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

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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 or for reducing export loads to downstream water bodies. This paper introduces new insights in nutrient sources and transport processes in a polder in the Netherlands situated below sea level 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 NO_3 concentration at the pumping station originated from N-loss from agricultural lands. The NO_3 loads appear as losses via tube drains after intensive rainfall events during the winter months due to preferential flow through the cracked clay soil. Transfer function-noise modelling of hourly NO_3 concentrations reveals that a large part of the dynamics in NO_3 concentrations during the winter months can be related to rainfall. The total phosphorus (TP) concentration and turbidity 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 NO_3 concentrations did not results in TP concentration peaks. The rainfall induced and NO_3 enriched quick interflow, may also be enriched in TP but retention of TP due to sedimentation of particulate P then results in the absence of rainfall induced TP concentration peaks. 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

primarily 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.

Keywords

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

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 (Bouwman et al., 2013a). Policy makers of national governments, the European Union and other authorities aim to improve water quality in surface water bodies that receive nutrient load from agriculture or other sources like sewage effluent (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 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., 2013b), due to a highly concentrated and productive agricultural sector.

For the evaluation of action programs and pilot studies, water authorities invest heavily in the monitoring of NO_3 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., 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 NO_3

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, 1997).

As a consequence of the dynamic behavior of nutrient transfer from land to surface water and in-stream 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 catchment 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 nutrient monitoring has revealed the 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). Large changes in concentrations or fluxes of materials over relatively short time periods are increasingly recognized as important pathways of nutrient delivery to surface water bodies (Kaushal et al., 2014). In the Netherlands, there is a still debate about the risk of incidental losses associated with manure application (Akkermans and Hermans, 2014). 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). The potential risk for incidental nutrient losses after manure application in February and March (before the start of the growing season) is not known. High-frequency monitoring is a powerful tool to detect such incidental losses.

In many low-lying areas worldwide, water levels are managed by inlet of diverted river water in dry periods and discharge via pumping stations in wet periods. Such an embanked land with a human controlled water regime is called a ‘polder’. 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 drainage catchments which may impact biogeochemical or hydrological 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.

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 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 in polder areas (2) to characterize the importance of incidental losses caused by intensive rainfall events whether or not 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 km^2, 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 confining layer of Holocene marine sediments, with a thickness of less than 0.5 m 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 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 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 Blocq van Kuffeler has four electrically powered pumps. Two pumps with a capacity of 750 m^3 min^{-1} each drain the Lage Afdeling. Operation of the pumping stations with one pump causes a flow velocity in the main channel of approximately 0.125 m sec^{-1} and with both pumps the flow velocity is approximately 0.25 m sec^{-1}. Up to 2008, the pumping station 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 renovation, the operational management of the pumping station is automatically controlled by a series of water level pressure sensors in the area. The pumps run predominantly during evening en night hours because of cheaper power supply during these hours. 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 Blocq van Kuffeler, is illustrated by arrows in Fig. 1. Pumping 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 Blocq van Kuffeler pumping station under normal meteorological conditions. There is a sewage treatment plant in the area that discharges its effluent to the Lage Vaart (Fig. 1). The average effluent discharge is 0.35 m^3 min^{-1}. The TP concentration in the effluent water is maximal 0.5 mg L^{-1} and the maximal NO_3 concentration is 1.5 mg N L^{-1} . The TP load to the Lage Vaart in the period October 2014 – October 2015 equals approximately 5400 kg and the NO_3 load 16400 kg N. There are no other sources of sewage discharge to the surface water within the Lage Afdeling drainage area.

2.2 Low-frequency monitoring

Grab samples were collected every two or four weeks from January 2014 to October 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. TP, dissolved reactive P (DRP), NO_3, NH_4 and Cl where determined using standard colorimetric methods (APHA-AWWA-WPCF, 1989). Organic-N was extracted by Kjeldahl extraction and measured by colorimetric method and sulphate was measured using IC (Ion Chromatography).

2.3 High-frequency measurements

Between October 2014 and October 2015 we measured the total-P (TP), total reactive P (TRP) and NO_3 concentration, turbidity, conductivity and water temperature semi-continuously at the polder outlet just before the pumping station. TRP include all P forms that are measured with the molybdenum blue method (Murphy and Riley, 1962) in unfiltered samples, those include acid labile phosphorus containing compounds (inorganic and organic) (Worsfold et al., 2005). The flow regime at the monitoring location is governed almost exclusively by the pumping station. The conductivity was measured continuously with a CTD-diver (Van Essen Instruments, Delft, the Netherlands).

The NO_3 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 NO_3 at a wavelength of 218 nm at a measuring receiver (EM – element for measuring) and at 228 nm at a reference receiver (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 (Huebsch et al., 2015). The Nitratax sensor covers a NOx-N detection range of 0.1 to 50.0 mg L^{-1}. The NO_3 concentrations were recorded every 5 minutes. There was a small drift in the signal of the Nitratax sensor (max 0.35 mg N L^{-1} per month). We, therefore, corrected the high-frequency NO_3 data using the NO_3 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 minutes. The Sigmatax was installed for the automated water sample collection and the pretreatment (ultrasonic homogenization). Next, the 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, the reagents were automatically added and the sample was measured at 880 nm using a LED photometer. The Phosphax Sigma was automatically cleaned and calibrated daily. 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 (R^2 = 0.982) and, therefore, no need to correct the high-frequency TP data (Fig. S1).

The turbidity (FTU) was measured using a OBS (optical back scatter) sensor (SOLITAX t-line sc, Hach Lange GmbH Düsseldorf, Germany) that receives the reflected light from the sediment-laden flow. Instead of directly obtaining the suspended sediment concentration, a turbidity sensor measures the turbidity of flow caused by suspended sediment (Gao, 2008). The FTU data was stored with a time interval of 5 minutes. There was a close agreement between the high-frequency turbidity data (FTU) and the suspended sediment concentrations (mg L^{-1}) of the grab samples (R^2 = 0.965) (Fig. S1).

2.4 Background 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 station 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 (Fig. 1).

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 (Cl between 7 and 4500 mg L^{-1}) and P-rich (TP between 0.01 and 3.6 mg P L^{-1}) with low NO_3 concentrations (between 0 and 7 mg NO_3 L^{-1}) (Fig. S2).

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 NO_3 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) or relate precipitation data to high-frequency observation of dissolved organic carbon (Jones et al., 2014), 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 NO_3 concentration measurements to rainfall using the following linear TFN model:

$$\log(NO_3) = \theta(B)p_t + \mu + n_t \quad (1)$$

and

$$n_t = \phi n_{t-1} + \varepsilon_t, \quad (2)$$

with p_t the precipitation at time t, $\theta(B) = \theta_0 + \theta_1 B + \cdots + \theta_r B^r$ 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 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 NO_3 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 groundwater dynamics:

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

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

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). To quantify the event-driven TP export load generated by changes in the water flow due to pumping, a hydrograph separation method was used to separate the high-frequency TP concentration data series into short-term TP concentration peaks and baseline TP concentration. In this study we used the same method as applied by Rozemeijer and Broers (2007). This method, originally developed by (Hewlett and Hibbert, 1963), separates the baseline concentration and the peak concentration by a separation line with a constant slope (Fig. S4). This line starts whenever the slope of the concentration series exceeds a specified constant separation slope. The separation line ends when it intersects the falling limb of the concentration series. For this study, a constant separation slope of 0.02 mg P L^{-1} d^{-1} was used. With this relatively low slope value, concentration peaks were also separated from the baseline concentration during situations of upward trends in TP concentrations.

