

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

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10 Abstract

11 Many agriculture-dominated lowland water systems worldwide suffer from eutrophication caused
12 by high nutrient loads. Insight in the hydrochemical functioning of embanked polder catchments is
13 highly relevant for improving the water quality in such areas or for reducing export loads to
14 downstream water bodies. This paper introduces new insights in nutrient sources and transport
15 processes in a polder in the Netherlands situated below sea level using high-frequency monitoring
16 technology at the outlet, where the water is pumped into a higher situated lake, combined with a
17 low-frequency water quality monitoring program at six locations within the drainage area. Seasonal
18 trends and short scale temporal dynamics in concentrations indicated that the NO₃ concentration at
19 the pumping station originated from N-loss from agricultural lands. The NO₃ loads appear as losses
20 via tube drains after intensive rainfall events during the winter months due to preferential flow
21 through the cracked clay soil. Transfer function-noise modelling of hourly NO₃ concentrations
22 reveals that a large part of the dynamics in NO₃ concentrations during the winter months can be
23 related to rainfall. The total phosphorus (TP) concentration and turbidity almost doubled during
24 operation of the pumping station which points to resuspension of particulate P from channel bed
25 sediments induced by changes in water flow due to pumping. Rainfall events that caused peaks in
26 NO₃ concentrations did not result in TP concentration peaks. The rainfall induced and NO₃ enriched
27 quick interflow, may also be enriched in TP but retention of TP due to sedimentation of particulate P
28 then results in the absence of rainfall induced TP concentration peaks. Increased TP concentrations
29 associated with run-off events is only observed during a rainfall event at the end of a freeze-thaw
30 cycle. All these observations suggest that the P retention potential of polder water systems is

1 primarily due to the artificial pumping regime that buffers high flows. As the TP concentration is
2 affected by operation of the pumping station, timing of sampling relative to the operating hours of
3 the pumping station should be accounted for when calculating P export loads, determining trends in
4 water quality or when judging water quality status of polder water systems.

5 Keywords

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

8 1 Introduction

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

21 For the evaluation of action programs and pilot studies, water authorities invest heavily in the
22 monitoring of NO_3 and P concentrations in surface water. Regional surface water quality networks in
23 EU member states are commonly sampled 12 times a year (Fraters et al., 2005). However, the
24 interpretation of grab sample data in terms of loads and fluxes is often problematic from such
25 monitoring networks (Rozemeijer et al., 2010). Grab sample frequencies are generally not sufficient
26 to capture the dynamical behavior of surface water quality and hydrological functioning of the
27 catchment (Kirchner et al., 2004;Johnes, 2007). It is increasingly recognized that incidental losses
28 and peak flows play an important role in the nutrient loads of surface water systems in the
29 Netherlands (Van der Salm et al., 2012;Regelink et al., 2013) and elsewhere (Withers et al., 2003).
30 Such incidental losses are considered to be related to peak flows after heavy rain storms and due to
31 overland flow or quick interflow via drains and cracked clay soils and related leaching of manure and
32 erosion of soil particles (Kaufmann et al., 2014). Some authors observed a lowering of NO_3

1 concentrations shortly after peak flow (e.g. Poor and McDonnell, 2007; Shrestha et al., 2013) caused
2 by dilution with NO₃-poor precipitation water. Others detected concentration peaks in response
3 events (e.g. Rozemeijer and Broers, 2007; Tiemeyer et al., 2008). Therefore, the NO₃ response to
4 rainfall events depends on the hydrochemical properties of the catchment (Rozemeijer et al., 2010).
5 In addition, the capacity of surface water bodies to retain nutrients is spatially and temporally
6 variable (e.g. Withers and Jarvie, 2008; Cirimo and McDonnell, 1997).

7 As a consequence of the dynamic behavior of nutrient transfer from land to surface water and in-
8 stream processes that impact nutrient retention combined with increasing demands for sound
9 assessments of the water system, there is an increasing interest in continuous or semi-continuous
10 monitoring of water quality at catchment outlets during the last decade (e.g. Bowes et al.,
11 2015; Wade et al., 2012; Jordan et al., 2007; Bieroza et al., 2014; Palmer-Felgate et al.,
12 2008; Rozemeijer et al., 2010; Kirchner et al., 2004; Cassidy and Jordan, 2011; Skeffington et al., 2015).
13 These studies showed catchment dependent non-stationary behavior of the concentration-discharge
14 relationships. High-frequency monitoring has proven to be a powerful tool to improve estimations of
15 annual export loads (e.g. Rozemeijer et al., 2010; Cassidy and Jordan, 2011), nutrients sources
16 (Bowes et al., 2015) and the hydrochemical functioning of a catchment (e.g. Wade et al.,
17 2012; Bieroza et al., 2014; Halliday et al., 2012). High-frequency nutrient monitoring has revealed the
18 presence of diurnal nutrient cycles in rivers and streams caused by biological processes or by P and N
19 inputs from sewage treatment works (e.g. Bowes et al., 2015; Halliday et al., 2012; Neal et al., 2012).
20 Large changes in concentrations or fluxes of materials over relatively short time periods are
21 increasingly recognized as important pathways of nutrient delivery to surface water bodies (Kaushal
22 et al., 2014). In the Netherlands, there is a still debate about the risk of incidental losses associated
23 with manure application (Akkermans and Hermans, 2014). The Netherlands adopted the European
24 Nitrate Directive in 1991 (EC, 1991), which regulates the use of nitrogen in agriculture through
25 national action plans. Among other measures, the regulation includes the period of manure
26 application. To reduce the risk of nutrient leaching to groundwater and surface water, manure
27 application on arable land is allowed from 1 February to 1 August and on grassland from 15 February
28 to 31 August (LNV, 2009). The potential risk for incidental nutrient losses after manure application in
29 February and March (before the start of the growing season) is not known. High-frequency
30 monitoring is a powerful tool to detect such incidental losses.

31 In many low-lying areas worldwide, water levels are managed by inlet of diverted river water in dry
32 periods and discharge via pumping stations in wet periods. Such an embanked land with a human
33 controlled water regime is called a 'polder'. In the Netherlands, these regulated polder catchments

1 cover 60% of the land surface (Van de Ven, 2003). The dense network of subsurface drains, ditches,
2 weirs, channels, pumping stations and the dynamic mixing of water from different sources (seepage,
3 precipitation and water inlet) results in a relatively complex hydrology. Many studies on nutrient
4 dynamics in natural catchments showed a relation between nutrient concentrations and discharge,
5 and this significantly improved the insight in the nutrient sources and pathways in the catchment.
6 The water flow in polders is, however, not a function of free discharge but is controlled by pumping
7 stations. The maximum discharge is controlled by the capacity of the pumping stations. Due to the
8 presence of a dense surface water system, the water storage capacity and the residence time of the
9 surface water in a polder is also higher when compared to natural, free drainage catchments which
10 may impact biogeochemical or hydrological in-stream processes controlling nutrient retention.
11 Insight in the hydrochemical functioning of polder catchments is highly relevant for improving the
12 water quality in the Netherlands.

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

19 The general aim of this study is to increase our understanding of the hydrochemical function of an
20 agriculture-dominated water system in a clay polder by analysis of high-frequency monitoring of
21 nutrient concentrations at the polder outlet combined with low-frequency surface water quality
22 data and groundwater quality data from different locations within the polder. The specific objectives
23 of this study are: (1) to increase insight in dynamics of nutrient concentrations and nutrient sources
24 in polder areas (2) to characterize the importance of incidental losses caused by intensive rainfall
25 events whether or not in combination with recent manure application and (3) to assess potential
26 effects of the operational management of the pumping station on the water quality.

27 2 Material and Methods

28 2.1 Study area

29 A continuous monitoring station was established in the Lage Vaart main channel nearby the
30 pumping station Blocq van Kuffeler (A in Fig. 1). This is one of the three pumping stations that
31 control the water level in Lage Afdeling pumped drainage area located within the Flevoland polder,
32 the most recent and at the same time biggest land reclamation project in the Netherland (Groen,

1 1997). The Flevoland polder consists of two pumped drainage areas, which are each drained by a
2 main channel. The Lage Afdeling drainage area drains into the Lage Vaart main channel (Fig. 1). The
3 size of the Lage Afdeling drainage area is 576 km², with altitude ranging between 3 and 5 m below
4 mean sea level. The Lage Afdeling drainage area is mainly rural. The land cover is dominated by
5 agriculture (76%), followed by woodlands and moors (18%) and urban or semi-urban areas (6%).

