Hydrol. Earth Syst. Sci. Discuss., 12, 8337–8380, 2015 www.hydrol-earth-syst-sci-discuss.net/12/8337/2015/ doi:10.5194/hessd-12-8337-2015 © Author(s) 2015. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Hydrology and Earth System Sciences (HESS). Please refer to the corresponding final paper in HESS if available.

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

B. van der Grift^{1,2}, H. P. Broers³, W. L. Berendrecht⁴, J. C. Rozemeijer², L. A. Osté², and J. Griffioen^{1,3}

 ¹Copernicus Institute of Sustainable Development, Faculty of Geosciences, Utrecht University, P.O. Box 80115, 3508 TA Utrecht, the Netherlands
 ²Deltares, P.O. Box 85467, 3508 AL Utrecht, the Netherlands
 ³TNO Geological Survey of the Netherlands, P.O. Box 80015, 3508 TA Utrecht, the Netherlands
 ⁴Berendrecht Consultancy, Stakenbergerhout 107, 3845 JE Harderwijk, the Netherlands

Received: 9 June 2015 - Accepted: 28 July 2015 - Published: 25 August 2015

Correspondence to: B. van der Grift (bas.vandergrift@deltares.nl)

Published by Copernicus Publications on behalf of the European Geosciences Union.



Abstract

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 highly relevant for improving the water quality in such

- areas. This paper introduces new insights in nutrient sources and transport processes in a low elevated polder in the Netherlands using high-frequency monitoring technology at the outlet, where the water is pumped into a higher situated lake, combined with a low-frequency water quality monitoring program at six locations within the drainage area. Seasonal trends and short scale temporal dynamics in concentrations indicated
- that the NO₃ concentration at the pumping station originated from N-loss from agricultural lands. The NO₃ loads appear as losses with drain water discharge after intensive rainfall events during the winter months due to preferential flow through the cracked clay soil. Transfer function-noise modelling of hourly NO₃ concentrations reveals that a large part of the dynamics in NO₃ concentrations during the winter months can be
- related to rainfall. The total phosphorus (TP) concentration almost doubled during operation of the pumping station which points to resuspension of particulate P from channel bed sediments induced by changes in water flow due to pumping. Rainfall events that caused peaks in NO₃ concentrations did not results in TP concentration peaks. The by rainfall induced and NO₃ enriched quick interflow, may also be enriched in TP but this
- is then buffered in the water system due to sedimentation of particulate P. 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 highly due to the artificial pumping regime that buffers high flows. As the TP concentration is affected by operation of the pumping sta-
- tion, 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.



1 Introduction

Many surface water bodies suffer from eutrophication caused by high nutrient loads. Eutrophication of surface waters can lead to turbid waters with decreased oxygen levels (hypoxia), toxin production by algae and bacteria, and fish kills. Policy makers of

- ⁵ national governments, the European Union and other authorities aim at improving water quality in surface water bodies that receive nutrient load from agriculture or other sources (EC, 2000). A sound assessment of pressures and impacts on the aquatic ecosystem and a reliable assessment of water status in catchments is, therefore, a topic of major importance. If the assessment of pressures is flawed, the action plans at the external data and the external data at the external data at
- will be ill founded and there is a risk that EU member states will not carry out their work where it is most needed and in a cost effective way (EC, 2015). This holds strongly for the Netherlands where nutrient surpluses and leaching are higher than elsewhere in Europe (van Grinsven et al., 2012) and the world (Bouwman et al., 2013), due to a highly concentrated and productive agricultural sector.
- ¹⁵ For the evaluation of action programs and pilot studies, water authorities invest heavily in the monitoring of NO₃ and P concentrations in surface water. Regional surface water quality networks in EU member states are commonly sampled 12 times a year (Fraters et al., 2005). However, the interpretation of grab sample data in terms of loads and fluxes is often problematic from such monitoring networks (Rozemeijer et al.,
- 20 2010). Grab sample frequencies are generally not sufficient to capture the dynamical behavior of surface water quality and hydrological functioning of the catchment (Kirchner et al., 2004; Johnes, 2007). It is increasingly recognized that incidental losses and peak flows play an important role in the nutrient loads of surface water systems in the Netherlands (Van der Salm et al., 2012; Regelink et al., 2013) and elsewhere (Withers
- et al., 2003). Such incidental losses are considered to be related to peak flows after heavy rain storms and due to overland flow or quick interflow via drains and cracked clay soils and related leaching of manure and erosion of soil particles (Kaufmann et al., 2014). Some authors observed a lowering of NO₃ concentrations shortly after peak flow



(e.g. Poor and McDonnell, 2007; Shrestha et al., 2013) caused by dilution with NO_3 poor precipitation water. Others detected concentration peaks in response events (e.g. Rozemeijer and Broers, 2007; Tiemeyer et al., 2008). Therefore, the NO_3 response to rainfall events depends on the hydrochemical properties of the catchment (Rozemeijer et al., 2010). In addition, the capacity of surface water bodies to retain nutrients is spatially and temporally variable (e.g. Withers and Jarvie, 2008; Cirmo and McDonnell,

As a consequence of the dynamic behavior of nutrient transfer from land to surface water and instream processes that impact nutrient retention combined with increasing demands for sound assessments of the water system, there is an increasing interest in continuous or semi-continuous monitoring of water quality at catchment outlets during the last decade (e.g. Bowes et 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., 2015). These studies showed catch-

1997).

- ¹⁵ ment dependent non-stationary behavior of the concentration–discharge relationships. High-frequency monitoring has proven to be a powerful tool to improve estimations of annual export loads (e.g. Rozemeijer et al., 2010; Cassidy and Jordan, 2011), nutrients sources (Bowes et al., 2015) and the hydrochemical functioning of a catchment (e.g. Wade et al., 2012; Bieroza et al., 2014; Halliday et al., 2012). High-frequency nutri-
- ent monitoring has revealed presence of diurnal nutrient cycles in rivers and streams caused by biological processes or by P and N inputs from sewage treatment works (e.g. Bowes et al., 2015; Halliday et al., 2012; Neal et al., 2012).

In many low-lying areas worldwide, water levels are human controlled by inlet of diverted river water in dry periods and discharge via pumping stations in wet periods.

Such an embanked land form with a human controlled water regime is called a "polder" (Wikipedia, 2015). In the Netherlands, these regulated polder catchments cover 60% of the land surface (Van de Ven, 2003). The dense network of subsurface drains, ditches, weirs, channels, pumping stations and the dynamic mixing of water from different sources (seepage, precipitation and water inlet) results in a relatively complex



hydrology. Many studies on nutrient dynamics in natural catchments showed a relation between nutrient concentrations and discharge, and this significantly improved the insight in the nutrient sources and pathways in the catchment. The water flow in polders is, however, not a function of free discharge but is controlled by pumping stations. The

maximum discharge is controlled by the capacity of the pumping stations. Due to the presence of a dense surface water system, the water storage capacity and the residence time of the surface water in a polder is also higher when compared to natural, free draining catchments which may impact in-stream processes controlling nutrient retention. Insight in the hydrochemical functioning of polder catchments is highly relevant
 for improving the water quality in the Netherlands.

To our knowledge, high-frequency monitoring of surface water quality has not been applied for polder catchments up to now. Discharge–concentration relationships and short scale variation in water quality in polder catchments are still unclear while nutrient sources and pathways are poorly understood (Rozemeijer et al., 2014). High-frequency measurements reveal the short-term variability in solute concentrations which may give valuable insight into the contribution of different sources or different flow routes to the surface water pollution in polders.

15

The general aim of this study is to increase our understanding of the hydrochemical function of an agriculture-dominated water system in a clay polder by analysis of high-frequency monitoring of nutrient concentrations at the polder outlet combined with

- ²⁰ high-frequency monitoring of nutrient concentrations at the polder outlet combined with low-frequency surface water quality 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 (2) to characterize the importance of incidental losses caused by intensive rainfall events whether or not
- ²⁵ in combination with recent manure application and (3) to assess potential effects of the operational management of the pumping station on the water quality.