Long term TP and NO_3 concentration measurements were available for the polder outlet. We used two frequently applied methods for trend analysis of concentration-time series: (1) seasonal Mann-Kendall tests (Hirsch and Slack, 1984) (2) Theil-Sen robust line (Hirsch et al., 1982) and (3) 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 seasonal Mann-

Kendall trend test is a robust, non-parametric test on the significance of an upward or downward trend. The Theil-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. We refer to Rozemeijer et al. (2014) for details on the statistical methods.

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.

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. There was a strong decline of the daily pumping hours from mid-April to the end of July. A wet period from mid-August to mid-September resulted in an increase of pumping hours. The pumping station pumped almost 70×10^6 m^3 water from the polder into the Markermeer during the period from October 2014 until March 2015 and 30×10^6 m^3 during the period from April 2015 until October 2015. This corresponds to approximately 350 mm distributed across the entire drainage area for the winter half year (Oct-March) and 150 mm for the summer half year (April-Sept.). The sum of the precipitation was 455 mm and 517 mm for the winter half year and summer half year, respectively.

3.2 Seasonal trends in high-frequency nutrient data

The high-frequency NO_3 concentration measured at the Blocq van Kuffeler pumping station ranged from 0.01 to 10.4 mg N L^{-1} and the total phosphorus (TP) concentration ranged from 0.07 to 1.16 mg P L^{-1}. (Fig. 2). The NO_3 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. The high-frequency NO_3 data showed a seasonal pattern and a response to rainfall. The NO_3 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 NO_3 concentration.

The NO_3 concentration increased from a level of 1 mg N L^{-1} to a maximum concentration of 9 mg N L^{-1} from mid-November to the third week of January. Major increases of the NO_3 concentration occurred during pumping from 18 to 21 November, 16 to 23 December and 13 to 18 January which showed that the NO_3 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 NO_3 concentration decreased to a level of 1 mg N L^{-1}. Next, the concentration reached a maximum of 10.4 mg N L^{-1} 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. During April the concentration declined to a level around 0.5 mg N L^{-1} or below and stayed at this low level until mid-August. The NO_3 concentration rapidly increased to approximately 3 mg N L^{-1} 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.

The high-frequency total-P (TP) data showed a seasonal variation, a response to rainfall and a response to pumping as well. The TP concentration was, with concentrations that ranged from 0.25 to 0.4 mg P L^{-1}, high during the first three weeks of the monitoring period. In October and November, the TP concentration decreased during wet periods to a concentration of approximately 0.15-0.2 mg P L^{-1} and increased again during the dryer periods to levels around 0.3 to 0.4 mg P L^{-1}. During the first two weeks of December, the TP concentration decreased to a level around 0.1 mg P L^{-1}. This baseline level remained at this level until halfway February. During the relatively dry period in February and March there was a gradual increase of the TP concentration to a level around 0.2 mg P L^{-1}. It remained at this level until mid-June. During the period from mid-June to mid-August the TP concentration gradually increased and peaked with a concentration of 1.2 mg P L^{1} during a wet period in mid-August. After this wet period in mid-August the TP concentration decreased to a level of approximately 0.1-0.2 mg P L^{-1}. Towards the end of the monitoring period the TP concentration peaked once more at a level of approximately 0.6 mg P L^{-1}. The high-frequency total-reactive P (TRP) data and the dissolved reactive P (DRP) data from the low-frequency monitoring program showed rather high concentrations from the start of the monitoring to early December 2014 and then declined to concentration below 0.1 mg P L^{-1}. The TRP and DRP concentration remained at this low level until the second half of May. During the period from mid-May to mid-August the TRP and DRP concentrations followed the trend of the increasing TP concentrations.

3.3 Short scale dynamics in high-frequency nutrient data

Significant increases of the NO_3 concentration up to 8 mg N L^{-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, 29 March-2 April, 14-18 August and 26-31 August (Fig. 3 and Table 2). The precipitation during these events peaked around 20 mm or above. The increase in NO_3 concentration did not appear after the precipitation events on 20-23 October, 3-4 November 17-23 June and 27-29 July. As it will be discussed in section 4, this is likely due to the absence of tube drain discharge upon these precipitation events. For the events from mid-November to early April, it applies that the response of the NO_3 concentration to rainfall was delayed and occurred about five days after the rainfall event. After this NO_3 concentration peak, the concentration declined during pumping. The period of five days between rainfall event and peak in the NO_3 concentration at the pumping station is representative for the average residence time of water in the Lage Afdeling drainage area during wet conditions. Catchment mean residence times are much shorter during wet periods compared dry periods (Van der Velde et al., 2012). The five days travel time of the water in the field ditches, sub-channels and main channel during wet conditions is in line with model calculated mean annual residence times of water in the Lage Vaart main channel of 6.6 days (Van den Eertwegh, 2002).

There is a structural response of the TP concentration and the turbidity on operation of the pumping station. The TP concentration and turbidity always peaked directly after the start of the pumping-engines and decreased again during the period of pumping and afterwards (Fig. 2 and Fig. 3). Pumping events with one pump resulted in an average increase of the TP concentration of 0.06 mg L^{-1} while events with two pumps resulted in an average increase of 0.13 mg L^{-1} (Table 3).The TP concentration was on average a factor of 1.30 and 1.83 higher during pumping with one pump and two pumps, respectively, compared to the concentration before pumping. The increase of the TP concentration and turbidity during operation of the pumping station and the larger increase during pumping with two pumps compared to one pump (Table 3) indicates that the increase of the TP concentration is related to resuspension of P from bed sediments due to increased flow velocities. The TRP concentrations also showed an increase in concentration during pumping. As the colorimetric measurement of TRP takes place in an acidic solution it is plausible to attribute the increase of the TRP concentration during pumping to the dissolution of particulate Fe or Ca bound inorganic P. The data shows the largest increase of TP concentrations (0.16-0.60 mg P L^{-1-}) 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). This indicates that during no-pumping conditions, an erodible layer builds up by sedimentation of particulate P. When the water flow velocities in the main channel increase upon pumping, the P becomes suspended and transported downstream. Short-term declines of the TP concentrations to values below the pre-pumping concentration were observed during pumping or shortly after pumping induced by rainfall periods in October, June and August (Fig. 3).

A significant short-term change in NO_3 and TP concentrations and the conductivity during a period without pumping appeared on 26 January (Fig. 2 and Fig. 3). The decrease in the NO_3 concentration (from 6.1 to 1.5 mg N L^{-1}) and increase in the TP concentration (from 0.09 to 0.21 mg P L^{-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). 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 L^{-1}) and decrease of the conductivity (from 235 to 122 mS cm^{-1}) (Fig. S3) were observed. 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 consisted of 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 NO_3 concentration and conductivity and increased the TP concentration and turbidity. This strongly indicates that the increase of the TP concentration was caused by erosion of soil surface particles. The TRP did not increase during this event, suggesting the TP largely existed of non-liable organic P.

3.4 Decomposition of high-frequency nitrate data

As shown in section 3.2, NO_3 concentrations were low from the start of the monitoring period until the rainfall event on 15 November and during April the NO_3 concentrations decreased again. Precipitation events before mid-November and after April only had a minor influence on the NO_3 concentration. For the period between15 November and 30 April a transfer function-noise modelling of hourly NO_3 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; short-term dynamics cannot be related to rainfall with the transfer model and are described by the stochastic model. The estimated autoregressive coefficient ($\phi = 0.98$) is quite low given the high sampling interval of 1 hour, 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 increase in concentration is modelled well, in January the concentration is overestimated, while in February and 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 and March (see section 4). The largest negative residuals appeared during the thaw event on 26 January (see section 3.3) while the largest positive residuals appeared on 24-25 February.