6 The geohydrology of the Flevoland polder area is generally described by a confining layer of
7 Holocene marine sediments, with a thickness of less than 0.5 m in the northeast to over 7 m
8 southwest, overlying a sandy aquifer deposited in the Pleistocene age. The soils consist for 50% of
9 clay soils, for 39% of silty clay loam and for 11% of sandy soils (Van den Eertwegh, 2002). A typical
10 characteristic of the soils in Flevoland is that the clay layer contains permanent and interconnected
11 cracks due to physical and chemical ripening of the soil after reclamation. The shrinkage cracks
12 disappeared in the plough layer by tillage activities, but are permanently present in the subsoil down
13 to about 1.0-1.5 m below the soil surface (Van den Eertwegh, 2002; Groen, 1997). From a depth of
14 1.2 to 1.5 m below the soil surface, clay deposits, if present, are permanently water saturated and
15 thus not ripened, resulting in a low-permeable soil layer. Due to altitudes below mean sea level and
16 below the water level of the surrounding lakes, there is upward groundwater seepage at most
17 locations within the Lage Afdeling drainage area.

18 The Lage Vaart main channel is connected via a series of secondary channels to a dense network of
19 field ditches and tube drains. Tube drains are generally installed at 0.95 m depth. The horizontal
20 spacing varies between less than 12 to 48 m, mainly dependent on the soil hydraulic conductivity
21 and groundwater seepage rate. The field ditches receive outflow from the tube drain, direct
22 drainage from subsurface flow, regional groundwater seepage and any surface run-off from the
23 connected field area. They drain freely into the secondary channels. The water level in the Lage
24 Afdeling is regulated by 97 weirs and three pumping stations that pump the excess water to the
25 higher situated Markermeer and Ketelmeer. The total pumping capacity is 11-12 mm d⁻¹. The Lage
26 Vaart main channel has a controlled constant water level of 6.2 m below mean sea level. The
27 pumping station Blocq van Kuffeler has four electrically powered pumps. Two pumps with a capacity
28 of 750 m³ min⁻¹ each drain the Lage Afdeling. Operation of the pumping stations with one pump
29 causes a flow velocity in the main channel of approximately 0.125 m sec⁻¹ and with both pumps the
30 flow velocity is approximately 0.25 m sec⁻¹. Up to 2008, the pumping station Blocq van Kuffeler was
31 powered with diesel engines. These diesel engines were replaced with electric engines during the
32 renovation of the pumping station in the autumn of 2008 and this conversion was finished in the
33 beginning of 2009. Since this renovation, the operational management of the pumping station is

1 automatically controlled by a series of water level pressure sensors in the area. The pumps run
2 predominantly during evening or night hours because of cheaper power supply during these hours.
3 The discharge generated by the pumping stations is measured continuously. The Blocq van Kuffeler
4 pumping station drains the south-western part of the Lage Afdeling drainage area. The flow direction
5 of the water in the channels that are drained by pumping station Blocq van Kuffeler, is illustrated by
6 arrows in Fig. 1. Pumping station B is an emergency pumping station and only operates during
7 extremely wet conditions. Although there is no physical boundary between the area drained by
8 Blocq van Kuffeler and pumping station C, location 5 can be considered as the most upstream
9 location in the Lage Vaart that is drained by the Blocq van Kuffeler pumping station under normal
10 meteorological conditions. There is a sewage treatment plant in the area that discharges its effluent
11 to the Lage Vaart (Fig. 1). The average effluent discharge is $0.35 \text{ m}^3 \text{ min}^{-1}$. The TP and NO_3
12 concentration in the effluent water is measured weakly. The average TP concentration is 0.5 mg L^{-1}
13 and the average NO_3 concentration is 1.5 mg N L^{-1} . The TP load to the Lage Vaart in the period
14 October 2014 – October 2015 equals approximately 5,400 kg and the NO_3 load 16,400 kg N. There
15 are no other sources of sewage discharge to the surface water within the Lage Afdeling drainage
16 area.

17 2.2 Low-frequency monitoring

18 Grab samples were collected every two or four weeks from January 2014 to October 2015 from the
19 polder outlet and 5 other monitoring locations within the part of the Lage Afdeling drainage area
20 that is drained by the Blocq van Kuffeler pumping station (Fig. 1). Four locations are representative
21 for different types of land use (Table 1). Electrical conductivity, oxygen concentration, transparency,
22 temperature and pH of the samples were measured directly in the field. Sub-samples for
23 determination of dissolved substances were filtered through a $0.45 \mu\text{m}$ poresize filter (Eijkelpamp).
24 The samples were transported and stored at 4°C . TP, dissolved reactive P (DRP), NO_3 , NH_4 and Cl
25 were determined using standard colorimetric methods (APHA-AWWA-WPCF, 1989). Organic-N was
26 extracted by Kjeldahl extraction and measured by colorimetric method and sulphate was measured
27 using IC (Ion Chromatography).

28 The water quality in the Lage Afdeling drainage area showed spatial differences in water quality
29 related to land use (Fig. S1). High NO_3 concentrations were observed in water from the agricultural
30 during winter (location 3 and 4 in Fig. 1). The highest TP concentrations were observed in water from
31 the nature area 'Oostvaardersplassen (location 6 in Fig. 1). The DRP concentration of all sampling
32 locations showed a seasonal variation with higher concentrations during the summer months.

1 2.3 High-frequency measurements

2 Between October 2014 and October 2015 we measured the total-P (TP), total reactive P (TRP) and
3 NO₃ concentration, turbidity, conductivity and water temperature semi-continuously at the polder
4 outlet just before the pumping station. TRP include all P forms that are measured with the
5 molybdenum blue method (Murphy and Riley, 1962) in unfiltered samples, those include acid labile
6 phosphorus containing compounds (inorganic and organic) (Worsfold et al., 2005). The flow regime
7 at the monitoring location is governed almost exclusively by the pumping station. The conductivity
8 was measured continuously with a CTD-diver (Van Essen Instruments, Delft, the Netherlands).

9 The NO₃ concentration was measured using a double wavelength spectrophotometric sensor (DWS),
10 (Nitratax plus sc, Hach Lange GmbH, Düsseldorf, Germany). The DWS measures UV absorbance of
11 dissolved NO₃ at a wavelength of 218 nm at a measuring receiver (EM – element for measuring) and
12 at 228 nm at a reference receiver (ER – element for reference). The recorded measurements at two
13 different wavelengths are designed to compensate interference of organic and/or suspended matter
14 by interpreting the difference between the absorbance values at EM and ER (Huebsch et al., 2015).
15 The Nitratax sensor covers a NO_x-N detection range of 0.1 to 50.0 mg L⁻¹. The NO₃ concentrations
16 were recorded every 5 minutes. There was a small drift in the signal of the Nitratax sensor (max 0.35
17 mg N L⁻¹ per month). We, therefore, corrected the high-frequency NO₃ data using the NO₃
18 concentrations from the biweekly grab samples by calculating a linear drift for the separate
19 maintenance intervals of the sensor.

20 For the total phosphorus (TP) concentration measurements, we installed a Sigmatax sampler and a
21 Phosphax Sigma auto-analyzer (both Hach Lange GmbH, Düsseldorf, Germany). The total-P
22 concentrations were recorded every 20 minutes. The Sigmatax was installed for the automated
23 water sample collection and the pretreatment (ultrasonic homogenization). Next, the sample was
24 delivered to the Phosphax Sigma auto-analyzer. This sample was digested using the sulphuric acid-
25 persulphate method (APHA-AWWA-WPCF, 1989). After mixing and quickly heating and cooling down
26 the sample, the reagents were automatically added and the sample was measured at 880 nm using a
27 LED photometer. The Phosphax Sigma was automatically cleaned and calibrated daily. There was a
28 close agreement between the high-frequency TP data and the TP concentrations of the
29 accompanying two weekly grab samples analyzed by standard laboratory assays ($R^2 = 0.982$) and,
30 therefore, no need to correct the high-frequency TP data (Fig. S2).