2 Material and methods

2.1 Study area

A continuous monitoring station was established in the Lage Vaart main channel nearby the pumping station Blocq van Kuffeler (A in Fig. 1). This is one of the three pumping stations that control the water level in Lage Afdeling pumped drainage area located within the Flevoland polder, the most recent and at the same time biggest land reclamation project in the Netherland (Groen, 1997). The Flevoland polder consists of two pumped drainage areas, which are each drained by a main channel. The Lage Afdeling drainage area drains into the Lage Vaart main channel (Fig. 1). The size of the Lage Afdeling drainage area is 576 km², with altitude ranging between 3 and 5 m below mean sea level. The Lage Afdeling drainage area is mainly rural. The land cover is dominated by agriculture (76%), followed by woodlands and moors (18%) and urban or semi-urban areas (6%).

The geohydrology of the Flevoland polder area is generally described by a confin-

- ¹⁵ ing layer of Holocene origin, with a thickness of nearly nil in the northeast to over 7 m southwest, overlying a sandy aquifer deposited in the Pleistocene age. The soils consist for 50 % of clay soils, for 39 % of silty clay loam and for 11 % of sandy soils (Van den Eertwegh, 2002). A typical characteristic of the soils in Flevoland is that the clay layer contains permanent and interconnected cracks due to physical and chemical ripening
- of the soil after reclamation. The shrinkage cracks disappeared in the plough layer by tillage activities, but are permanently present in the subsoil down to about 1.0–1.5 m below the soil surface (Van den Eertwegh, 2002; Groen, 1997). From a depth of 1.2 to 1.5 m below the soil surface, clay deposits, if present, are permanently water saturated and thus not ripened, resulting in a low-permeable soil layer. Due to altitudes below
- ²⁵ mean sea level and below the water level of the surrounding lakes, there is upward groundwater seepage at most locations 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 and groundwater seepage rate. The field ditches receive outflow from the tube drain, direct drainage from subsurface flow, regional groundwater seepage and any surface run-off from the connected field area. They drain freely into the secondary channels. The water level in the Lage Afdeling 5 is regulated by 97 weirs and three pumping stations that pump the excess water to the higher situated Markermeer and Ketelmeer. The total pumping capacity is 11-12 mm d⁻¹. The Lage Vaart main channel has a controlled constant water level of 6.2 m below mean sea level. The pumping station Blocg van Kuffeler has two electrically powered pumps with a capacity of $750 \text{ m}^3 \text{ h}^{-1}$ each. The operational management of the 10 pumping station is automatically controlled by a series of water level pressure sensors in the area. The discharge generated by the pumping stations is measured continuously. The Blocq van Kuffeler pumping station drains the south-western part of the Lage Afdeling drainage area. The flow direction of the water in the channels that are drained by pumping station Blocg van Kuffeler, is illustrated by arrows in Fig. 1. Pump-15 ing station B is an emergency pumping station and only operates during extremely wet conditions. Although there is no physical boundary between the area drained by Blocq van Kuffeler and pumping station C, location 5 can be considered as the most upstream location in the Lage Vaart that is drained by the Blocg van Kuffeler pumping

²⁰ station under normal meteorological conditions.

2.2 High-frequency measurements

Between October 2014 and April 2015 we measured the total-P concentration, NO₃ concentration, conductivity and water temperature semi-continuously at the polder outlet just before the pumping station. The flow regime at the monitoring location is gov-²⁵ erned almost exclusively by the pumping station. The conductivity and water temperature was measured continuously with a CTD-diver (Van Essen Instruments, Delft, the Netherlands).



The NO₃ concentration was measured using a double wavelength spectrophotometric sensor (DWS), (Nitratax plus sc, Hach Lange GmbH, Düsseldorf, Germany). The DWS measures UV absorbance of dissolved NO₃ at a wavelength of 218 nm at a measuring receiver (EM – element for measuring) and at 228 nm at a reference receiver

- $_{5}$ (ER element for reference). The recorded measurements at two different wavelengths are designed to compensate interference of organic and/or suspended matter by interpreting the difference between the absorbance values at EM and ER. A UV sensor using only one single wavelength is not able to compensate additional interferences (Huebsch et al., 2015). The Nitratax sensor covers a NO_x-N detection range of 0.1 to
- ¹⁰ 50.0 mg L⁻¹. The NO₃ concentrations were recorded every 5 min. There was a small drift in the signal of the Nitratax sensor (max 0.35 mg N L⁻¹ month⁻¹). We, therefore, corrected the high-frequency NO₃ data using the NO₃ concentrations from the biweekly grab samples by calculating a linear drift for the separate maintenance intervals of the sensor.
- For the total phosphorus (TP) concentration measurements, we installed a Sigmatax sampler and a Phosphax Sigma auto-analyzer (both Hach Lange GmbH, Düsseldorf, Germany). The total-P concentrations were recorded every 20 min. The Phosphax Sigma was automatically cleaned and calibrated daily. The Sigmatax was installed for the automated water sample collection and the pretreatment (ultrasonic homogeniza-
- tion) of the 100 mL samples. A 10 mL sub-sample was delivered to the Phosphax Sigma auto-analyzer. This sample was digested using the sulphuric acid-persulphate method (APHA-AWWA-WPCF, 1989). After mixing and quickly heating and cooling down the sample, molybdate, antimony and ascorbic acid were automatically added and mixed with the sample and the sample was measured at 880 nm using a LED photometer.
- ²⁵ There was a close agreement between the high-frequency TP data and the TP concentrations of the accompanying two weekly grab samples analyzed by standard laboratory assays and, therefore, no need to correct the high-frequency TP data.



2.3 Low-frequency monitoring

In addition to the automatic water quality measurements, grab samples were collected every two or four weeks from January 2014 to March 2015 from the 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 for different types of land use (Table 1). Electrical conductivity, oxygen concentration, transparency, temperature and pH of the samples were measured directly in the field. Sub-samples for determination of dissolved substances were filtered through a 0.45 μm poresize filter. The samples were transported and stored at 4 °C. Total-P,
 dissolved reactive P, NO₃, NH₄ and Cl where determined using standard colorimetric methods (APHA-AWWA-WPCF, 1989). Organic-N was extracted by Kjeldahl extraction.
- tion and measured by colorimetric method and sulphate was measured using IC (Ion Chromatography).

2.4 Supporting information

- Precipitation data on an hourly basis for the Lage Afdeling were abstracted from HydroNet (http://portal.hydronet.nl/). This is an online database with precipitation data based on calibrated radar images. The precipitation of the radar pixels were averaged over the Lage Afdeling drainage area. Temperature data were retrieved from the Royal Dutch Meteorological Institute (KNMI, De Bilt, the Netherlands) weather sta-
- tion Lelystad, located in the center of the Lage Afdeling. The Flevoland polder has a moderate maritime climate with an average annual temperature of 9.9 °C, an average annual precipitation of 850 mm and an average of 8 days per year with a maximum temperature below 0 °C. Groundwater levels were monitored continuously with pressure sensors in five phreatic groundwater wells located within the agricultural area of the Lage Afdeling.

The groundwater quality data set from Griffioen et al. (2013) was used as background information. This database was assembled from the national database of the TNO



Geological Survey of the Netherlands and contains complete groundwater analyses down to a depth of about 30 m with sampling dates later than 1945. The groundwater in the Lage Afdeling is characterized as anoxic fresh to saline and P-rich with low NO_3 concentrations, CI concentrations between 7 and 4500 mg L⁻¹ and P concentrations between 0.01 and 3.6 mg PL⁻¹ (Fig. S1).

2.5 Transfer function-noise modelling

To increase insight in the driving forces of measured dynamics of nutrient concentrations, preliminary research was done on the application of time series analysis, and more specifically transfer function-noise (TFN) modelling, to estimate the impact of rainfall on NO₃ concentrations. TFN models are very popular for describing dynamic causal relationships between time series and have been widely applied in the field of groundwater modelling (e.g. Berendrecht et al., 2003; Knotters and van Walsum, 1997). Although a small number of studies has used TFN models to relate streamflow data to nutrient concentrations (Schoch et al., 2009; Worrall et al., 2003), to our knowledge TFN models have not been applied yet on high-frequency monitoring data of nutrients such as available in this study. Therefore, as a first step, we tried to relate the time

series of hourly NO₃ concentration measurements to rainfall using the following linear TFN model:

 $\log(NO_3) = \theta(B)\rho_t + \mu + n_t$

20 and

5

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

with p_t the precipitation at time t, $\theta(B) = \theta_0 + \theta_1 B + \ldots + \theta_r B^r$ the transfer function (*B* is backward shift operator, $B^i p_t = p_{t-i}$), μ is the reference or baseline level, n_t a stochastic first-order autoregressive process, ϕ the autoregressive coefficient ($0 < \phi < 1$), and

Discussion HESSD 12, 8337-8380, 2015 Paper **Transport processes** in an agriculturedominated lowland Discussion water system B. van der Grift et al. Paper **Title Page** Introduction Abstract **Discussion** Paper Conclusions References **Figures** Back Discussion Full Screen / Esc **Printer-friendly Version** Paper Interactive Discussion

(1)

(2)

 ε_t a zero-mean normally distributed process (Box and Jenkins, 1970). As ε_t is assumed to be normally distributed, the time series of NO₃ data was log-transformed to better satisfy this assumption. For reasons of flexibility and model parsimony, we used a predefined transfer function as described by von Asmuth et al. (2002), which has the form of a Gamma distribution function and has been successfully applied for describing

form of a Gamma distribution function and has been successfully applied for describing groundwater dynamics.