The estimated model parameters and their standard deviation are given in Table S1. The estimated impulse response function for transferring an impulse of 1 mm rainfall into log-NO_3 concentration is given in Fig. S5. 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 5.4 days with a response of 0.033 log(mg NO_3-N mg L^{-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 events and peak concentrations (Fig. 2).

The reference or baseline level follows from the model estimation and has a value of μ = -1.13, or back-transformed from logarithm: $e^{-1.13}$ = 0.32 mg N L^{-1} which means that after a long no-rain period, the NO_3 concentration will decline to 0.32 mg N L^{-1}. The current time series does not include seasonal patterns; during spring and summer season the NO_3 concentration cannot be related to rainfall only. The groundwater levels drop below the tube drain levels (i.e. precipitation may not lead to discharge) and denitrification or in-stream nutrient uptake processes reduce the NO_3 concentration, so other driving forces and non-linearity have to be included in the TFN model for modelling the summer season.

3.5 Nutrient loads and fluxes at polder outlet

Cumulative loads at the polder outlet based on either linear interpolation within the low-frequency dataset or the high-frequency dataset are given in Fig. 5. For TP the cumulative 'baseline' load calculated from the high frequency dataset after separation of the pumping event-driven short-term TP peaks are given in Fig. 5 as well. The annual loads based on the high-frequency dataset equaled 19,500 kg for TP and 388,500 kg for NO_3-N. The TP load during the winter months (October – March) was almost equal to the load during the summer months (April – September) while for NO_3 almost 80% of the annual load occurred during the winter months. The annual loads calculated from the low-frequency data equaled 18200 for TP and 372500 kg for NO_3-N. The annual baseline TP load after separation of the TP concentration peaks was 15400 kg. The difference between the total load and the baseline load equaled 4100 kg, i.e., 21 % of the annual TP load can be attributed to resuspension of TP due to changes in water flow induced by the pumping station.

During the period from 1 Oct 2014 to 1 April 2015 the cumulative TP load calculated from the low-frequency data matched the baseline TP load and underestimated the high frequency load with 17%. The low-frequency NO_3 load overestimated the high-frequency load by 6.5%. From April to mid-August 2015 there was almost no NO_3 export load. During the period from April 2015 to October 2015 the difference between the baseline load and grab sample load increase. The annual grab sample load underestimated the best available data load with 6%.

Time series of TP and NO_3 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 NO_3 concentration showed no significant 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 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 mg P L^{-1} per year) over the years 2000-2015. This downward trend was significant according the seasonal Mann-Kendall trend tests.

The blue and green lines give the Theil-Sen slopes for the periods 2000-2008 and 2009-2015, respectively, before and after renovation of the pumping station. Where the Theil-Sen slope showed a decline of TP concentration over the years 2000-2015, it showed upward trends of 0.0023 mg P L^{-1} per year and 0.011 mg P L^{-1} per year over the separate periods 2000-2008 and 2009-2015, respectively. The upward trend for the period 2009-2015 was significant according the seasonal Mann-Kendall trend tests. The NO_3 concentrations showed no significant 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 almost two years 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). Chloride is an indicator for the contribution of deep groundwater to the surface water. Chloride concentrations above 500 mg L^{-1} were commonly observed in the deeper groundwater in the area upstream of location 3 and 5 (Fig. S2). Location 3 shows an inverse relation between the NO_3 and Cl concentrations (R^2 = -0.67) which illustrates the soil and shallow groundwater as source of NO_3 in the surface water. 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 Cl concentrations of location 1 during summer.

Low NO_3 concentrations were observed in discharge water from the nature area Oostvaardersplassen (location 6) throughout the year whereas high NO_3 concentrations were observed in water from the agricultural areas Lepelaartocht and Gruttotocht (location 3 and 4) in the winter (8.3 and 13 mg N L^{-1} in February 2014 and 2015, respectively). The NO_3 concentration in the urban area water (location 2) did not exceed 2 mg N L^{-1}. The NO_3 concentrations of the Lage Vaart channel water at the pumping station (location 1) during the winter months were lower compared to the NO_3 concentrations at the outlet of the agricultural areas. As denitrification is limited during winter time, this indicates dilution of agriculture-dominated water with water from nature areas or urban areas. This is confirmed by the SO_4 data that demonstrate some dilution of the agriculture-dominated water as well. The locations with high SO_4 concentrations exhibit an inverse pattern with the Cl concentration (R^2 = -0.45 for location 3). This shows the occurrence of pyrite oxidation in the shallow subsurface (Griffioen et al., 2013) in the Lage Afdeling drainage 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 mg N L^{-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 mg P L^{-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 mg P L^{-1} from January to July 2014. The concentration dropped to a level around 0.3 mg P L^{-1} or lower in August 2014 and stayed at this level until April 2015. From April 2015 to mid-September 2015 the TP concentration ranged between 0.35 and 0.74 mg P L^{-1}. 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 2014 as well compared with concentrations in other recent years (Fig. 6.). We do not have a clear explanation for this observation. The DRP concentrations were low during the first half year of 2014 and 2015. There was an increase of the DRP concentration in July 2014 and July 2015. During the first half year of 2014 and 2015 the TP concentration was dominated (> 90 %) by particulate P while in the second half year about 50% of the TP concentration consisted of DRP.

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. S2)

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 NO_3 data for identification of NO_3 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 NO_3 concentrations in groundwater (Fig. S2) and the high NO_3 concentrations in the surface water at the outlet of the agriculture-dominated areas during winter months (Fig. 7), it is clear that almost all NO_3 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 NO_3 delivery to the surface water.

The high-frequency NO_3 data showed a seasonal trend with a gradually increase from mid-November to mid-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 NO_3 concentrations are controlled by a combination of effluent loads from sewage treatment works and dilution by rainfall commonly show a decline in NO_3 from summer to winter (Bowes et al., 2015;Wade et al., 2012). The NO_3 pattern is therefore thought to be due to a combination of interflow or shallow draining groundwater with high fertilizer or manure inputs and NO_3 enrichment during autumn and winter.

Increased crop uptake of NO_3 during the growing season combined with the effect of in-stream processes result in declined NO_3 concentrations during the summer months.

The annual NO_3 load from the WWTP to the Lage Vaart is approximately 4 % of the NO_3 export load at the polder outlet. The low NO_3 concentrations during the summer months and the rapid increase after a very wet period during August additionally indicate that the influence of sewage effluent on the NO_3 concentrations is limited. The discharge from the channel that drains the nature area Oostvaarderplassen (location 6) enters the Lage Vaart between the WWTP and the pumping station and is 2 to 3 times higher than the discharge from the WWTP. This implies that there is limited flow of the WWTP effluent towards the pumping station during no pumping conditions.