31 The turbidity (FTU) was measured using a OBS (optical back scatter) sensor (SOLITAX t-line sc, Hach
32 Lange GmbH Düsseldorf, Germany) that receives the reflected light from the sediment-laden flow.

1 Instead of directly obtaining the suspended sediment concentration, a turbidity sensor measures the
2 turbidity of flow caused by suspended sediment (Gao, 2008). The FTU data was stored with a time
3 interval of 5 minutes. There was a close agreement between the high-frequency turbidity data (FTU)
4 and the suspended sediment (SS) concentrations (mg L^{-1}) of the grab samples ($R^2 = 0.965$) (Fig. S2).
5 The measured turbidity could thus be taken as a proxy for the SS concentration.

6 2.4 Background information

7 Precipitation data on an hourly basis for the Lage Afdeling were abstracted from HydroNet
8 (<http://portal.hydro.net.nl/>). This is an online database with precipitation data based on calibrated
9 radar images. The precipitation of the radar pixels were averaged over the Lage Afdeling drainage
10 area. Temperature data were retrieved from the Royal Dutch Meteorological Institute (KNMI, De Bilt,
11 the Netherlands) weather station Lelystad, located in the center of the Lage Afdeling. The Flevoland
12 polder has a moderate maritime climate with an average annual temperature of 9.9°C , an average
13 annual precipitation of 850 mm and an average of 8 days per year with a maximum temperature
14 below 0°C . Groundwater levels were monitored continuously with pressure sensors in five phreatic
15 groundwater wells located within the agricultural area of the Lage Afdeling (Fig. 1).

16 The groundwater quality data set from Griffioen et al. (2013) was used as background information.
17 This database was assembled from the national database of the TNO Geological Survey of the
18 Netherlands and contains complete groundwater analyses down to a depth of about 30 m with
19 sampling dates later than 1945. The groundwater in the Lage Afdeling is characterized as anoxic
20 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
21 NO_3 concentrations (between 0 and $7 \text{ mg NO}_3 \text{ L}^{-1}$) (Fig. S3).

22 2.5 Transfer function-noise modelling

23 To increase insight in the driving forces of measured dynamics of nutrient concentrations,
24 preliminary research was done on the application of time series analysis, and more specifically
25 transfer function-noise (TFN) modelling, to estimate the impact of rainfall on NO_3 concentrations.
26 TFN models are very popular for describing dynamic causal relationships between time series and
27 have been widely applied in the field of groundwater modelling (e.g. Berendrecht et al.,
28 2003; Knotters and van Walsum, 1997). Although a small number of studies has used TFN models to
29 relate streamflow data to nutrient concentrations (Schoch et al., 2009; Worrall et al., 2003) or relate
30 precipitation data to high-frequency observation of dissolved organic carbon (Jones et al., 2014), to
31 our knowledge TFN models have not been applied yet on high-frequency monitoring data of

1 nutrients such as available in this study. Therefore, as a first step, we tried to relate the time series
2 of hourly NO₃ concentration measurements to rainfall using the following linear TFN model:

$$3 \quad \log(NO_3) = \theta(B)p_t + \mu + n_t \quad (1)$$

4 and

$$5 \quad n_t = \phi n_{t-1} + \varepsilon_t, \quad (2)$$

6 with p_t the precipitation at time t , $\theta(B) = \theta_0 + \theta_1 B + \dots + \theta_r B^r$ the transfer function (B is
7 backward shift operator, $B^i p_t = p_{t-i}$), μ is the reference or baseline level, n_t a stochastic first-order
8 autoregressive process, ϕ the autoregressive coefficient ($0 < \phi < 1$), and ε_t a zero-mean normally
9 distributed process (Box and Jenkins, 1970). As ε_t is assumed to be normally distributed, the time
10 series of NO₃ data was log-transformed to better satisfy this assumption. For reasons of flexibility
11 and model parsimony, we used a predefined transfer function as described by von Asmuth et al.
12 (2002), which has the form of a Gamma distribution function and has been successfully applied for
13 describing groundwater dynamics:

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

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

16 2.6 Export loads calculations and trend analysis

17 True NO₃ and TP export loads from the drainage area into the Markermeer were based on our high-
18 frequency concentration measurements and discharge data of the pumping station. In addition NO₃
19 and TP loads were estimated from linear interpolation of the low-frequency grab sample data
20 combined with the discharge data. Although advanced methods have been developed to improve
21 load estimates from low-frequency concentration data, none of the methods clearly outperformed
22 the methods that were based on simple linear or stepwise interpolation (Rozemeijer et al., 2010). To
23 quantify the event-driven TP export load generated by changes in the water flow due to pumping, a
24 hydrograph separation method was used to separate the high-frequency TP concentration data
25 series into short-term TP concentration peaks and baseline TP concentration. In this study we used
26 the same method as applied by Rozemeijer and Broers (2007). This method, originally developed by
27 (Hewlett and Hibbert, 1963), separates the baseline concentration and the peak concentration by a
28 separation line with a constant slope (Fig. S5). This line starts whenever the slope of the
29 concentration series exceeds a specified constant separation slope. The separation line ends when it

1 intersects the falling limb of the concentration series. For this study, a constant separation slope of
2 $0.02 \text{ mg P L}^{-1} \text{ d}^{-1}$ was used. With this relatively low slope value, concentration peaks were also
3 separated from the baseline concentration during situations of upward trends in TP concentrations.

4 Long term TP and NO_3 concentration measurements were available for the polder outlet. We used
5 two frequently applied methods for trend analysis of concentration-time series: (1) seasonal Mann-
6 Kendall tests (Hirsch and Slack, 1984) (2) Theil-Sen robust line (Hirsch et al., 1982) and (3) locally
7 weighted scatterplot smoothing (LOWESS) trend lines (Cleveland, 1979). These methods are
8 relatively insensitive to extreme values and missing data in the time series. The seasonal Mann-
9 Kendall trend test is a robust, non-parametric test on the significance of an upward or downward
10 trend. The Theil-Sen method is a robust non-parametric trend slope estimator. The LOWESS trend
11 lines were used to examine possible changes in trend slopes within the concentration time-series
12 period. We refer to Rozemeijer et al. (2014) for details on the statistical methods.

13 3 Results

14 3.1 Water discharge

15 The Blocq van Kuffeler pumping station responds rapidly to rainfall events in the drainage area by
16 automatically switching on one or two pumps (Fig. 2A). The interval in which the pumping station is
17 in operation decreased during the autumn months. During the winter months the pumping station
18 runs almost at a daily basis and continuously for several days during very wet periods. There was a
19 strong decline of the daily pumping hours from mid-April to the end of July. A wet period from mid-
20 August to mid-September resulted in an increase of pumping hours. The pumping station pumped
21 almost $67 \times 10^6 \text{ m}^3$ water from the polder into the Markermeer during the period from October 2014
22 until March 2015 and $33 \times 10^6 \text{ m}^3$ during the period from April 2015 until October 2015 (Fig. 3). This
23 corresponds to approximately 350 mm distributed across the entire drainage area for the winter half
24 year (Oct-March) and 170 mm for the summer half year (April-Sept.). The sum of the precipitation
25 amounted to 455 mm and 517 mm for the winter half year and summer half year, respectively.

26 3.2 Seasonal trends in high-frequency nutrient data

27 The high-frequency NO_3 concentration ranged from 0.01 to 10.4 mg N L^{-1} and showed a seasonal
28 pattern and a response to rainfall with high concentrations in winter and an increase during wet
29 periods (Fig. 2B). The NO_3 concentration was low from the start of the monitoring until half
30 November. From mid-November to the third week of January, the NO_3 concentration gradually
31 increased to a maximum of 9 mg N L^{-1} . During the dry period in the first three weeks of February, the

1 NO₃ concentration decreased to a level of 1 mg N L⁻¹. Next, the concentration peaked at 24-25
2 February upon rainfall and gradually decreased towards the end of March where it showed an
3 increase again during the wet period in late March and early April. During April the concentration
4 declined to a level around 0.5 mg N L⁻¹ or below and stayed at this low level until mid-August. The
5 NO₃ concentration rapidly increased after a wet period during mid-August and gradually decreased
6 afterward.