2.6 Export loads calculations and trend analysis

True NO_3 and TP export loads from the drainage area into the Markermeer were based on our high-frequency concentration measurements and discharge data of the pumping station. In addition NO_3 and TP loads were estimated from linear interpolation of the low-frequency grab sample data combined with the discharge data. Although advanced methods have been developed to improve 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).

- ¹⁵ Long term TP and NO₃ concentration measurements were available for the polder outlet. We used two frequently applied methods for trend analysis of concentrationtime series: (1) Theil–Sen robust line (Hirsch et al., 1982) and (2) locally weighted scatterplot smoothing (LOWESS) trend lines (Cleveland, 1979). These methods are relatively insensitive to extreme values and missing data in the time series. The Theil– Sen method is a robust new parametric trend along actimator. The LOWESS trend
- ²⁰ Sen method is a robust non-parametric trend slope estimator. The LOWESS trend lines were used to examine possible changes in trend slopes within the concentration time-series period.

3 Results

The results of the high-frequency monitoring at the pumping station Blocq van Kuffeler and low-frequency monitoring within the Lage Afdeling drainage area will be presented



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

5 3.1 Water discharge

The Blocq van Kuffeler pumping station responds rapidly to rainfall events in the drainage area by automatically switching on one or two pumps (Fig. 2). The interval in which the pumping station is in operation decreased during the autumn months. During the winter months the pumping station runs almost at a daily basis and continuously for

several days during very wet periods. The pumping station pumped almost 70 × 10⁶ m³ water from the polder into the Markermeer during the period from October 2014 until March 2015. This corresponds to approximately 350 mm distributed across the entire drainage area. The precipitation during this period equaled 470 mm.

3.2 Mid-term trends in high-frequency nutrient data

- ¹⁵ The high-frequency NO₃ concentration measured at the Blocq van Kuffeler pumping station ranged from 0.45 to 10.4 mgNL⁻¹ and the total phosphorus (TP) concentration ranged from 0.07 to 0.57 mgPL⁻¹. (Fig. 2). The NO₃ and TP concentrations from the biweekly grab samples and the accompanying one day antecedent precipitation and flow data are shown in Fig. 2 as well. Although the data do not cover a whole
 ²⁰ year, the high-frequency NO₃ data show a seasonal pattern and a response to rainfall. The NO₃ concentrations were low at the start of the monitoring in October 2014 and stayed low until the rainfall event on 15–17 November. Precipitation events before mid-November only had a minor influence on the NO₃ concentration. The NO₃ concentration of 9 mgNL⁻¹
- ²⁵ from mid-November to the third week of January. Major increases of the NO₃ concentration occurred during pumping from 18 to 21 November, 16 to 23 December and 13



to 18 January which showed that the NO₃ concentration responded to rainfall during this period. The concentration slightly decreased during dryer periods after these individual wet periods. During the dry period in the first three weeks of February, the NO₃ concentration decreased to a level of 1 mgNL^{-1} . Next, the concentration reached a maximum of 10.4 mgNL^{-1} at 24–25 February and gradually decreased towards the

end of March where it showed an increase again.

The high-frequency total-P (TP) data shows a seasonal variation and a response to pumping as well. The TP concentration was, with concentrations that ranged from 0.25 to 0.4 mg PL^{-1} , high during the first three weeks of the monitoring period. In October and November, the TP concentration decreased upon wet periods to a concentration

- ¹⁰ and November, the TP concentration decreased upon wet periods to a concentration level around 0.15–0.2 mg PL⁻¹ and increased again during the dryer periods to levels around 0.3 to 0.4 mg PL⁻¹. During the first two weeks of December, the TP concentration decreased to a level around 0.1 mg PL⁻¹. This baseline level remained at this level until halfway February. During the relatively dry period in February and March there
- ¹⁵ was a gradual increase of the TP concentration to a level around 0.2 mg PL⁻¹. The dissolved reactive P (DRP) data from the low-frequency monitoring program showed relatively a high concentration until early December and then declined to concentration below 0.05 mg PL⁻¹. The DRP concentration remained at this low level until the end of the monitoring program.

20 3.3 Short scale dynamics in high-frequency nutrient data

Significant increases of the NO₃ concentration up to 8 mgNL⁻¹ in short time scales appeared during pumping within five days after major rainfall events on 15–18 November, 10–12 December, 19–20 December, 7–9 January, 12–14 January, 21–22 February and 29 March–2 April (Fig. 2 and Table 2). The precipitation during these events peaked around 20 mm or above (Figs. 2 and 3). The increase in NO₃ concentration did not appear after the precipitation events on 20–23 October and 3–4 November. As it will be discussed in Sect. 4, this is likely due to the absence of tube drain discharge upon these precipitation events. For the events after mid-November applies that the re-



sponse of the NO₃ concentration to rainfall was delayed and occurred about five days after the rainfall event. After this NO₃ concentration peak, the concentration declined during pumping. The period of five days between rainfall event and peak in the NO₃ concentration at the pumping station is representative for the average residence time

of water in the Lage Afdeling drainage area. This is in line with model calculated mean annual residence times of water in the Lage Vaart main channel of 6.6 days for the period 1988–1998 (Van den Eertwegh, 2002).

There is a structural response of the TP concentration on operation of the pumping station. The TP concentration always peaked directly after the start of the pumping-engines and decreased again during the period of pumping and afterwards (Figs. 2 and 3). The maximum TP concentration during pumping was a factor 1.5 to 2 higher than the concentration before pumping. The abrupt increase of the TP concentration as caused by operation of the pumping station indicates that the additional TP (the TP concentration during pumping compared to the concentration before pumping) is

10

related to resuspension of particulate P (PP) from bed sediments due to increased flow velocities. Due to low flow conditions during no-pumping conditions, an erodible layer builds up by sedimentation of PP. When the water flow velocities in the main channel increase upon pumping, the PP becomes suspended and transported downstream.

A significant short-term change in NO₃ and TP concentrations and the conductivity during a period without pumping appeared on 26 January (Figs. 2 and 3). The decrease in the NO₃ concentration (from 6.1 to 1.5 mgNL⁻¹) and increase in the TP concentration (from 0.07 to 0.21 mgPL⁻¹) as observed on 26 January cannot be explained by operation of the pumping station or by antecedent precipitation (5.5 mm on 24 January and 2.1 mm on 25–26 January). A cold period with daily average temperatures below

0°C started at 20 January and ended on 24 January (Fig. 3). As a consequence the top soil was frozen, the precipitation during the night of 24 January fell as snow and this resulted in a snow cover of a few centimeters. Soil freeze-thaw processes significantly increase the potential erosion during run-off events that follow thaw in hill slope areas (Ferrick and Gatto, 2005) but also in relatively flat areas (Gentry et al., 2007). Where



under normal conditions rainfall infiltrates into the soil, the thaw and precipitation on 25 January likely resulted in run-off. This temporally diluted the NO₃ concentration and increased the TP concentration. Thus, the increase of the TP concentration must be caused by erosion of soil surface particles.

5 3.4 Decomposition of high-frequency nitrate data

As shown in Sect. 3.2, NO₃ concentrations were low until the rainfall event on 15 November and precipitation events before mid-November only had a minor influence on the NO₃ concentration. For the period after 15 November a transfer function-noise modelling of hourly NO₃ concentrations reveals that the model can relate quite a large part of the dynamics to rainfall: the coefficient of determination $R^2 = 0.7$. The measured time series together with the model simulation and the residual series are shown in Fig. 4.