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 NO_3 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 l increase implies that run-off, which dilutes the NO_3 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 NO_3 dynamics during the winter months can be related to rainfall. Meinardi and Van den Eertwegh (1997) ran a monitoring program on tube drain water composition 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 NO_3 concentrations of 14 - 18 mg N L^{-1} (van Boekel et al., 2012). These concentrations can only explain the observed NO_3 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. S6) that shows a direct response of the groundwater level on rainfall combined with a seasonal trend that shows rising groundwater levels during the months October and November and quite stable levels from December to March. Rainfall events between the start of the monitoring and mid-November and between April and mid-August did not result in tube drain discharge. The low NO_3 concentration of the surface water during these periods, are thus, explained by the absence of tube drain discharge. Extensive rainfall during the second half of August resulted in a rising of the groundwater level close to the tube drain level (Fig. S6) and thus to leaching of NO_3, stored in the soil profile, to the surface water. This is also the reason that we started the TFN model on 15 November. As rainfall is not a driving force for the NO_3 concentration before mid-November and after April, starting the TFN model on 1 October and continuing after 1 May 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 NO_3 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 quickly contributes to tube drain discharge. Due to short residence time of this water in the soil, the influence of denitrification on the NO_3 concentration is limited. This implies that the NO_3 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 NO_3 concentration, the TP concentration at the pumping station decreased after the wet periods in the autumn of 2014 and the late summer of 2015 (Fig. 2). The interflow discharge via subsurface tube drains, cracks or other macropores that resulted in an increase of NO_3 concentrations diluted the TP concentrations. Likely this can be attributed to the relative decrease of the groundwater contribution to the channel water during periods of increased interflow discharge. This indicates that the sources of TP in the channel water at the polder outlet can largely be attributed to exfiltration of P-rich groundwater that occurs throughout the year, presumably combined with effluent loads from the WWTP and biogeochemical remobilization of P from channel sediments during the 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 2015 (Fig. 7) can be explained by transition of dissolved P to particulate P at the groundwater-surface water interface. 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 annual TP load from the WWTP to the Lage Vaart is approximately 27 % of the TP export load at the polder outlet. As discussed previously for NO_3, the effect of the WWTP on the NO_3 concentration at the pumping station seems to be small. For TP, however, the WWTP load cannot be neglected. The discharge water from the Oostvaardersplassen has relatively high TP concentrations (Fig. 7) and may contribute to the increase in TP concentration at the pumping station during no pumping periods. The source of the TP in the Oostvaardersplassen is groundwater and feces of wildlife. The Oostvaardersplassen is an important wintering area for birds that import nutrients from elsewhere.

Additional to this groundwater input signal, the high DRP:TP ratios of the low-frequency monitoring program during the second half year of 2014 and the summer of 2015 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 when the TP concentration reached a maximum level between 0.8 and 1.2 mg P L^{-1}. 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 O_2 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. 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 mg P L^{-1} coming from 47 rainfall events over a year. Particulate P (PP) increases up to a factor of 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 P L^{-1} in al lowland stream during high discharge conditions while the mean concentration equaled

0.1 mg P L^{-1}. Haygarth et al. (2005) reported 10 to 20 times higher mean TP concentrations during storm flow conditions compared to base flow 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 all considerably larger than the average factor of 1.30 and 1.83 that we observed at the pumping station during pumping with one and two pumps, respectively. The P export from natural catchments during pulses at high flow in less than 10% of the time may amount to about 80% of the annual export (Kaushal et al., 2014). For our polder catchment we calculated that only 21% of the annual TP export load can be related to resuspension of TP due to changes in water flow induced by the pumping station. With 143 pumping events during the period from October 2014 to October 2015, discharge-related changes that lead to resuspension of P appear more frequent in polders compared to natural catchments. The TP concentrations that increase during dry periods in the summer and autumn, likely as a result of DRP release from the bed sediments additionally contributes the TP export loads. Therefore, it can be concluded that total P export loads from polder catchment can 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 in combination with recent manure application.

The NO_3 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 NO_3 concentration is almost two times higher compared to the other peaks in NO_3 concentration after a rainfall event (Table 2). This suggests that the NO_3 peak of 10.4 mg N L^{-1} was caused by an incidental loss after manure application that started on 1 February. The TFN model revealed high residual NO_3 concentrations up to almost 8 mg N L^{-1} during this NO_3 peak that cannot be explained by rainfall (Fig. 4). The NO_3 concentration peaks on 27 February and 3 March also showed large positive residuals of 4.2 and 3.4 mg N L^{-1}, respectively. The wet period in January resulted, however, in predicted NO_3 concentrations that were higher than the measured concentrations. The negative residuals in January can be explained by leaching of the NO_3 stored in the soil profile during the winter season in combination with the appearance of some degree of dilution of the remaining NO_3 by precipitation water during this period. Dilution of the NO_3 concentration upon rainfall events commonly observed in catchments (e.g. Rozemeijer et al., 2010;Wade et al., 2012). A plausible explanation for the large positive residuals in February and

March 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 during the beginning of the rainfall event, simultaneously with a turbidity peak after the start-up of the pumps following upon a relatively dry period of more than one week without pumping (Fig. 3). It is, therefore, not likely that this peak was caused by an incidental loss after manure application but 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 interflow 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. Several other studies ask attention for elevated TP concentrations in drain and trench flow within a few weeks after application of fertilizers or liquid farm manure (Hodgkinson et al., 2002;Simard et al., 2000;Djodjic et al., 2000). 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 NO_3 peaks at the polder outlet can be attributed to sedimentation of PP from agricultural sources in the field ditches or sub-channels where it may become a source for DRP release from bed sediments during the summer and autumn months 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 with a high affinity to retain P, at the oxic/anoxic interface around the tube drains and ditch sediment (van der Grift et al., 2014;Baken et al., 2015). The relevance of this process in the Lage Afdeling is unknown.

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. Since the renovation of the pumping station in the autumn of 2008, it runs typically overnight during normal meteorological conditions, as reason of cheaper power supply. The low-frequency sampling is always performed during daytime. The distribution of pumping hours and sampling moments over the day during the period October 2014 – September 2015 and boxplots of measured TP concentrations over the day during the months

January and February 2015 are shown in Fig. S7. These two months were selected because boxplots for longer time series are dominated by the seasonal trends in the TP concentration. 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 and consequently does not measure diurnal cycles in water quality caused by the pumping station. The reported time series from the low-frequency sampling program is, thus, not fully representative for the 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). The NO_3 concentration showed no structural response on pumping, further illustrating the importance of resuspension of 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 may be caused by the sudden decrease of concentrations after renovation of the pumping station which is an artifact of a change in pumping regimes.

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 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.

5 Conclusions

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 via clay cracks, has a dominant contribution to NO_3 loads to surface water, mainly originating from N-losses from agricultural lands during the winter. Transfer function-noise modelling of hourly NO_3 concentrations reveals that quite a large part of the dynamics in NO_3 concentrations during the winter months can be related to rainfall once groundwater tables have risen close to the tube drain levels. The NO_3 loads appear as incidental losses upon intensive rainfall events and cause high NO_3 concentrations at the polder outlet within approximately five days after the rainfall event. Such dynamics are difficult to detect with grab samples.

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. High DRP/TP ratios in grab samples from different location within the polder in the summer and autumn months further suggest that biogeochemical remobilization from bed sediments or mineralization of organic P from algae of plant debris additionally contributed to the TP concentration. The effluent load of a wastewater treatment plant finally attributes the TP concentration. Agriculture did not seem to be a direct source of the TP concentration at the polder outlet. At the moments when water at the polder outlet was enriched in NO_3, originated from the agricultural land, it had low TP concentrations.

Short-scale responses of the NO_3 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 NO_3 concentration of the channel water (caused by dilution with NO_3-poor run-off water) in combination 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-thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO_3 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 generated by the pumping station initiates short-scale hydrodynamic resuspension of particulate P from the channel bed sediment and thus an increase of the TP concentration in the surface water during pumping. This process is responsible for 21% of the annual TP export load from the polder catchment. Changes in the TP concentration upon pumping are considerably smaller compared to discharge-driven concentration 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.

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 in surface water quality.

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References

APHA-AWWA-WPCF: Standard Methods for the Examination of Water and Waste Water, edited by: Clesceri, G., Trussell, American Public Health Association, 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 Research, 71, 160-170, 2015.

Berendrecht, W. L., Heemink, A. W., van Geer, F. C., and Gehrels, J. C.: Decoupling of modeling and 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.

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, Environmental Sciences: Processes and Impacts, 16, 1676-1691, 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 Research, 22, 355-363, 1988.

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, 2013a.