7 The high-frequency total-P (TP) concentration ranged from 0.07 to 1.16 mg P L⁻¹ (Fig. 2C). The TP
8 concentration was relatively high during the first three weeks of the monitoring period (0.25 to 0.4
9 mg P L⁻¹). In October and November, the TP concentration decreased during wet periods and
10 increased during the dryer periods. During the wet first two weeks of December, the TP
11 concentration decreased to a level around 0.1 mg P L⁻¹ and remained low until halfway February.
12 During the relatively dry period in February and March the TP concentration increased to a level
13 around 0.2 mg P L⁻¹ and remained at this level until mid-June. From mid-June to mid-August the TP
14 concentration gradually increased and peaked in mid-August. With higher concentrations during the
15 summer season and a decrease during wet periods, the TP concentration showed a seasonal
16 variation and a response to rainfall that was opposite to the NO₃ concentration.

17 The high-frequency total-reactive P (TRP) data and the dissolved reactive P (DRP) data from the low-
18 frequency monitoring program showed rather high concentrations from the start of the monitoring
19 to early December 2014 and then declined to a low level (Fig 2C). The TRP and DRP concentration
20 remained low until the second half of May. During the period from mid-May to mid-August the TRP
21 and DRP concentrations followed the trend of the increasing TP concentrations.

22 The baseline level of the suspended sediment (SS) concentration was low during the period
23 October to January (Fig 2D). In January the SS concentration increased and it stayed at a relative high
24 level to April. During the end of April and May the SS concentration decreased again.

25 3.3 Short scale dynamics in high-frequency nutrient data

26 Significant increases of the NO₃ concentration up to 8 mg N L⁻¹ in short time scales appeared during
27 pumping within five days after major rainfall events on 15-18 November, 10-12 December, 19-20
28 December, 7-9 January, 12-14 January, 21-22 February, 29 March-2 April, 14-18 August and 26-31
29 August (Fig. 4 and Table 2). The precipitation during these events was around 20 mm or above. After
30 these NO₃ concentration peaks, the concentration declined during pumping. The increase in NO₃
31 concentration did not appear after the precipitation events on 20-23 October, 3-4 November 17-23
32 June and 27-29 July.

1 There is a structural response of the TP concentration and the turbidity on operation of the pumping
2 station. The TP concentration and turbidity always peaked directly after the start of the pumping-
3 engines and decreased again during the period of pumping and afterwards (Fig. 4). Pumping events
4 with one pump resulted in an average increase of the TP concentration of 0.06 mg L^{-1} and turbidity of
5 4.4 FTU while events with two pumps resulted in an average increase of 0.13 mg L^{-1} and turbidity of
6 22 FTU (Table 3). The TP concentration was on average a factor of 1.30 and 1.83 higher during
7 pumping with one pump and two pumps, respectively, compared to the concentration before
8 pumping. The TRP concentrations also showed an increase in concentration during pumping. As the
9 colorimetric measurement of TRP takes place in an acidic solution it is plausible to attribute the
10 increase of the TRP concentration during pumping to the dissolution of particulate Fe or Ca bound
11 inorganic P. The data shows the largest increase of TP concentrations ($0.16\text{-}0.60 \text{ mg P L}^{-1}$) during
12 pumping with two pumps after longer periods without pumping (21 Oct., 2 Nov., 8 Dec., 20 Feb., 23
13 June, 25 July and 15 Aug.) and decreasing TP peaks were observed with subsequent pumping events
14 (Fig.4). Short-term declines of the TP concentrations to values below the pre-pumping concentration
15 were observed during pumping or shortly after pumping induced by rainfall periods in October, June
16 and August (Fig. 4).

17 A significant short-term change in NO_3 and TP concentrations and the conductivity that was not
18 linked to pumping appeared during rainfall on 25 and 26 January (Fig. 4). This period marked the end
19 of a freeze-thaw cycle that started on 20 January. During this period the top soil became frozen. The
20 precipitation during the night of 24 January consisted of snow and this resulted in a snow cover of a
21 few centimeters. Upon rainfall on the frozen soil on 25 January, the NO_3 concentration decreased
22 from 6.1 to 1.5 mg N L^{-1} and the TP concentration increased from 0.09 to 0.21 mg P L^{-1} . Together
23 with the changes in NO_3 and TP concentrations, the turbidity increased from 8 to 57 FTU , the TRP
24 concentration decrease from 0.06 to 0.02 mg P L^{-1} and the conductivity decreased from 235 to 122
25 mS cm^{-1} (Fig. S4).

26 3.4 Decomposition of high-frequency nitrate data

27 As shown in section 3.2, NO_3 concentrations were low from the start of the monitoring period until
28 the rainfall event on 15 November and during April the NO_3 concentrations decreased again.
29 Precipitation events before mid-November and after April only had a minor influence on the NO_3
30 concentration. For the period between 15 November and 30 April a transfer function-noise modelling
31 of hourly NO_3 concentrations reveals that the model can relate quite a large part of the dynamics to
32 rainfall: the coefficient of determination $R^2 = 0.7$. The measured time series together with the model
33 simulation and the residual series are shown in Fig. 5.

1 Overall, the transfer model describes slow dynamics well; short-term dynamics cannot be related to
2 rainfall with the transfer model and are described by the stochastic model. The estimated
3 autoregressive coefficient ($\phi = 0.98$) is quite low given the high sampling interval of 1 hour,
4 indicating that most of the temporal structure in the time series has been captured by the transfer
5 model.

6 The estimated model parameters and their standard deviation are given in Table S1. The estimated
7 impulse response function for transferring an impulse of 1 mm rainfall into log-NO₃ concentration is
8 given in Fig. S6. The smooth character of the function is due to predefined structure of the function,
9 which is the Gamma distribution function. The time to peak is 5.4 days with a response of 0.033
10 log(mg NO₃-N mg L⁻¹), while 95% of the total response happens within 43 days. The time to peak as
11 revealed by the TFN model matches well with the delay of approximately five days between rainfall
12 events and peak concentrations (Fig. 4).

13 The reference or baseline level follows from the model estimation and has a value of $\mu = -1.13$, or
14 back-transformed from logarithm: $e^{-1.13} = 0.32$ mg N L⁻¹ which means that after a long no-rain
15 period, the NO₃ concentration will decline to 0.32 mg N L⁻¹. The current time series does not include
16 seasonal patterns; during spring and summer season the NO₃ concentration cannot be related to
17 rainfall only. The groundwater levels drop below the tube drain levels (i.e. precipitation may not lead
18 to discharge) and denitrification or in-stream nutrient uptake processes reduce the NO₃
19 concentration, so other driving forces and non-linearity have to be included in the TFN model for
20 modelling the summer season.

21 3.5 Nutrient loads and fluxes at polder outlet

22 The annual loads based on the high-frequency dataset equaled 19,500 kg for TP, 388,500 kg for NO₃-
23 N and 1,788,000 kg for SS which corresponds to 0.98 kg ha⁻¹ for TP, 19.4 kg ha⁻¹ for NO₃-N and 89.4
24 kg ha⁻¹ for SS (Fig. 3). The TP load during the winter months (October – March) was almost equal to
25 the load during the summer months (April – September) while for NO₃ almost 80% of the annual
26 load occurred during the winter months, with January and February as most important months. The
27 annual loads calculated from the grab sample data equaled 18,200 kg for TP and 372,500 kg for NO₃-
28 N. The annual baseline TP load after separation of the TP concentration peaks was 15,400 kg. The
29 difference between the total load and the baseline load equaled 4100 kg, i.e., 21 % of the annual TP
30 load can be attributed to resuspension of TP due to changes in water flow induced by the pumping
31 station.

1 During the period from 1 Oct 2014 to 1 April 2015 the cumulative TP load calculated from the grab
2 sample data matched the baseline TP load and underestimated the high frequency load with 17%.
3 The months December and January showed the largest difference between the grab sample load
4 and the high-frequency load. The winter low-frequency NO₃ load overestimated the high-frequency
5 load by 6.5%, mainly due to a higher monthly low-frequency load in February. From May to mid-
6 August 2015 there was almost no NO₃ load. In August and September the grab sample load was
7 lower than the high-frequency load. The annual grab sample load underestimated the high-
8 frequency load with 4%.