Overall, the transfer model describes slow dynamics well; high-frequency dynamics cannot be related to rainfall with the transfer model and are described by the stochastic

⁵ model. The estimated autoregressive coefficient ($\phi = 0.98$) is quite low given the high sampling interval of 1 h, indicating that most of the temporal structure in the time series has been captured by the transfer model.

The results in Fig. 4 show that during no-rain periods the decline in concentration is modelled well. The various periods of rainfall show different results: in December the in-

crease in concentration is modelled well, in January the concentration is overestimated, while in February/March the concentration is underestimated. The overestimation in January can be explained by dilution while recent manure application is a plausible explanation for the underestimation of modelled concentrations in February/March (see Sect. 4). The largest negative residuals appeared during the thaw event on 26 January
 (see Sect. 3.3) while the largest positive residuals appeared on 24–25 February.

The estimated impulse response function for transferring an impulse of 1 mm rainfall into $log-NO_3$ concentration is given in Fig. S2. The smooth character of the function is due to predefined structure of the function, which is the Gamma distribution function.



The time to peak is 5.5 days with a response of 0.033 log(mgNO₃L⁻¹), while 95% of the total response happens within 43 days. The time to peak as revealed by the TFN model matches well with the delay of approximately five days between rainfall event and peak concentrations (Fig. 2).

- ⁵ The estimated reference or baseline level is 0.54 mgNO₃ L⁻¹, which means that after a long no-rain period, the NO₃ concentration will decline to 0.54 mg L⁻¹. A longer time series (at least 1 year) would be necessary to give any physical interpretation of this value (e.g. estimate of background concentration). The current time series does not include seasonal patterns; during spring and summer season the NO₃ concentration tion cannot be related to rainfall only, so other driving forces have to be included. As
- tion cannot be related to rainfall only, so other driving forces have to be included. As it will be discussed in Sect. 4, in-stream nutrient uptake processes reduce the NO₃ concentration and rainfall may not lead to discharge.

3.5 Nutrient loads and fluxes at polder outlet

Cumulative loads at the polder outlet based on either linear interpolation within the low-

- ¹⁵ frequency data set or the high-frequency data set are given in Fig. 5. The total measured loads based on the high-frequency dataset from 1 October 2014 to 1 April 2015 were 10 500 kg for P and 308 000 kg for NO₃-N. These loads overestimate the TP load calculated from the low-frequency data by 20 % and underestimate the low-frequency NO₃ load by 5.5 %.
- ²⁰ Time series of TP and NO₃ concentrations in grab samples at the Blocq van Kuffeler pumping-station over the period 2000–2015 are given in Fig. 6. The red lines in Fig. 6 show the LOWESS trend line and the black lines show the Theil–Sen slope over the period 2000–2015. The NO₃ concentration showed no upward or downward trend over the period 2000–2015. The time series of TP concentration showed different trends over the period 2000–2015. After a period with miner increase for 2000 to 2000, the
- over the period 2000–2015. After a period with minor increase for 2000 to 2009, the LOWESS trend line reveals a decline in TP concentrations in the period 2009–2010



followed by an increase from 2011 to 2015. The Theil–Sen slope showed a decline of TP concentration $(-0.0053 \text{ mg PL}^{-1} \text{ yr}^{-1})$ over the years 2000–2015.

The blue and green lines give the Theil–Sen slopes for the periods 2000–2008 and 2009–2015, respectively. As it will be discussed in Sect. 4, the pumping-station was renovated in the autumn of 2008 and this likely had an impact on the TP dataset time series. Where the Theil–Sen slope showed a decline of TP concentration over the

years 2000–2015, it showed upward trends of 0.0023 and 0.0088 mg PL^{-1} yr⁻¹ over the separate periods 2000–2008 and 2009–2015, respectively. The NO₃ concentration showed no upward or downward trend over the separate periods 2000–2008 and 2009–2015.

3.6 Water quality within Lage Afdeling drainage area

The low frequency dataset of 11/4 yr with analyses from 6 locations within the Lage Afdeling drainage area showed spatial differences in water quality related to land use and subsurface characteristics. High chloride concentrations were observed at monitoring locations 1, 3 and 5, where location 1 and 3 showed higher concentrations during summer than during winter (Fig. 7). The salinity of the surface water was high with CI concentrations above approximatly 250 mg L⁻¹ when the groundwater in the vicinity of the monitoring location had high CI concentrations. Chloride concentrations above 500 mg L⁻¹ were commonly observed in the groundwater in the area upstream of location 3 and 5 (Fig. S1). The Lage Vaart channel acts as a drainage channel for

of location 3 and 5 (Fig. S1). The Lage Vaart channel acts as a drainage channel for groundwater under the confining Holocene layer, which is often brackish/saline (Van den Eertwegh, 2002). This explains the relatively high CI concentrations of location 1 during summer.

Low NO₃ concentrations were observed in discharge water from the nature area Oostvaardersplassen (location 6) throughout the year whereas high NO₃ concentrations were observed in water from the agricultural areas Lepelaartocht and Gruttotocht (location 3 and 4) in the winter. The overall highest NO₃ concentrations of 8.3 and 13 mgNL⁻¹ were observed at these locations in February 2014 and 2015, respectively.



The NO₃ concentration in the urban area water (location 2) did not exceed 2 mgNL^{-1} and showed only a minor seasonal variation. The NO₃ concentrations of the Lage Vaart channel water at the pumping station (location 1) during the winter months were lower compared to the NO₃ concentrations at the outlet of the agricultural areas. This

- ⁵ indicating some dilution of the agriculture-dominated water with water from nature or urban areas. This is confirmed by the SO₄ data that demonstrate some dilution of the agriculture-dominated water as well. The locations with high SO₄ concentrations exhibit an inverse pattern with the CI concentration. This shows the occurrence of pyrite oxidation in the shallow subsurface (Griffioen et al., 2013) in the Lage Afdeling drainage
- ¹⁰ area except for location 6 that drains the Oostvaarderplassen which has no tube drains and high groundwater levels throughout the year. The N-Kjeldahl concentrations varied between 0.77 and 5.8 mgNL⁻¹ but showed little variation over the year for the individual agriculture-dominated and urban-dominated sampling locations. The N-Kjeldahl concentration in the water from the Gruttotocht (location 3) was almost twice as high as from the Lepelaartocht (location 4).

The TP concentration of the low-frequency monitoring program varied between 0.05 and 0.72 mgPL^{-1} (Fig. 7). From all sampling locations within the Lage Afdeling, the water from the Oostvaardersplassen (location 6) had the highest TP concentrations. The TP concentration of this water ranged between 0.37 and 0.72 mgPL^{-1} from Jan-

- ²⁰ uary to July 2014. The concentration dropped to a level around 0.3 mg P L⁻¹ or lower in August and stayed at this level until the end of the monitoring program. The TP concentration at the Oostvaarderplassen and Blocq van Kuffeler were higher during the first months of 2014 compared with the same period in 2015. The long-term data series for Blocq van Kuffeler showed high TP concentrations during the first months of
- 25 2014 as well compared with concentrations in other recent years (Fig. 6.) We do not have a clear explanation for this observation. Together with a decrease of the TP concentration at the Oostvaardersplassen and Blocq van Kuffeler, there was an increase of the DRP concentration. During the first half year of 2014 the TP concentration was dominated (> 90 %) by particulate P while in the second half year of 2014 about 50 %



of the TP concentration consisted of DRP. The DRP concentration dropped again to levels around the detection limit during the winter of 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.

⁵ Although less pronounced, this seasonal variation applied as well for the agriculturedominated 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. S1)

10 **4 Discussion**

4.1 Identification of nutrients sources and dynamics in nutrient concentrations

The first objective of our study was gaining insight in the dynamics of nutrient concentrations and nutrient sources of a typical agriculture-dominated lowland water system. We examine the added value of TFN modelling of high-frequency NO₃ data for iden-¹⁵ tification of NO₃ sources and dynamics and, in addition, combining high-frequency monitoring data at the polder outlet with low-frequency surface water quality data and groundwater data from the drainage area.