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, Proceedings of the National Academy of Sciences, 110, 20882-20887, 10.1073/pnas.1012878108, 2013b.

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.

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, Journal of Hydrology, 405, 182-193, http://dx.doi.org/10.1016/j.jhydrol.2011.05.020, 2011.

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

Cleveland, W. S.: Robust locally weighted regression and smoothing scatterplots, Journal of the American Statistical Association, 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 Resources Research, 35, 2513-2521, 1999.

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.

Duan, S., Kaushal, S. S., Groffman, P. M., Band, L. E., and Belt, K. T.: Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed, Journal of Geophysical Research: Biogeosciences, 117, G01025, 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, Science of The Total Environment, 329, 165-182, 10.1016/j.scitotenv.2004.02.023, 2004.

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, 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.

Gao, P.: Understanding watershed suspended sediment transport, Progress in Physical Geography, 32, 243-263, 2008.

Gemalen: Available from: http://www.gemalen.nl/ (Accessed 12 May 2015), 2015.

Geurts, J. J. M., Hetjens, H., and Lamers, L. P. M.: Remobilization of nutrients after un-deepening of lakes (in dutch), Radbouduniversiteit Nijmegen,, Nijmegen, 2013.

Griffioen, J., Vermooten, S., and Janssen, G.: Geochemical and palaeohydrological controls on the composition of shallow groundwater in the Netherlands, Applied Geochemistry, 39, 129-149, http://dx.doi.org/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.

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, Science of The Total Environment, 434, 186-200, http://dx.doi.org/10.1016/j.scitotenv.2011.10.052, 2012.

Haygarth, P. M., Wood, F. L., Heathwaite, A. L., and Butler, P. J.: Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study, Science of The Total Environment, 344, 83-106, http://dx.doi.org/10.1016/j.scitotenv.2005.02.007, 2005.

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.

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.

Hirsch, R. M., and Slack, J. R.: A Nonparametric Trend Test for Seasonal Data With Serial Dependence, Water Resources Research, 20, 727-732, 10.1029/WR020i006p00727, 1984.

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.

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. Sci., 19, 1589-1598, 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, Journal of Hydrology, 350, 261-273, 2008.

Johnes, P. J.: Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density, Journal of Hydrology, 332, 241-258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.

Jones, T. D., Chappell, N. A., and Tych, W.: First Dynamic Model of Dissolved Organic Carbon Derived Directly from High-Frequency Observations through Contiguous Storms, Environmental Science & Technology, 48, 13289-13297, 10.1021/es503506m, 2014.

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, 53-64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.

Kaushal, S. S., Mayer, P. M., Vidon, P. G., Smith, R. M., Pennino, M. J., Newcomer, T. A., Duan, S., Welty, C., and Belt, K. T.: Land use and climate variability amplify carbon, nutrient, and contaminant pulses: A review with management implications, Journal of the American Water Resources Association, 50, 585-614, 10.1111/jawr.12204, 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, Hydrological Processes, 18, 1353-1359, 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, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.

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.

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 inundated floodplain soils, Environmental Pollution, 156, 325-331, 10.1016/j.envpol.2008.02.006, 2008.

Meinardi, C. R., and Van den 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.

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.

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, Science of The Total Environment, 434, 3-12, http://dx.doi.org/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 settlements, Hydrol. Earth Syst. Sci., 18, 1009-1025, 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, Journal of Hydrology, 351, 87-97, http://dx.doi.org/10.1016/j.jhydrol.2007.11.036, 2008.

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.

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 Asymmetric Flow Field-Flow Fractionation, J. Environ. Qual., 42, 464-473, 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), Environmental Pollution, 148, 695-706, 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, Environmental Science and Technology, 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, Environmental Monitoring and Assessment, 186, 8981-8995, 10.1007/s10661-014-4059-0, 2014.

Schoch, A. L., Schilling, K. E., and Chan, K.-S.: 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.

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.

Simard, R. R., Beauchemin, S., and Haygarth, P. M.: Potential for preferential pathways of phosphorus transport, Journal of Environmental Quality, 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, 10.5194/hess-19-2491-2015, 2015.

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.

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.

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.

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, 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, 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, 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.

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.

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.

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.

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.

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.

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.

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.

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.

Tables

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 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”

Table 2. Rainfall events and response of NO_3 concentration (in mg N L^{-1}).

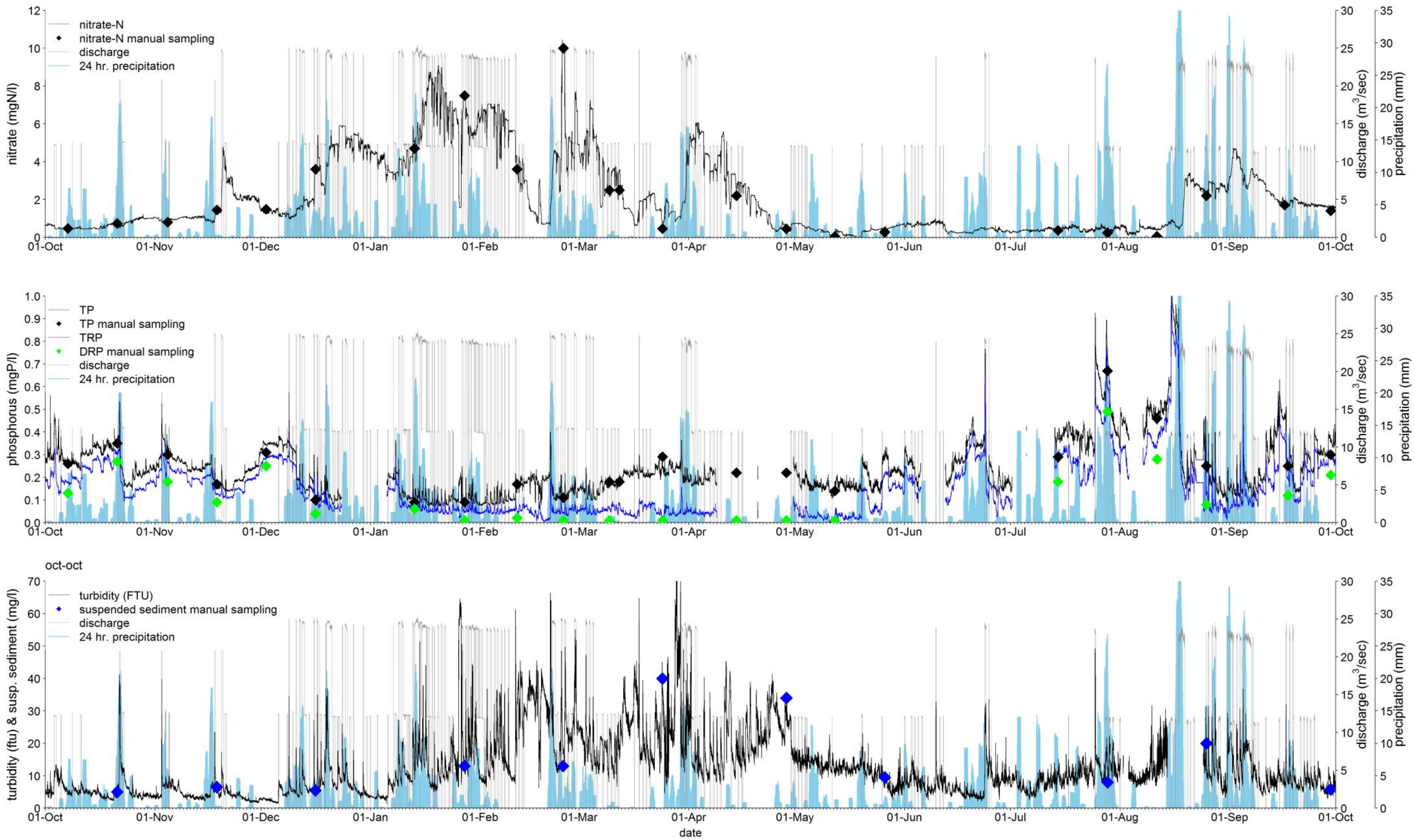
Rainfall event	date	mm	NO_3 concentration before event	Maximum NO_3 concentration after event
1	20-23 Oct	31	0.7	0.8
2	3-4 Nov	16	0.8	0.9
3	15-18 Nov	23	0.8	4.6
4	10-12 Dec	29	1.0	5.3
5	19-20 Dec	24	2.4	5.9
6	7-9 Jan	14	3.0	5.8
7	12-14 Jan	24	4.1	9.0
8	20-21 Feb	26	0.8	10.4
9	29 Mar-2-Apr	43	0.8	6.1
10	17-23 June	40	0.2	0.5
11	27-29 July	47	0.5	0.7
12	14-18 Aug	87	0.6	3.4
13	26-31 Aug	59	2.4	4.7