9 Time series of TP and NO₃ concentrations in grab samples at the Blocq van Kuffeler pumping-station
10 over the period 2000-2015 are given in Fig. 6. The red lines in Fig. 6 show the LOWESS trend line and
11 the black lines show the Theil-Sen slope over the period 2000-2015. The NO₃ concentration showed
12 no significant upward or downward trend over the period 2000-2015. The time series of TP
13 concentration showed different trends over the period 2000-2015. After a period with minor
14 increase for 2000 to 2009, the LOWESS trend line reveals a decline in TP concentrations in the period
15 2009-2010 followed by an increase from 2011 to 2015. The Theil-Sen slope showed a decline of TP
16 concentration ($-0.0053 \text{ mg P L}^{-1}$ per year) over the years 2000-2015. This downward trend was
17 significant according the seasonal Mann-Kendall trend tests.

18 The blue and green lines give the Theil-Sen slopes for the periods 2000-2008 and 2009-2015,
19 respectively, before and after renovation of the pumping station. Where the Theil-Sen slope showed
20 a decline of TP concentration over the years 2000-2015, it showed upward trends of $0.0023 \text{ mg P L}^{-1}$
21 per year and $0.011 \text{ mg P L}^{-1}$ per year over the separate periods 2000-2008 and 2009-2015,
22 respectively. The upward trend for the period 2009-2015 was significant according the seasonal
23 Mann-Kendall trend tests. The NO₃ concentrations showed no significant upward or downward
24 trend over the separate periods 2000-2008 and 2009-2015.

25 4 Discussion

26 4.1 Identification of nutrients sources and dynamics in nutrient concentrations

27 4.1.1 Nitrate

28 The high-frequency NO₃ data showed a seasonal trend with higher concentrations during winter
29 compared summer. Low-frequency surface water data showed high NO₃ concentrations at the outlet
30 of the agriculture-dominated areas within the drainage area during winter months (Fig. S1), whereas
31 the groundwater has low NO₃ concentrations (Fig. S3). From this, it is clear that NO₃ in the surface

1 water at the polder outlet has an agricultural source. An increase of NO₃ concentrations from
2 summer to winter is observed in a large majority of agriculture-dominated headwater in The
3 Netherlands (Rozemeijer et al., 2014) and natural catchments elsewhere (Wade et al., 2012).
4 Catchments where NO₃ concentrations are controlled by a combination of effluent loads from
5 sewage treatment works and dilution by rainfall commonly show a decline in NO₃ from summer to
6 winter (Bowes et al., 2015; Wade et al., 2012). The NO₃ pattern is therefore thought to be due to a
7 combination of interflow or shallow draining groundwater with high fertilizer or manure inputs and
8 NO₃ enrichment during autumn and winter. Increased crop uptake of NO₃ during the growing season
9 combined with the effect of in-stream processes result in declined NO₃ concentrations during the
10 summer months.

11 The annual NO₃ load from the WWTP to the Lage Vaart is approximately 4 % of the NO₃ export load
12 at the polder outlet. The low NO₃ concentrations during the summer months and the rapid increase
13 after a very wet period during August additionally indicate that the influence of sewage effluent on
14 the NO₃ concentrations is limited. The discharge from the channel that drains the nature area
15 Oostvaarderplassen (Fig. 1, location 6) enters the Lage Vaart between the WWTP and the pumping
16 station and is 2 to 3 times higher than the discharge from the WWTP. This implies that there is
17 limited flow of the WWTP effluent towards the pumping station during no pumping conditions.

18 Beside the seasonal variation, we structurally observed an increase of NO₃ concentrations after
19 intensive rainfall events during the winter months. A reduction in NO₃ concentrations coinciding
20 with periods of intensive rainfall is commonly reported in high-frequency monitoring studies in
21 natural catchments and attributed to dilution of the surface water by surface run-off (Bowes et al.,
22 2015; Rozemeijer et al., 2010). Our structurally observed increase implies that run-off, which dilutes
23 the NO₃ concentration of the surface water does not commonly occur in the polder. Dilution of the
24 NO₃ concentration upon rainfall was only observed during the thaw on 25 January. Soil freeze-thaw
25 processes significantly increase the potential erosion during run-off events that follow thaw in hill
26 slope areas (Ferrick and Gatto, 2005) but also in relatively flat areas (Gentry et al., 2007). Where
27 during normal conditions rainfall infiltrates into the soil, the thaw and precipitation on 25 January
28 likely resulted in run-off. This temporally diluted the NO₃ concentration and conductivity and
29 increased the TP concentration and turbidity.

30 During normal conditions with soil temperatures above 0 °C, rainfall initiates a sudden increase of
31 quick interflow via subsurface tube drains, cracks or other macropores to the Lage Vaart channel
32 water which results in leaching for NO₃ stored in the soil profile to the surface water.

1 This is confirmed by the TFN model which showed that quite a large part of the NO₃ dynamics during
2 the winter months can be related to rainfall. The results in Fig. 5 show that during no-rain periods
3 the decline in concentration is modelled well. The various periods of rainfall show different results:
4 in December the increase in concentration is modelled well, in January the concentration is
5 overestimated, while in February and March the concentration is underestimated. The
6 overestimation in January can be explained by dilution in combination with a decrease of in the NO₃
7 stock stored in the soil profile due to leaching with rain during previous months. The largest positive
8 residuals appeared on 24-26 February. Recent manure application is a plausible explanation for the
9 underestimation of measured concentrations in February and March (see section 3.3). The largest
10 negative residuals appeared during the thaw on 25 and 26 January. The residuals of the TFN model
11 help to get a better understanding of the dynamic NO₃ behavior of the polder catchment.

12 *Drainage water*

13 The tube drain water in the Flevoland polder contains relatively high NO₃ concentrations. Meinardi
14 and Van den Eertwegh (1997) ran a monitoring program on tube drain water composition at 14
15 farms in the Flevoland polder during 1992-1995 and reported concentrations between 5 - 25 mg N L⁻¹.
16 Another monitoring program on nutrient concentration of tube drain water at 6 farms in Flevoland
17 from 2004 to 2008 gave farm-average NO₃ concentrations of 14 - 18 mg N L⁻¹ (van Boekel et al.,
18 2012). These concentrations can only explain the observed NO₃ concentration at the pumping
19 station during wet conditions when the tube drain water is the dominant contributor of the Lage
20 Vaart channel water. Groundwater levels within the polder are commonly low and tube drainage is
21 rare during the summer and early autumn (Van den Eertwegh, 2002; Groen, 1997). In autumn, when
22 evapotranspiration decreases, the groundwater levels rise upon rainfall events to around or above
23 the level of the tube drains, which are present at a depth of 0.95 m below the soil surface, and this
24 initiates drain discharge. This is illustrated by the measured groundwater levels within the Lage
25 Afdeling drainage area (Fig. S7) that shows a direct response of the groundwater level on rainfall
26 combined with a seasonal trend that shows rising groundwater levels during the months October
27 and November and quite stable levels from December to March. Rainfall events between the start of
28 the monitoring and mid-November and between April and mid-August did not result in tube drain
29 discharge. The low NO₃ concentration of the surface water during these periods, are thus, explained
30 by the absence of tube drain discharge. Extensive rainfall during the second half of August resulted
31 in a rising of the groundwater level close to the tube drain level (Fig. S7) and thus to leaching of NO₃,
32 stored in the soil profile, to the surface water. As our TFN model is weak in explaining the processes

1 that might control NO₃ concentration such as biogeochemical processes in surface waters we did not
2 include the summer period in our model.

3 *Preferential transport*

4 The high-frequency data showed a quick response of the NO₃ concentration at the pumping station
5 to rainfall once the groundwater level is at the tube drain level. This can be explained by the
6 presence of cracked clay soils that results in a rapid response of drainage to rainfall events in winter
7 (Groen, 1997; Van den Eertwegh, 2002). Preferential transport of water and nutrients through cracks
8 and macropores is known to play an important role in heavy clay soils (e.g. Van der Salm et al., 2012).
9 Due to regular plowing rainwater easily infiltrates into the top soil layer where exchange of NO₃ from
10 manure, fertilizers and plant debris occurs. The top soil or plough layer is commonly well aerated,
11 and therefore, quite optimal for conversion of organic nitrogen and ammonium to NO₃. After
12 leaching of this water from the plough layer to the cracked soil layer it quickly contributes to tube
13 drain discharge. Due to short residence time of this water in the soil, the influence of denitrification
14 on the NO₃ concentration is limited. This implies that the NO₃ concentration at the polder outlet and
15 the related export load from the polder are strongly controlled by quick interflow including tube
16 drain discharge during the winter months.