4.1.1 Nitrate

Given the low NO₃ concentrations in groundwater (Fig. S1) and the high NO₃ concentrations in the surface water at the outlet of the agriculture-dominated areas during winter months (Fig. 7), it is clear that almost all NO₃ in the surface water at the polder outlet has an agricultural source. The high-frequency monitoring data at the Blocq van Kuffeler pumping stations additionally provides insights in the processes and dynamics of NO₃ delivery to the surface water.



The high-frequency NO_3 data showed a seasonal trend with a gradually increase from half November to half January. An increase of NO_3 concentrations from summer to winter is observed in a large majority of agriculture-dominated headwater in the Netherlands (Rozemeijer et al., 2014) and natural catchments elsewhere (Wade

- et al., 2012). Catchments where NO₃ concentrations are controlled by a combination of effluent loads from sewage treatment works and dilution by rainfall commonly show a decline in NO₃ from summer to winter (Bowes et al., 2015; Wade et al., 2012). The NO₃ pattern is therefore thought to be due to a combination of interflow or shallow draining groundwater with high fertilizer or manure inputs and NO₃ enrichment during autumn and winter. Increased crop uptake of NO₃ during the growing season combined
- with the effect of instream processes result in declined NO_3 concentrations during the summer months.

Beside the seasonal variation, we structurally observed an increase of NO_3 concentrations after intensive rainfall events, except for the rainfall event during the thaw

- on 24–25 January. A reduction in NO₃ concentrations coinciding with periods of intensive rainfall is commonly reported in high-frequency monitoring studies in natural catchments and attributed to dilution of the surface water by run-off (Bowes et al., 2015; Rozemeijer et al., 2010). Our structurally observed / increase implies that run-off, which dilutes the NO₃ concentration of the surface water does not commonly occur
- in the polder. It, therefore, indicates that rainfall initiates a sudden increase of quick interflow via subsurface tube drains, cracks or other macropores to the Lage Vaart channel water. This is confirmed by the TFN model which showed that quite a large part of the NO₃ dynamics during the winter months can be related to rainfall. Meinardi and Van der Eertwegh (1997) ran a monitoring program on tube drain water composi-
- tion at 14 farms in the Flevoland polder during 1992–1995 and reported concentrations between 5–25 mg N L⁻¹. Another monitoring program on nutrient concentration of tube drain water at 6 farms in Flevoland from 2004 to 2008 gave farm-average NO₃ concentrations of 14–18 mg N L⁻¹ (van Boekel et al., 2012). These concentrations levels can only explain the observed NO₃ concentration at the pumping station when tube drain



water is a dominant source of the Lage Vaart channel water. Groundwater levels within the polder are commonly low and tube drainage is rare during the summer and early autumn (Van den Eertwegh, 2002; Groen, 1997). In autumn, when evapotranspiration decreases, the groundwater levels rise upon rainfall events to around or above the level

- of the tube 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 area (Fig. S3) that shows a direct response of the groundwater level on rainfall combined with a seasonal trend that shows increasing groundwater levels during the months October and November and quite stable levels
- from December to March. Rainfall events unit half November did not result in tube drain discharge and the low NO₃ concentration of the surface water until half November is, thus, explained by the absence of tube drain discharge. This is also the reason that we started the TFN model on 15 November. As rainfall is not a driving force for the NO₃ concentration before mid-November, starting the TFN model on 1 October would serenely be unfavorable for the transfer model.

The presence of cracked clay soils results in a rapid response of drainage to rainfall events in winter (Groen, 1997; Van den Eertwegh, 2002). Preferential 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), which explains the quick response of NO₃ concentration of the surface water to rainfall events. Due to regular plowing

rainwater easily infiltrates into the top soil layer where exchange of NO_3 from manure, fertilizers and plant debris occurs. The top soil or plough layer is commonly well aerated, and therefore, quite optimal for conversion of organic nitrogen and ammonium to NO_3 . After leaching of this water from the plough layer to the cracked soil layer it

20

²⁵ quickly contributes to tube drain discharge. Due to short residence time of this water in the soil, the influence of denitrification on the NO₃ concentration is limited. This implies that the NO₃ concentration at the polder outlet and the related export load from the polder are strongly controlled by quick interflow including tube drain discharge during the winter months.



4.1.2 Phosphorus

In contrast to the NO₃ concentration, the TP concentration at the pumping station decreased after the wet periods in the autumn of 2014. The interflow discharge via subsurface tube drains, cracks or other macropores that resulted in an increase of NO₃

- ⁵ concentrations diluted the TP concentration. This indicates that the sources of TP in the channel water at the polder outlet can largely be attributed to exfiltration of dissolved P-rich groundwater that occurs throughout the year, presumably combined with biogeochemical remobilization from channel sediments in summer and autumn. The low DRP:TP ratio of the surface water within the Lage Afdeling as observed during
- the first half year of 2014 and the winter of 2015 (Fig. 7) can be explained by transition of dissolved P to particulate P. This commonly occurs after exfiltration of anaerobic groundwater into surface water due to oxidation processes (e.g. van der Grift et al., 2014; Baken et al., 2015). The decrease of the groundwater contribution to the channel water due to an increase in interflow discharge during autumn, results in a decline of
- the TP concentration in the channel water. Additional to this groundwater input signal, the high DRP: TP ratios of the low-frequency monitoring program during the second half year of 2014 indicates that mineralization of organic P from algae or plant debris, or release of DRP from bed sediments can be considered as a second P source during summer and autumn. Mineralization of organic P mainly occurs after the growing
- season and the release of DRP from bed sediments is reported during summer and autumn due to temperature and redox dependent biogeochemical remobilization processes for lakes (e.g. Lavoie and Auclair, 2012; Boers and van Hese, 1988), wetlands, fens and floodplain soils (e.g. Zak et al., 2006; Loeb et al., 2008) but also for streams and rivers (e.g. Duan et al., 2012; Jarvie et al., 2008). Low O₂ concentrations in the
 water column are reported as an indicator for remobilization of P from bed sediments
- (Geurts et al., 2013). The decline of the O_2 concentrations in the surface water at low-frequency monitoring locations during the summer and autumn months (Fig. 7), thus,



indicates that biogeochemical remobilization may occur in the channels of the Lage Afdeling.

As a result of resuspension of particulate P from bed sediments due to increased flow velocities, we structurally observed an increase of TP concentrations during pumping.

- ⁵ Resuspension of particulate P retained by sediments during high discharge events is an important transport mechanism in natural catchments (e.g. Evans et al., 2004; Mulholland et al., 1985; Nyenje et al., 2014; Haygarth et al., 2005; Palmer-Felgate et al., 2008). Our data shows that this mechanism is also relevant for P transport in polders where flow velocities vary more abruptly and are maximized by the capacity
- of the pumping station. The changes in TP concentration during pumping are, however, significantly lower than reported during peak water discharge amongst storms in natural catchments. For an agriculture-dominated lowland catchment in the Netherlands, Rozemeijer et al. (2010) reported a mean increase in TP concentration during discharge from 0.15 to 0.95 mgPL⁻¹ comming from 47 rainfall events over a year. Par-
- ticulate P (PP) increases up to a factor 100 were reported by Stutter et al. (2008) in response to storm events. Evans et al. (2004) measured PP concentrations up to 3.93 mg PL⁻¹ in al lowland stream during high discharge conditions while the mean concentration equaled 0.1 mg PL⁻¹. Haygarth et al. (2005) reported 10 to 20 times higher mean TP concentrations during storm flow conditions compared to base flow
- ²⁰ conditions. With data from 76 storms Correll et al. (1999) showed that concentrations of PP increased up to three orders of magnitude during storms. These changes are significantly higher than the factor 1.5 to 2 that we observed at the pumping station but with 79 pump cycles during the period October 2014–March 2015, discharge-related changes that lead to resuspension of particulate P appear more frequent in polders
- ²⁵ compared to natural catchments. Total P export loads from polders can thus be characterized as less incidental and less peak flow controlled than those from natural catchments.