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

	Δ TP (mg L^{-1})	Δ turbidity (FTU)	Δ TP (mg L^{-1})	Δ turbidity (FTU)
	1 pump	1 pump	2 pumps	2 pumps
n peaks	72	79	59	60
average	0.06	4.4	0.13	22.1
median	0.04	4.4	0.10	21.1
P25	0.01	1.8	0.07	14.0
P75	0.08	8.3	0.14	29.2
max	0.58	26.2	0.61	52.0
min	-0.01	-1.5	0.03	5.9

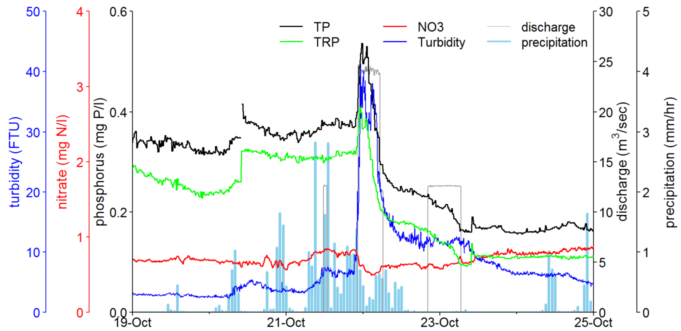
Figures

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

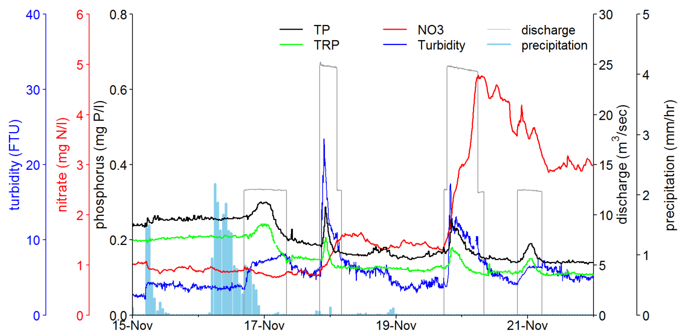


nitrate-N
nitrate-N manual sampling
discharge
24 hr. precipitation
nitrate (mgN/l)
discharge (m³/sec)
precipitation (mm)
TP
TP manual sampling
TRP
DRP manual sampling
phosphorus (mgP/l)
oct-oct
turbidity (FTU)
suspended sediment manual sampling
turbidity (ftu) & susp. sediment (mg/l)
01-Oct
01-Nov
01-Dec
01-Jan
01-Feb
01-Mar
01-Apr
01-May
01-Jun
01-Jul
01-Aug
01-Sep
date

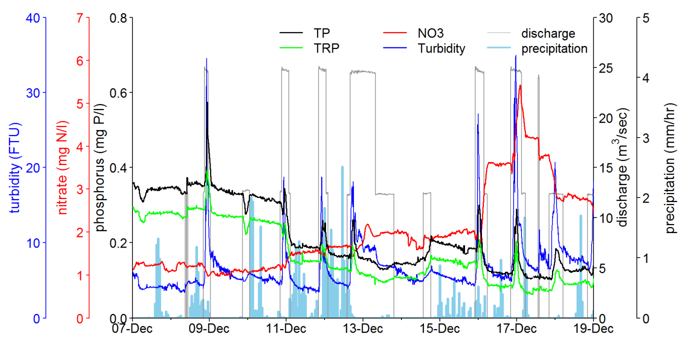
Figure 2. High-frequency monitoring data for the Lage Vaart channel at the pumping station Blocq van Kuffeler together with the 1 day antecedent precipitation and discharge as generated by the pumping station: (top) nitrate-N 5 minutes data, with NO_3-N manual sampled biweekly data; (middle) total phosphorus and total reactive phosphorus 20 minutes data, with TP and DRP manual sampled biweekly data; (bottom) turbidity 5 minutes data, with suspended sediment manual sampled monthly data.


TP
TRP
NO3
Turbidity
discharge
precipitation
turbidity (FTU)
nitrate (mg N/l)
phosphorus (mg P/l)
discharge (m^3/sec)
precipitation (mm/hr)
19-Oct
21-Oct
23-Oct
25-Oct

1


TP
TRP
NO3
Turbidity
discharge
precipitation
turbidity (FTU)
nitrate (mg N/l)
phosphorus (mg P/l)
discharge (m^3/sec)
precipitation (mm/hr)
15-Nov
17-Nov
19-Nov
21-Nov

2


TP
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turbidity (FTU)
nitrate (mg N/l)
phosphorus (mg P/l)
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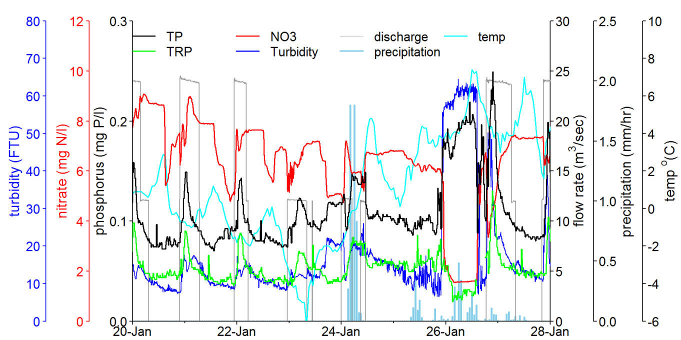
precipitation (mm/hr)
07-Dec
09-Dec
11-Dec
13-Dec
15-Dec
17-Dec
19-Dec

3


TP
TRP
NO3
Turbidity
discharge
precipitation
temp
turbidity (FTU)
nitrate (mg N/l)
phosphorus (mg P/l)
flow rate (m^3/sec)
precipitation (mm/hr)
temp ^{o}(C)
20-Jan
22-Jan
24-Jan
26-Jan
28-Jan