17 The period of five days between rainfall event and peak in the NO₃ concentration at the pumping
18 station is representative for the average residence time of water in the Lage Afdeling drainage area
19 during wet conditions. Catchment mean residence times are much shorter during wet periods
20 compared dry periods (Van der Velde et al., 2012). The five days travel time of the water in the field
21 ditches, sub-channels and main channel during wet conditions is in line with model calculated mean
22 annual residence times of water in the Lage Vaart main channel of 6.6 days (Van den Eertwegh,
23 2002).

24 *4.1.2 Phosphorus*

25 In contrast to the NO₃ concentration, the TP concentration at the pumping station decreased after
26 the wet periods (Fig. 2C). The interflow discharge via subsurface tube drains, cracks or other
27 macropores that resulted in an increase of NO₃ concentrations diluted the TP concentrations. Likely
28 this can be attributed to the relative decrease of the groundwater contribution to the channel water
29 during periods of increased interflow discharge. This indicates that the sources of TP in the channel
30 water at the polder outlet can largely be attributed to exfiltration of P-rich groundwater that occurs
31 throughout the year, presumably in combination with effluent loads from the WWTP and
32 biogeochemical remobilization of P from channel sediments during the summer and autumn. The

1 low DRP:TP ratio of the surface water within the Lage Afdeling as observed during the first half year
2 of 2014 and 2015 (Fig. S1) can be explained by transition of dissolved P to particulate P at the
3 groundwater-surface water interface. This commonly occurs after exfiltration of anaerobic
4 groundwater into surface water due to oxidation processes (e.g. van der Grift et al., 2014; Baken et
5 al., 2015).

6 The annual TP load from the WWTP to the Lage Vaart is approximately 27 % of the TP export load at
7 the polder outlet. As discussed previously for NO₃, the effect of the WWTP on the NO₃ concentration
8 at the pumping station seems to be small. For TP, however, the WWTP load cannot be neglected.
9 The discharge water from the Oostvaardersplassen has relatively high TP concentrations (Fig. S1)
10 and may contribute to the increase in TP concentration at the pumping station during no pumping
11 periods. The source of the TP in the Oostvaardersplassen is groundwater and feces of wildlife. The
12 Oostvaardersplassen is an important wintering area for birds that import nutrients from elsewhere.

13 The high DRP:TP ratios of the low-frequency monitoring program during the second half year of
14 2014 and the summer of 2015 indicates that mineralization of organic P from algae or plant debris,
15 or release of DRP from bed sediments can be considered as an additional P source during summer
16 and autumn when the TP concentration reached a maximum level between 0.8 and 1.2 mg P L⁻¹.
17 Mineralization of organic P mainly occurs after the growing season and the release of DRP from bed
18 sediments is reported during summer and autumn due to temperature and redox dependent
19 biogeochemical remobilization processes for lakes (e.g. Lavoie and Auclair, 2012; Boers and van Hese,
20 1988), wetlands, fens and floodplain soils (e.g. Zak et al., 2006; Loeb et al., 2008) but also for streams
21 and rivers (e.g. Duan et al., 2012; Jarvie et al., 2008). Low O₂ concentrations in the water column are
22 reported as an indicator for remobilization of P from bed sediments (Geurts et al., 2013). The surface
23 water at low-frequency monitoring locations showed a decline of the O₂ concentrations in during the
24 summer and autumn months (Fig. S1), thus, indicates that biogeochemical remobilization may occur
25 in the channels of the Lage Afdeling.

26 Surface run-off as a source of P in the surface water was only observed at the end of the freeze-thaw
27 cycle on 25-26 January. The TRP did not increase during this event, suggesting the TP largely existed
28 of non-labile organic P. Run-off is generally not an important transport process controlling P dynamic
29 in the polder catchment.

30 *Resuspension of particulate P*

31 The increase of the TP concentration and turbidity during operation of the pumping station and the
32 larger increase during pumping with two pumps compared to one pump (Table 3) indicate that the

1 increase of the TP concentration is related to resuspension of P from bed sediments due to
2 increased flow velocities. During no-pumping conditions, an erodible layer builds up by
3 sedimentation of particulate P. When the water flow velocities in the main channel increase upon
4 pumping, the P becomes suspended and transported downstream. The largest increase of the TP
5 concentration during pumping with two pumps after longer periods without pumping and the
6 decreasing TP peaks with subsequent pumping events supports this mechanism.

7 Resuspension of particulate P retained by sediments during high discharge events is an important
8 transport mechanism in natural catchments (e.g. Evans et al., 2004; Mulholland et al., 1985; Nyenje et
9 al., 2014; Haygarth et al., 2005; Palmer-Felgate et al., 2008). Our data shows that this mechanism is
10 also relevant for P transport in polders where flow velocities vary more abruptly and are maximized
11 by the capacity of the pumping station. The changes in TP concentration during pumping are,
12 however, significantly lower than reported during peak water discharge amongst storms in natural
13 catchments. For an agriculture-dominated lowland catchment in the Netherlands, Rozemeijer et al.
14 (2010) reported a mean increase in TP concentration during discharge from 0.15 to 0.95 mg P L⁻¹
15 coming from 47 rainfall events over a year. Particulate P (PP) increases up to a factor of 100 were
16 reported by Stutter et al. (2008) in response to storm events. Evans et al. (2004) measured PP
17 concentrations up to 3.93 mg P L⁻¹ in a lowland stream during high discharge conditions while the
18 mean concentration equaled 0.1 mg P L⁻¹. Haygarth et al. (2005) reported 10 to 20 times higher
19 mean TP concentrations during storm flow conditions compared to base flow conditions. With data
20 from 76 storms Correll et al. (1999) showed that concentrations of PP increased up to three orders
21 of magnitude during storms.

22 These changes are all considerably larger than the average factor of 1.30 and 1.83 that we observed
23 at the pumping station during pumping with one and two pumps, respectively. The P export from
24 natural catchments during pulses at high flow in less than 10% of the time may amount to about 80%
25 of the annual export (Kaushal et al., 2014). With 143 pumping events during the period from
26 October 2014 to September 2015, discharge-related changes that lead to resuspension of P appear
27 more frequent in this polder catchment compared to natural catchments. As only 21% of the annual
28 TP export load can be related to resuspension this cannot be considered as the dominant P transport
29 mechanism. The artificial pumping regime that buffers high flows in polder area thus results in a
30 high potential of polder areas to retain P by sedimentation of PP. Consequently, this may result in a
31 higher potential of polder areas for DRP release from the bed sediments during summer months by
32 biogeochemical remobilization which attributes to TP export loads during the summer period.
33 Therefore, it can be concluded that P transport mechanisms in polder catchment can be

1 characterized as less incidental and peak flow controlled and more controlled by biogeochemical
2 remobilization from bed sediments than those from natural catchments.

3 4.2 Incidental nutrient losses to surface water after manure application

4 The NO₃ concentration peaked at the polder outlet on 24 February, four days after an intensive
5 rainfall event that marked the end of a relative dry period that started early February. The increase
6 of the NO₃ concentration is almost two times higher compared to the other peaks in NO₃
7 concentration after a rainfall event (Table 2). This suggests that the NO₃ peak of 10.4 mg N L⁻¹ was
8 caused by an incidental loss after manure application that started on 1 February. The TFN model
9 revealed high residual NO₃ concentrations up to almost 8 mg N L⁻¹ during this NO₃ peak that cannot
10 be explained by rainfall (Fig. 5). The NO₃ concentration peaks on 27 February and 3 March also
11 showed large positive residuals of 4.2 and 3.4 mg N L⁻¹, respectively. The wet period in January
12 resulted, however, in predicted NO₃ concentrations that were higher than the measured
13 concentrations. The negative residuals in January can be explained by leaching of the NO₃ stored in
14 the soil profile during the winter season in combination with the appearance of some degree of
15 dilution of the remaining NO₃ by precipitation water during this period. Dilution of the NO₃
16 concentration upon rainfall events commonly observed in catchments (e.g. Rozemeijer et al.,
17 2010;Wade et al., 2012). A plausible explanation for the large positive residuals in February and
18 March is recent manure application that started on 1 February and temporary soil storage of applied
19 N during the first dry weeks of February.