4.2 Incidental nutrient losses to surface water after manure application

The second objective of our study was to determine the relevance of incidental nutrient losses caused by intensive rainfall events whether or not in combination with recent manure application. the Netherlands adopted the European Nitrate Directive in 1991

- (EC, 1991), which regulates the use of nitrogen in agriculture through national action plans. Among other measures, the regulation includes the period of manure application. To reduce the risk of nutrient leaching to groundwater and surface water, manure application on arable land is allowed from 1 February to 1 August and on grassland from 15 February to 31 August (LNV, 2009). There is still debate about potential ef-
- fects of manure application in February and March (before the start of the growing season) on the water quality. Several studies ask attention for elevated nutrient concentrations in quickflow within a few weeks after application of fertilizers or liquid farm manure. However, the individual conditions varied between those studies: high losses were reported after installation of drains following application of liquid farm manure
- (Hodgkinson et al., 2002), with a rainfall event after P fertilizer application on frozen soil (Gentry et al., 2007), in drain water with a rainfall event after fertilizer application on clayey grassland (Simard et al., 2000), in drain water after harvest and superphosphate fertilizer application on clay soil (Djodjic et al., 2000), in drain and trench water after application of fertilizer or cattle manure (Van der Salm et al., 2012). The associated incidental loss may even amount to about 50% of the annual loss. Next, the
- question arises if this affects water quality at a more regional scale. High-frequency monitoring is a powerful tool to detect such incidental losses.

The NO₃ concentration peaked at the polder outlet on 24 February, four days after an intensive rainfall event that marked the end of a relative dry period that started early February. The increase of the NO₃ concentration is almost two times higher compared to the other peaks in NO₃ concentration after a rainfall event (Table 2). This suggests that the NO₃ peak of 10.4 mg NL⁻¹ was caused by an incidental loss after recent manure application. The TFN model revealed high residual NO₃ concentrations up to al-



most 8 mg NL⁻¹ during this NO₃ peak that cannot be explained by rainfall (Fig. 4). The NO₃ concentration peaks on 27 February and 3 March also showed high positive residuals of 4.2 and 3.4 mg NL^{-1} , respectively. The wet period in January resulted, however, in predicted NO₃ concentrations that were higher than the measured concentrations.

⁵ There was probably some degree of dilution during this period. A plausible explanation for this behavior is recent manure application that started on 1 February and temporary soil storage of applied N during the first dry weeks of February.

The TP concentration peaked on 21 February. It is, however, not likely that this peak was caused by an incidental loss after manure application. This peak appeared during the basis of the reinfoll event simultaneously with the start up of the number of the start up of t

- the beginning of the rainfall event, simultaneously with the start-up of the pumps after a relatively dry period. Therefore, it is more likely caused by hydrodynamic resuspension of the Lage Vaart bed sediment. The absence of a TP peak after the rainfall event on 21–22 February can be attributed to the soil characteristics of the area. We already discussed that the water quality at the polder outlet is strongly controlled by quick in-
- ¹⁵ terflow via tube drains or cracks and that surface run-off only influenced the water quality when it rained during the end of a freeze-thaw cycle. Although it is known that tube drain discharge after rainfall events in combination with recent manure application on cracked clay soils may contain significant TP concentrations (Van der Salm et al., 2012), these peaks did not appear at the polder outlet. It is unknown if these peaks
- appear after rainfall events in the tube drain discharge or in the receiving field ditches in the Lage Afdeling drainage area. Therefore, it is unclear if the absence of TP peaks simultaneously with the NO₃ peaks at the polder outlet can be attributed to sedimentation of PP in the field ditches or sub-channels or that there is almost no particulate or dissolved P leaching from the top-soil to the surface water due to the sorption capacity
- of the top-soil. From other areas it is known that the dissolved P loads to surface water from tube drains and shallow groundwater discharge are low due to precipitation with Fe hydroxides at the oxic/anoxic interface around the tube drains and ditch sediment (van der Grift et al., 2014; Baken et al., 2015). It is unknown if this process is relevant in the Lage Afdeling.



4.3 Water quality affected by the operational management of the pumping station

The third objective of our study was to assess the potential effects of the operational management of the pumping station on the water quality. Up to 2008, the pumping sta-

- tion Blocq van Kuffeler was powered with diesel engines. These diesel engines were replaced with electric engines during the renovation of the pumping station in the autumn of 2008 and this conversion was finished in the beginning of 2009. Since this transition, the pumping station runs typically overnight during normal meteorological conditions, because night power supply is cheaper than daytime power supply. The low-frequency compliance of pumping and during a daytime. The distribution of pumping heaven and
- ¹⁰ sampling is always performed during daytime. The distribution of pumping hours and sampling moments over the day during the period October 2014–March 2015 and boxplots of measured TP concentrations over the day during the months January and February 2015 are shown in Fig. S4. These two months were selected because boxplots for longer time series are dominated by the seasonal trends in the TP concentra-
- tion. The median, quartile and maximum TP concentrations were higher during night hours than during daytime. As a result, the monitoring program systematically misses the TP peak that occurs during pumping hours and consequently does not measure diurnal cycles caused by the operation of the pumping station. The reported time series from the low-frequency sampling program is, thus, not fully representative for the
- ²⁰ TP concentration at the polder outlet. As a consequence, export fluxes from the polder as calculated from low-frequency sample data underestimate the true export P-loads (Fig. 5). Similar results have been reported for load calculations in natural catchments with rapid run-off (e.g. Rozemeijer et al., 2010; Cassidy and Jordan, 2011). The NO₃ concentration showed no structural response on pumping, further illustrating the im-²⁵ portance 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 is 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 a.m. and 3 p.m. result in ⁵ a dataset time series that is not fully representative of the actual trends in water quality.

The number of diesel powered pumping stations in the Netherlands has rapidly declined during the last decades. There were around 200 diesel or hybrid (diesel + electric) powered pumping stations in operation in 1990. Currently, there are only 40 remaining and these pumping stations have mainly a function for emergency situations

(Gemalen, 2015). During the same period, electric powered pumping stations have 10 been equipped with automatic switching systems. Nowadays, a large majority of pumping stations operates predominantly during night hours. As the pumping station is the outlet of a (artificial) water system it is often a monitoring location for surface water quality as well. The renovation of pumping stations may thus have had a substantial

impact on reported trends in water quality on a regional or even a national scale. 15

Conclusions 5

High-frequency monitoring at the outlet of an agriculture-dominated lowland water system in combination with low-frequency monitoring within the area significantly improves insight in nutrient sources and transport processes.

Discharge water from subsurface drains, likely in combination with quick interflow 20 via clay cracks, has a dominant contribution to NO₃ loads to surface water, mainly originating from N-losses from agricultural lands during the winter. Transfer functionnoise modelling of hourly NO₃ concentrations reveals that guite a large part of the dynamics in NO₃ concentrations during the winter months can be related to rainfall once groundwater tables have risen above the tube drain levels. The NO₃ loads appear as incidental losses upon intensive rainfall events and cause high NO₃ concentrations at the polder outlet within approximately five days after the rainfall event.



Total P cannot be linked to a dominant source. The TP concentration decreases in response to wet periods, this implies that groundwater seepage is an important source of TP during dry periods. High DRP/TP ratios in the autumn months further suggest that biogeochemical remobilization from bed sediments or mineralization of organic P from

- ⁵ algae of plant debris additionally attributes to the TP concentration. Water discharge from the polder as generated by the pumping station initiates hydrodynamic resuspension of particulate P from the channel bed sediment and thus an increase of the TP concentration in the surface water during pumping. Changes in the TP concentration upon pumping are significantly smaller compared to discharge-driven concentration
- ¹⁰ changes in response to rainfall events in natural catchments. These findings suggest that the P retention capacity of polder water systems is high because flow velocities are maximized by the power of the pumping station. This result in a large P retention compared with natural catchments where incidental losses during peak flow conditions control the export load.
- Short-scale responses of the NO₃ and TP concentration on rainfall events indicate that run-off is not an important process that controls nutrient export from the polder. A decline of the NO₃ concentration of the channel water (caused by dilution with NO₃-poor run-off water) in combination with an increase in the TP concentration (by surface erosion and associated particulate P transport) was only observed at the polder outlet
- ²⁰ 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 NO₃ 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.
- A change in pumping regime caused by a transformation of the pumping station from powering with diesel engines to electric engines leads to a trend suggesting decreasing TP concentrations in the surface water that now should be considered artificial. Our data suggest increasing TP concentrations when analysing the individual time series before and after the transformation. The timing of sampling relative to the operating



hours of the pumping station affects the concentration and this should be accounted for when calculating P export loads, determining trends in water quality or when judging water quality against ecological thresholds and standards. High-frequency monitoring appears to be an effective tool to reveal this kind of difficult to notice artificial responses 5 in surface water quality.