4

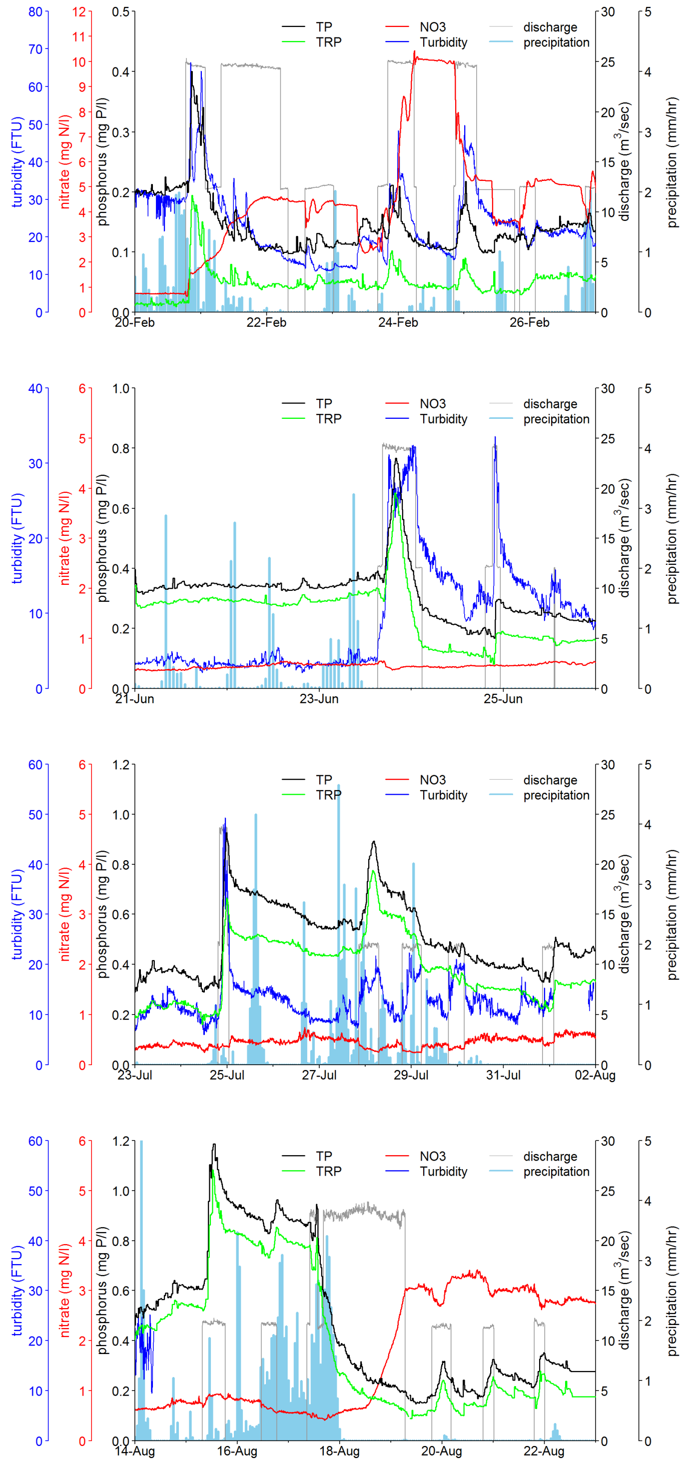


Figure 3. Examples of surface water NO_3, TP and turbidity dynamics at the pumping station Blocq van Kuffeler during meteorological events between October 2014 and August 2015 together with the pumping regime and precipitation (in mm hr^{-1}). The January event demonstrates the effect of freeze-thaw on the nutrient concentrations while the other events show the nutrient dynamics upon rainfall events.

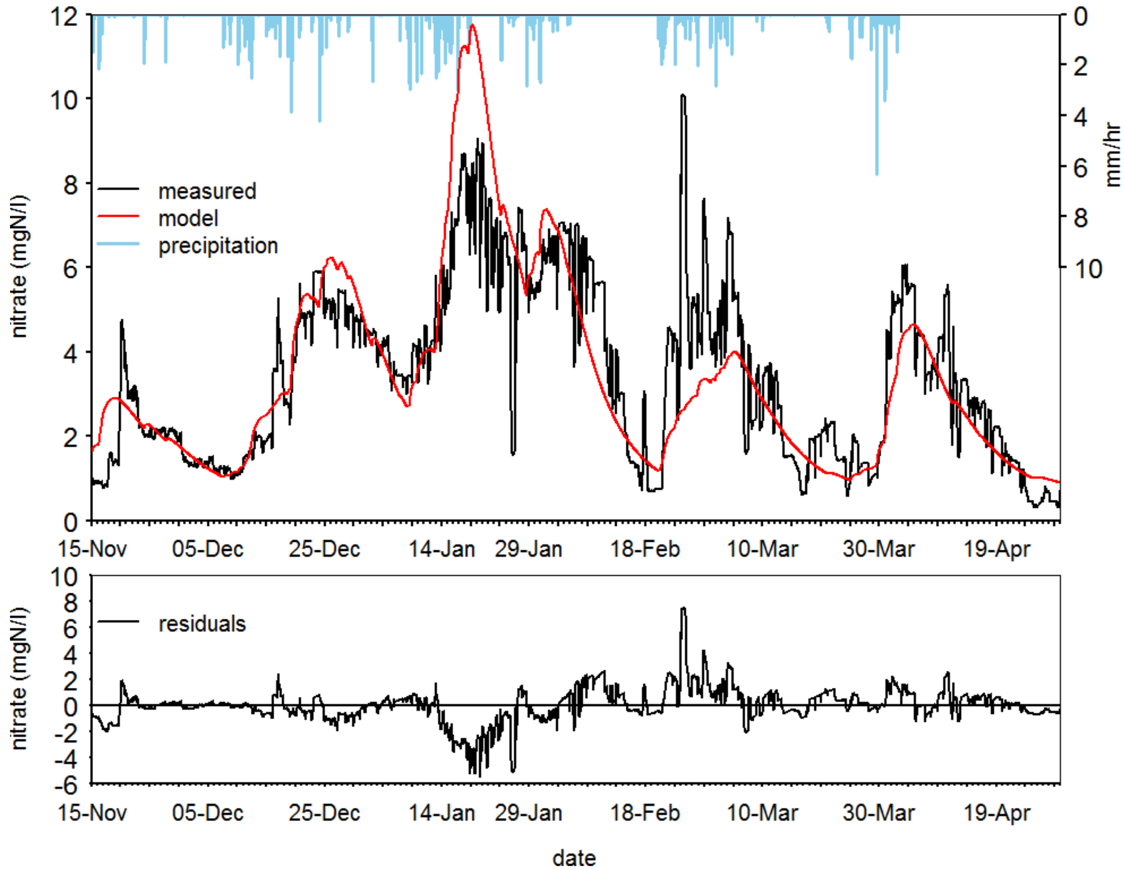


Figure 4. Measured and simulated NO_3 concentrations and rainfall data (top); and residual NO_3 series (bottom).