20 The TP concentration peaked on 21 February during the beginning of the rainfall event,
21 simultaneously with a turbidity peak after the start-up of the pumps following upon a relatively dry
22 period of more than one week without pumping (Fig. 4). It is, therefore, not likely that this peak was
23 caused by an incidental loss after manure application but caused by hydrodynamic resuspension of
24 the Lage Vaart bed sediment. The absence of a TP peak after the rainfall event on 21-22 February
25 can be attributed to the soil characteristics of the area. We already discussed that the water quality
26 at the polder outlet is strongly controlled by quick interflow via tube drains or cracks and that
27 surface run-off only influenced the water quality when it rained during the end of a freeze-thaw
28 cycle. Although it is known that tube drain discharge after rainfall events in combination with recent
29 manure application on cracked clay soils may contain significant TP concentrations (Van der Salm et
30 al., 2012), these peaks did not appear at the polder outlet. Several other studies ask attention for
31 elevated TP concentrations in drain and trench flow within a few weeks after application of
32 fertilizers or liquid farm manure (Hodgkinson et al., 2002;Simard et al., 2000;Djodjic et al., 2000). It is
33 unknown if these peaks appear after rainfall events in the tube drain discharge or in the receiving

1 field ditches in the Lage Afdeling drainage area. Therefore, it is unclear if the absence of TP peaks
2 simultaneously with the NO_3 peaks at the polder outlet can be attributed to sedimentation of PP
3 from agricultural sources in the field ditches or sub-channels where it may become a source for DRP
4 release from bed sediments during the summer and autumn months or that there is almost no
5 particulate or dissolved P leaching from the top-soil to the surface water due to the sorption
6 capacity of the top-soil. From other lowland areas it is known that the dissolved P loads to surface
7 water from tube drains and shallow groundwater discharge are low due to precipitation with Fe
8 hydroxides with a high affinity to retain P, at the oxic/anoxic interface around the tube drains and
9 ditch sediment (van der Grift et al., 2014; Baken et al., 2015).

10 4.3 Water quality affected by the operational management of the pumping station

11 Since the renovation of the pumping station in the autumn of 2008, it runs typically overnight during
12 normal meteorological conditions, as reason of cheaper power supply. The low-frequency sampling
13 is always performed during daytime. The distribution of pumping hours and sampling moments over
14 the day during the period October 2014 – September 2015 and boxplots of measured TP
15 concentrations over the day during the months January and February 2015 are shown in Fig. S8.
16 These two months were selected because boxplots for longer time series are dominated by the
17 seasonal trends in the TP concentration. The median, quartile and maximum TP concentrations were
18 higher during night hours than during daytime. As a result, the monitoring program systematically
19 misses the TP peak that occurs during pumping and consequently does not measure diurnal cycles in
20 water quality caused by the pumping station. The reported time series from the low-frequency
21 sampling program is, thus, not fully representative for the TP concentration at the polder outlet. As a
22 consequence, export fluxes from the polder as calculated from low-frequency sample data
23 underestimate the true export P-loads (Fig. 3). The NO_3 concentration showed no structural
24 response on pumping, further illustrating the importance of resuspension of P by pumping.

25 The preferred timing of sampling during regular working-hours is also critical for trend detection in
26 the resulted dataset time series (Fig. 6). Trend analysis before and after replacement of the diesel
27 engines compared with trend analysis over the years 2000-2015 indicates that the trend of slightly
28 decreasing concentrations over the years 2000-2015 may be caused by the sudden decrease of
29 concentrations after renovation of the pumping station which is an artifact of a change in pumping
30 regimes.

31 The number of diesel powered pumping stations in the Netherlands has rapidly declined during the
32 last decades. There were around 200 diesel or hybrid (diesel + electric) powered pumping stations in

1 operation in 1990. Currently, there are only 40 remaining and these pumping stations have mainly a
2 function for emergency situations (Gemalen, 2015). During the same period, electric powered
3 pumping stations have been equipped with automatic switching systems. Nowadays, a large
4 majority of pumping stations operates predominantly during night hours. As the pumping station is
5 the outlet of a (artificial) water system it is often a monitoring location for surface water quality as
6 well. The renovation of pumping stations may thus have had a substantial impact on reported trends
7 in water quality on a regional or even a national scale.

8 5 Conclusions

9 High-frequency monitoring at the outlet of an agriculture-dominated lowland water system
10 combined with low-frequency monitoring at several other locations in the polder appears to be an
11 effective tool to reveal difficult to notice responses in surface water quality. P and NO₃ react
12 differently. Conclusions regarding P are the following:

- 13 • The P retention potential of the polder water systems is enhanced compared to natural
14 catchments due to the artificial pumping regime that prevents high discharge flow and
15 therefore limits resuspension of particulate P.
- 16 • Groundwater seepage, biogeochemical remobilization and wastewater treatment plant
17 effluent are sources of TP in the surface water. The relative importance of these sources,
18 however, cannot be determined.
- 19 • Rainfall events do not result in TP concentration peaks. Transport of particulate P that
20 originates from groundwater and (agricultural) drains discharge is strongly retained but
21 particulate P can be remobilized due to biogeochemical processes in the sediment layer at
22 other moments. This makes it difficult to link agricultural practice to P concentrations in the
23 surface water and this should be accounted for when judging measures to reduce P loads
24 from agriculture.
- 25 • The artificial pumping regime and high retention capacity of polder catchments, however,
26 enables the potential for measures to reclaim P from the water systems after being leached
27 from the soil but before being transported to downstream surface water bodies.

28 Conclusions with respect to N:

- 29 • The NO₃ load to surface water originates from subsurface drains in the agricultural area,
30 likely in combination with quick interflow via clay cracks, that start discharging upon
31 intensive rainfall events and result in a quick response of the NO₃ concentration at the
32 polder outlet.

- 1 • Intensive rainfall events within a few weeks after manure application in February results in
2 incidental losses of NO₃.

3 In general it can furthermore be concluded that:

- 4 • Surface run-off is generally not an important transport mechanism controlling NO₃, P and SS
5 dynamics in the polder catchment, expect at the end of a freeze-thaw cycle.
6 • The timing of sampling relative to the operating hours of a pumping station affects the
7 concentration of TP and SS and this should be accounted for when calculating P export loads,
8 determining trends in water quality or when evaluating water quality against ecological
9 thresholds and standards.

10 Acknowledgements

11 The Regional Water Authority Zuiderzeeland is gratefully acknowledged for the financial support for
12 installation and maintenance of the high-frequency monitoring station and providing the water
13 quality and groundwater level data. The useful comments of two anonymous reviewers are greatly
14 appreciated. Funding of the project was provided by Deltares (project SO2015: From catchment to
15 coast).

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1 Tables

2 Table 1. Locations of the low-frequency monitoring program in Lage Afdeling pumped drainage area
3 that is drained by the Blocq van Kuffeler pumping station.