The Supplement related to this article is available online at doi:10.5194/hessd-12-8337-2015-supplement.

Acknowledgements. The Waterboard Zuiderzeeland is gratefully acknowledged for the financial support for installation and maintenance of the high-frequency monitoring station and pro viding the water quality and groundwater level data. Funding of the project was provided by Deltares (project SO2015: From catchment to coast).

References

15

20

- APHA-AWWA-WPCF: Standard Methods for the Examination of Water and Waste Water, edited by: Clesceri, G., American Public Health Association, American Water Works Association, Water Environment Federation, W. W. Norton & Company, Washington, D.C., 1989.
- Baken, S., Verbeeck, M., Verheyen, D., Diels, J., and Smolders, E.: Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches, Water Res., 71, 160–170, 2015.

Berendrecht, W. L., Heemink, A. W., van Geer, F. C., and Gehrels, J. C.: Decoupling of modelling and measuring interval in groundwater time series analysis based on response characteris-

tics, J. Hydrol., 278, 1–16, doi:10.1016/S0022-1694(03)00075-1, 2003.

- Bieroza, M. Z., Heathwaite, A. L., Mullinger, N. J., and Keenan, P. O.: Understanding nutrient biogeochemistry in agricultural catchments: the challenge of appropriate monitoring frequencies, Environ. Sci. Proc. Imp., 16, 1676–1691, doi:10.1039/c4em00100a, 2014.
- Boers, P. C. M. and van Hese, O.: Phosphorus release from the peaty sediments of the Loosdrecht Lakes (the Netherlands), Water Res., 22, 355–363, 1988.



- Bouwman, L., Goldewijk, K. K., Van Der Hoek, K. W., Beusen, A. H. W., Van Vuuren, D. P., Willems, J., Rufino, M. C., and Stehfest, E.: Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900–2050 period, P. Natl. Acad. Sci., 110, 20882–20887, doi:10.1073/pnas.1012878108, 2013.
- ⁵ 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, Sci. Total Environ., 511, 608–620, doi: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 Francisco, 575 pp., 1970.
 - Cassidy, R. and Jordan, P.: Limitations of instantaneous water quality sampling in surface-water catchments: comparison with near-continuous phosphorus time-series data, J. Hydrol., 405, 182–193, doi:10.1016/j.jhydrol.2011.05.020, 2011.

Cirmo, C. P. and McDonnell, J. J.: Linking the hydrologic and biogeochemical controls of nitro-

- gen transport in near-stream zones of temperate-forested catchments: a review, J. Hydrol., 199, 88–120, doi:10.1016/S0022-1694(96)03286-6, 1997.
 - Cleveland, W. S.: Robust locally weighted regression and smoothing scatterplots, J. Am. Stat. Assoc., 74, 829–836, 1979.

Correll, D. L., Jordan, T. E., and Weller, D. E.: Transport of nitrogen and phosphorus from Rhode River watersheds during storm events, Water Resour. Res., 35, 2513–2521, 1999.

20

Djodjic, F., Ulén, B., and Bergström, L.: Temporal and spatial variations of phosphorus losses and drainage in a structured clay soil, Water Res., 34, 1687–1695, doi:10.1016/S0043-1354(99)00312-7, 2000.

Duan, S., Kaushal, S. S., Groffman, P. M., Band, L. E., and Belt, K. T.: Phosphorus export across

²⁵ an urban to rural gradient in the Chesapeake Bay watershed, J. Geophys. Res.-Biogeo., 117, G01025, doi:10.1029/2011JG001782, 2012.

- 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, Sci. Total Environ., 329, 165–182, doi:10.1016/j.scitotenv.2004.02.023, 2004.
- ³⁰ Ferrick, M. G. and Gatto, L. W.: Quantifying the effect of a freeze–thaw cycle on soil erosion: laboratory experiments, Earth Surf. Proc. Land., 30, 1305–1326, doi:10.1002/esp.1209, 2005.



- Fraters, B., Kovar, K., Willems, W., Stockmarr, J., and Grant, R.: Monitoring effectiveness of the EU Nitrates Directive Action Programmes. Results of the international MonNO3 workshop in the Netherlands, 11–12 June 2003, RIVM, Bilthoven, the Netherlands, 2005. Gemalen: available at: http://www.gemalen.nl/, last access: 12 May 2015.
- 5 Gentry, L. E., David, M. B., Royer, T. V., Mitchell, C. A., and Starks, K. M.: Phosphorus transport pathways to streams in tile-drained agricultural watersheds, J. Environ. Qual., 36, 408–415, doi:10.2134/jeg2006.0098, 2007.
 - Geurts, J. J. M., Hetjens, H., and Lamers, L. P. M.: Remobilization of Nutrients After Un-Deepening of Lakes, Radbouduniversiteit Nijmegen, Nijmegen, 2013.
- Griffioen, J., Vermooten, S., and Janssen, G.: Geochemical and palaeohydrological controls on 10 the composition of shallow groundwater in the Netherlands, Appl. Geochem., 39, 129–149, doi:10.1016/j.apgeochem.2013.10.005, 2013.
 - Groen, K. P.: Pesticide leaching in polders, Field and model studies on cracked clays and loamy sand, van land tot zee, Ministerie van Verkeer en Waterstaat, Directoraat-Generaal Rijkswaterstaat, Lelystad, 1997.

15

- Halliday, S. J., Wade, A. J., Skeffington, R. A., Neal, C., Reynolds, B., Rowland, P., Neal, M., and Norris, D.: An analysis of long-term trends, seasonality and short-term dynamics in water quality data from Plynlimon, Wales, Sci. Total Environ., 434, 186-200, doi:10.1016/j.scitotenv.2011.10.052, 2012.
- Haygarth, P. M., Wood, F. L., Heathwaite, A. L., and Butler, P. J.: Phosphorus dynamics ob-20 served through increasing scales in a nested headwater-to-river channel study, Sci. Total Environ., 344, 83–106, doi:10.1016/j.scitotenv.2005.02.007, 2005.
 - Hirsch, R. M., Slack, J. R., and Smith, R. A.: Techniques of trend analysis for monthly water guality data, Water Resour. Res., 18, 107–121, doi:10.1029/WR018i001p00107, 1982.
- 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, Agr. Water Manage., 57, 155-173, doi:10.1016/S0378-3774(02)00057-4, 2002.
 - Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K. G., Jordan, P., Sawarieh, A., Blum, P., and Goldscheider, N.: Technical Note: Field experiences using
- UV/VIS sensors for high-resolution monitoring of nitrate in groundwater, Hydrol. Earth Syst. 30 Sci., 19, 1589–1598, doi:10.5194/hess-19-1589-2015, 2015.



- Jarvie, H. P., Mortimer, R. J. G., Palmer-Felgate, E. J., Quinton, K. S., Harman, S. A., and Carbo, P.: Measurement of soluble reactive phosphorus concentration profiles and fluxes in river-bed sediments using DET gel probes, J. Hydrol., 350, 261–273, 2008.
- Johnes, P. J.: Uncertainties in annual riverine phosphorus load estimation: impact of load esti-
- mation methodology, sampling frequency, baseflow index and catchment population density, J. Hydrol., 332, 241–258, doi:10.1016/j.jhydrol.2006.07.006, 2007.
 - Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrol. Earth Syst. Sci., 11, 372–381, doi:10.5194/hess-11-372-2007, 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, J. Contam. Hydrol., 160, 53–64, doi:10.1016/j.jconhyd.2014.02.005, 2014.
 - 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, Hydrol. Process., 18, 1353–1359, doi:10.1002/hyp.5537, 2004.
- ¹⁵ doi:10.1002/hyp.5537, 2004.
 - Knotters, M. and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, J. Hydrol., 197, 25–46, doi:10.1016/S0022-1694(96)03278-7, 1997.

Lavoie, M. and Auclair, J.-C.: Phosphorus mobilization at the sediment-water interface in soft-

- water shield lakes: the role of organic carbon and metal oxyhydroxides, Aquat. Geochem., 18, 327–341, doi:10.1007/s10498-012-9166-3, 2012.
 - LNV: Fourth Dutch Action Programme (2010–2013) concerning the Nitrates Directive; 91/676/EEC, the Hague, 2009.