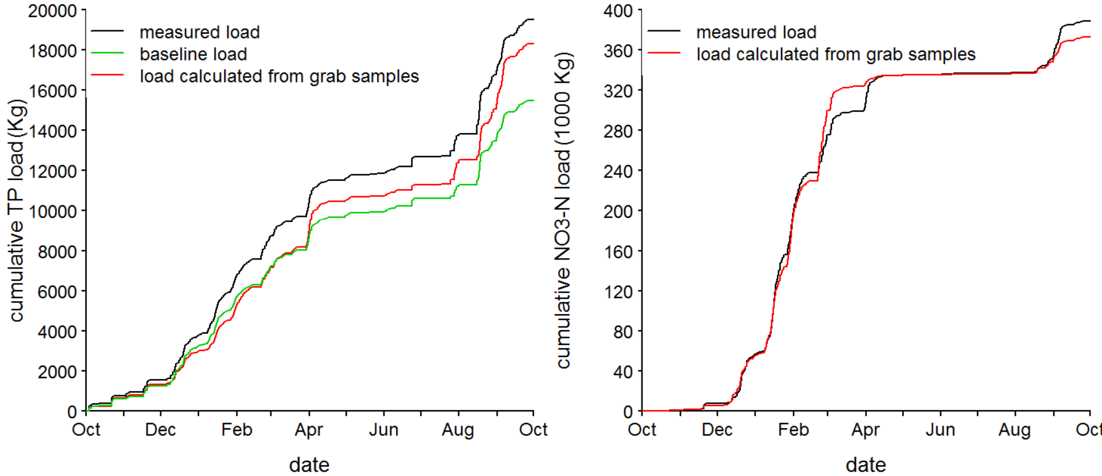
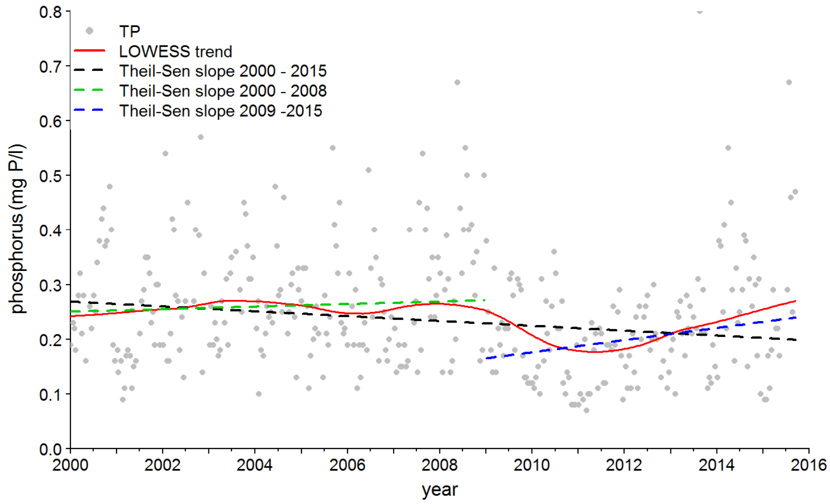


Figure 5: Measured and calculated TP and NO_3 loads at the pumping station Blocq van Kuffeler, the baseline load was calculated with the high-frequency TP data after separation of the short-scale concentration peaks generated by the pumping station.



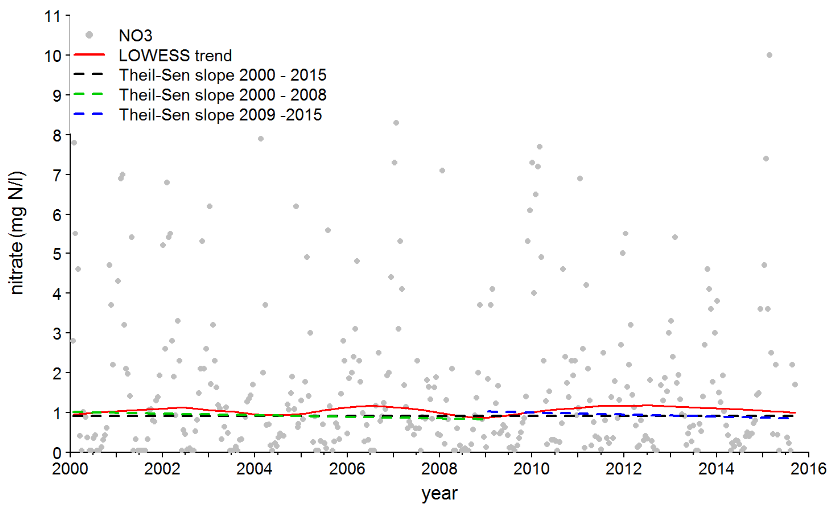


Figure 6: Trends in TP and NO_3 concentrations over the period 2000-2015 at location 1 (Blocq van Kuffeler).

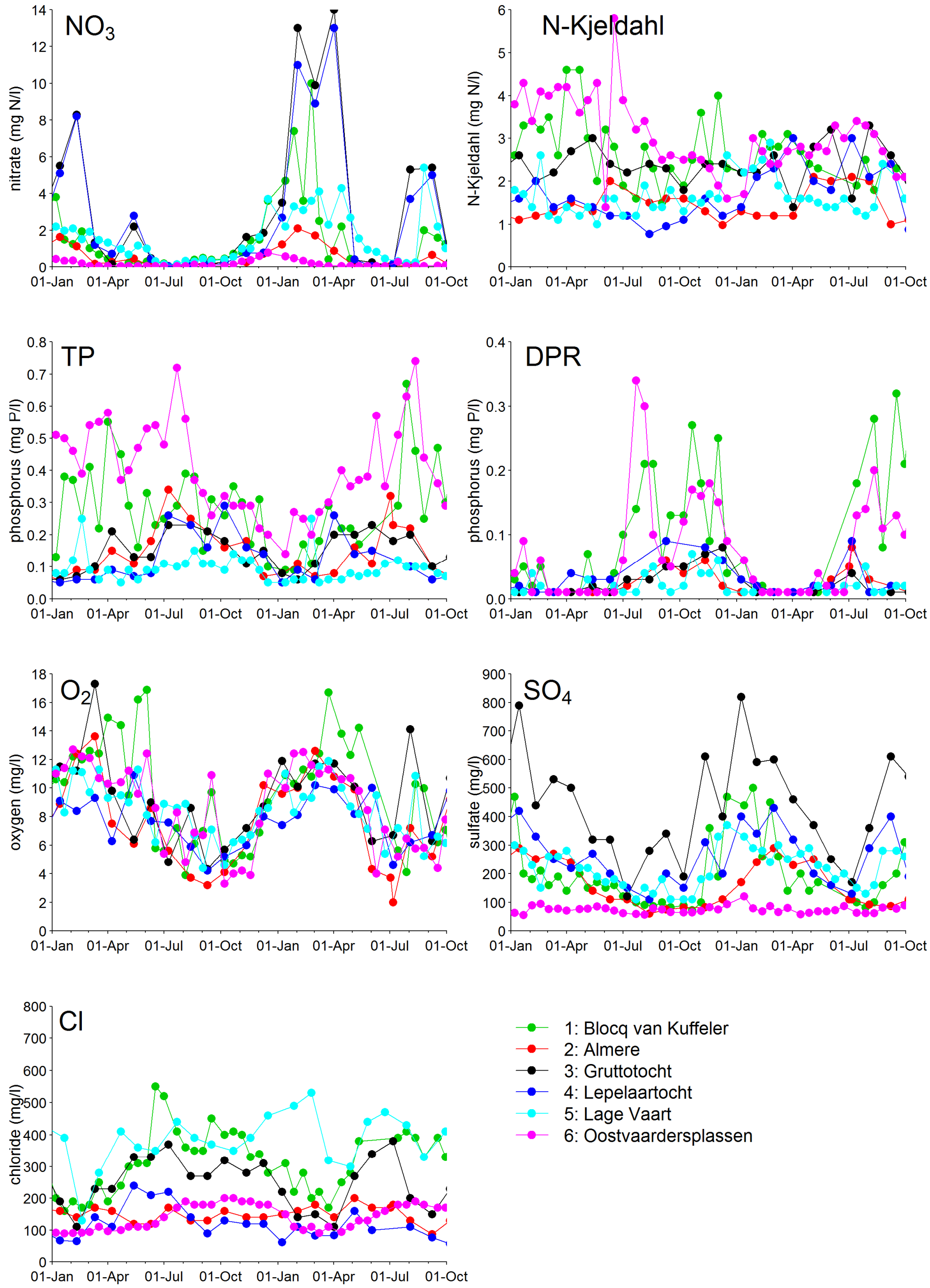


Figure 7. Low-frequency time series of NO_3, N-kjeldahl, TP, DRP, O_2, SO_4 and Cl concentration at surface water sampling location in the Lage Afdeling drainage area during the period January 2014 to October 2015. Fig. 1 shows the positions of the monitoring locations.