Loeb, R., Lamers, L. P. M., and Roelofs, J. G. M.: Prediction of phosphorus mobilisation in

- ²⁵ inundated floodplain soils, Environ. Pollut., 156, 325–331, doi:10.1016/j.envpol.2008.02.006, 2008.
 - Meinardi, C. R. and Van der Eertwegh, G. A. P. H.: Investigations on Tile Drains in Clayey Regions of the Netherlands, Part II: Interpretation of Data, RIVM, Bilthoven, the Netherlands, 1997.
- Mulholland, P. J., Newbold, J. D., Elwood, J. W., Ferren, L. A., and Jackson, R. W.: Phosphorus spiralling in a woodland stream: seasonal variations, Ecology, 66, 1012–1023, 1985.
 - Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J. W., Neal, M., Sleep, D., Lawlor, A., Woods, C., Thacker, S., Guyatt, H., Vincent, C., Hockenhull, K., Wickham, H., Harman, S.,



and Armstrong, L.: High-frequency water quality time series in precipitation and streamflow: from fragmentary signals to scientific challenge, Sci. Total Environ., 434, 3–12, doi:10.1016/j.scitotenv.2011.10.072, 2012.

Nyenje, P. M., Meijer, L. M. G., Foppen, J. W., Kulabako, R., and Uhlenbrook, S.: Phosphorus transport and retention in a channel draining an urban, tropical catchment with informal set-

- tlements, Hydrol. Earth Syst. Sci., 18, 1009–1025, doi:10.5194/hess-18-1009-2014, 2014. Palmer-Felgate, E. J., Jarvie, H. P., Williams, R. J., Mortimer, R. J. G., Loewenthal, M., and
- Neal, C.: Phosphorus dynamics and productivity in a sewage-impacted lowland chalk stream, J. Hydrol., 351, 87–97, doi:10.1016/j.jhydrol.2007.11.036, 2008.
- Polder, available at: http://en.wikipedia.org/wiki/Polder (last access: 12 May 2014), 2015. Poor, C. J. and McDonnell, J. J.: The effects of land use on stream nitrate dynamics, J. Hydrol., 332, 54–68, doi:10.1016/j.jhydrol.2006.06.022, 2007.

Regelink, I. C., Koopmans, G. F., van der Salm, C., Weng, L., and van Riemsdijk, W. H.: Characterization of colloidal phosphorus species in drainage waters from a clay soil using asymmet-

- ric flow field–flow fractionation, J. Environ. Qual., 42, 464–473, doi:10.2134/jeq2012.0322, 2013.
 - 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), Environ. Pollut., 148, 695–706, doi:10.1016/j.envpol.2007.01.028, 2007.
- 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, Environ. Sci. Technol., 44, 6305–6312, 2010.
 - 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, Environ. Monit. Assess., 186, 8981–8995, doi:10.1007/s10661-014-4059-0, 2014.
 - Schoch, A. L., Schilling, K. E., and Chan, K.-S.: Time-series modelling of reservoir effects on river nitrate concentrations, Adv. Water Resour., 32, 1197–1205, doi:10.1016/j.advwatres.2009.04.002, 2009.
- ³⁰ 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, Hydrol. Res., 44, 995–1012, doi:10.2166/nh.2013.087, 2013.



- Simard, R. R., Beauchemin, S., and Haygarth, P. M.: Potential for preferential pathways of phosphorus transport, J. Environ. Qual., 29, 97–105, 2000.
- 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, doi:10.5194/hess-19-2491-2015, 2015. Stutter, M. I., Langan, S. J., and Cooper, R. J.: Spatial contributions of diffuse inputs and withinchannel processes to the form of stream water phosphorus over storm events, J. Hydrol., 350, 203–214, doi:10.1016/j.jhydrol.2007.10.045, 2008.
- Tiemeyer, B., Lennartz, B., and Kahle, P.: Analysing nitrate losses from an artificially drained lowland catchment (North-Eastern Germany) with a mixing model, Agr. Ecosyst. Environ.,
 - 123, 125–136, doi:10.1016/j.agee.2007.05.006, 2008. 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 U.B. Wageningen, 2012

Alterra Wageningen UR, Wageningen, 2012.

20

- Van de Ven, G. P.: Man-made Lowlands, History of Water Management and Land Reclamation in the Netherlands, Uitgeverij Matrijs, Utrecht, 2003.
- 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, Wageningen, 2002.
- 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, doi:10.5194/hess-18-4687-2014, 2014.

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, J. Environ. Qual., 41, 229–241, doi:10.2134/jeq2011.0292, 2012.
 - 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 environ-
- ³⁰ mental impacts of nitrogen fertilization in northwestern Europe under the Nitrates Directive; a benchmark study, Biogeosciences, 9, 5143–5160, doi:10.5194/bg-9-5143-2012, 2012.



von Asmuth, J. R., Bierkens, M. F. P., and Maas, K.: Transfer function-noise modelling in continuous time using predefined impulse response functions, Water Resour. Res., 38, 23-1–23-13, doi:10.1029/2001WR001136, 2002.

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, Hydrol. Earth Syst. Sci., 16, 4323–4342, doi:10.5194/hess-16-4323-2012, 2012.
 - Withers, P. J. A. and Jarvie, H. P.: Delivery and cycling of phosphorus in rivers: a review, Sci. Total Environ., 400, 379–395, 2008.

10

Withers, P. J. A., Ulén, B., Stamm, C., and Bechmann, M.: Incidental phosphorus losses – are they significant and can they be predicted?, J. Plant Nutr. Soil Sc., 166, 459–468, doi:10.1002/jpln.200321165, 2003.

Worrall, F., Swank, W. T., and Burt, T. P.: Changes in stream nitrate concentrations due to land

- ¹⁵ management practices, ecological succession, and climate: developing a systems approach to integrated catchment response, Water Resour. Res., 39, HWC11–HWC114, 2003.
 - 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.

	HESSD 12, 8337–8380, 2015 Transport processes in an agriculture-				
	dominated lowland water system				
200	B. van der Grift et al.				
	Title	Page			
_	Abstract	Introduction			
	Conclusions	References			
	Tables	Figures			
5	14	►I			
5	•	•			
-	Back	Close			
	Full Scr	een / Esc			
2.	Printer-frier	ndly Version			
	Interactive	Discussion			
7	œ	() BY			

cussion apa

Discussion Pa	HESSD 12, 8337–8380, 2015					
iper D	Transport processes in an agriculture- dominated lowland					
iscussion F	B. van der Grift et al.					
aper	Title Page					
Disc	AbstractIntroductionConclusionsReferences					
ussion F	Tables Figures					
aper	• • • •					
Discussi	Back Close Full Screen / Esc Printer-friendly Version					
on Paper	Interactive Discussion					
_						

Table 1. Locations of the low-frequency monitoring program in Lage Afdeling pumped drainage area 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 Aldeling 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"	

Rainfall event	Date	mm	NO ₃ concentration before event	Maximal NO ₃ concentration after event
1	20–23 Oct	31	0.7	0.8
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

Table 2. Rainfall events and response of NO_3 concentration (in mgNL⁻¹).





Figure 1. Map of the Lage Afdeling pumped drainage area. The flow direction of the water in the channels that are drained by pumping station Blocq van Kuffeler is illustrated by arrows.





Figure 2. High-frequency monitoring data for the Lage Vaart channel at the pumping station Blocq van Kuffeler together with the 1 day antecedent precipitation and the pumping regime: top panel: total phosphorus 20 min data, with TP and DRP manual sampled biweekly data, precipitation data and discharge as generated by the pumping station; middle panel: nitrate-N 5 min data, with NO₃-N manual sampled biweekly data; bottom panel: conductivity, air temperature (from KNMI weather station Lelystad) and water temperature.





Figure 3. Examples surface water NO₃ and TP dynamics at the pumping station Blocq van Kuffeler during meteorological events between November 2014 and February 2015 together with the pumping regime and precipitation (in mmh^{-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_3 concentrations and rainfall data (top panel); and residual NO_3 series (bottom panel).





Figure 5. Measured and calculated P and NO₃ loads at the pumping station Blocq van Kuffeler.





Interactive Discussion



8379



Figure 7. Low-frequency time series of NO_3 , N-kjeldahl, TP, DRP, O_2 , SO_4 and Cl concentration at surface water sampling location in the Lage Afdeling drainage area during the period January 2014 to March 2015. Figure 1 for locations.