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

4

5 Table 2. Rainfall events and response of NO₃ 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

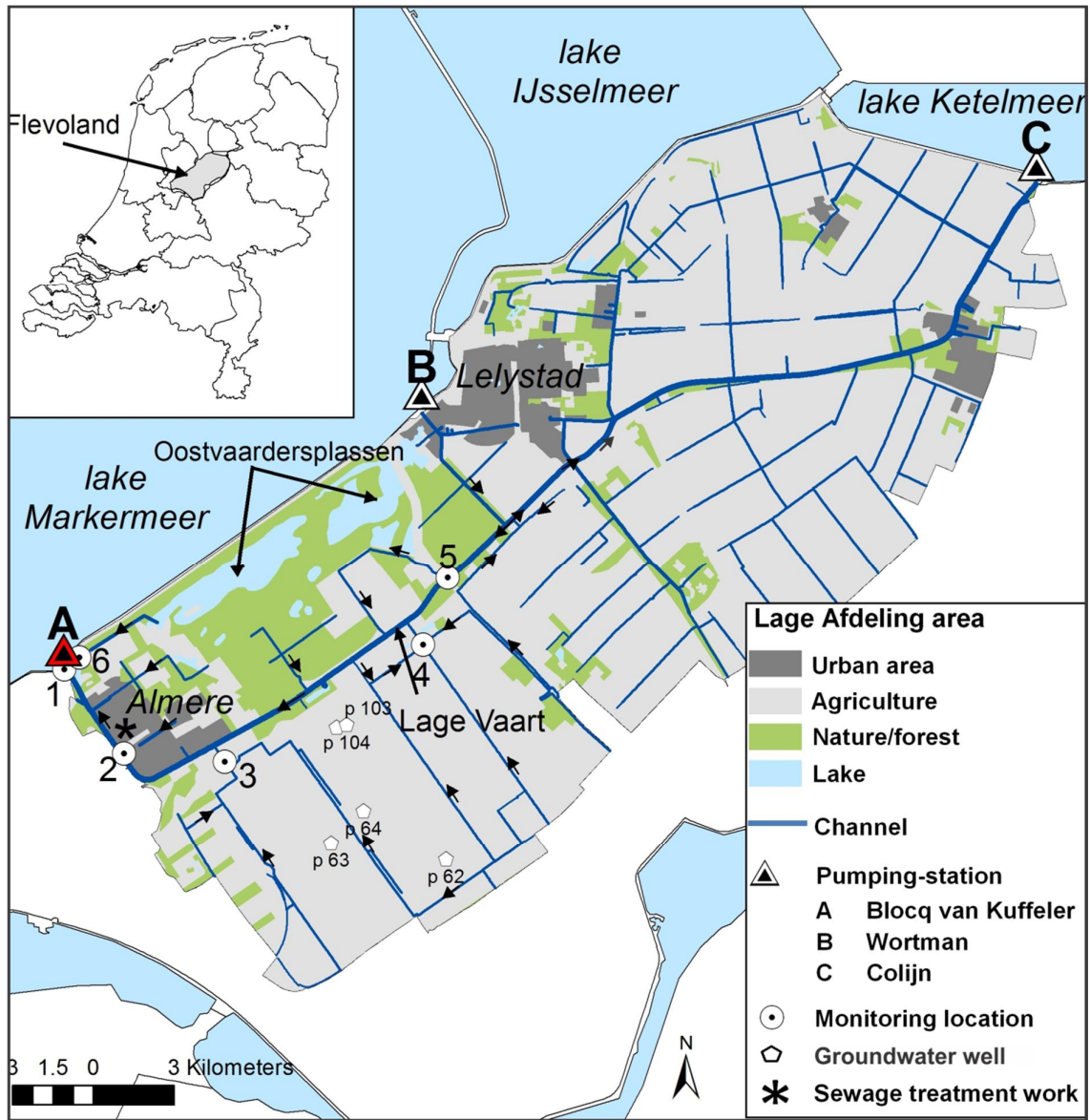
6

7 Table 3. Summary of TP and turbidity peaks, calculated as difference between the maximum value
8 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

9

1 Figures

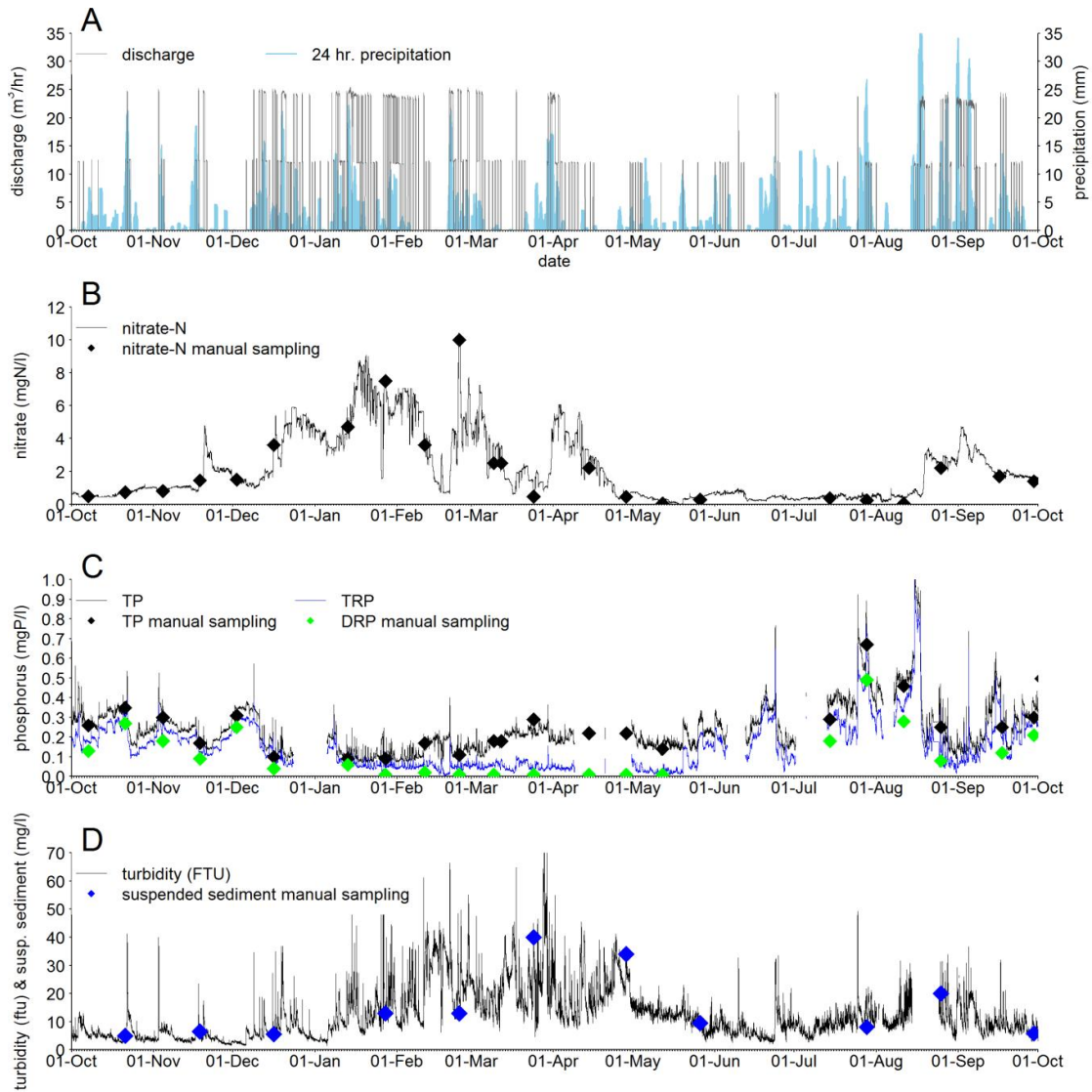


2

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

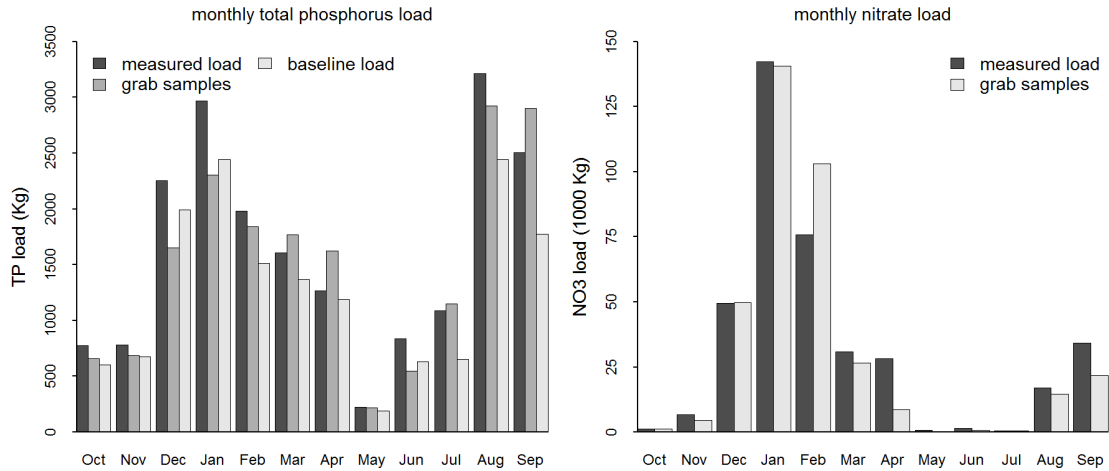
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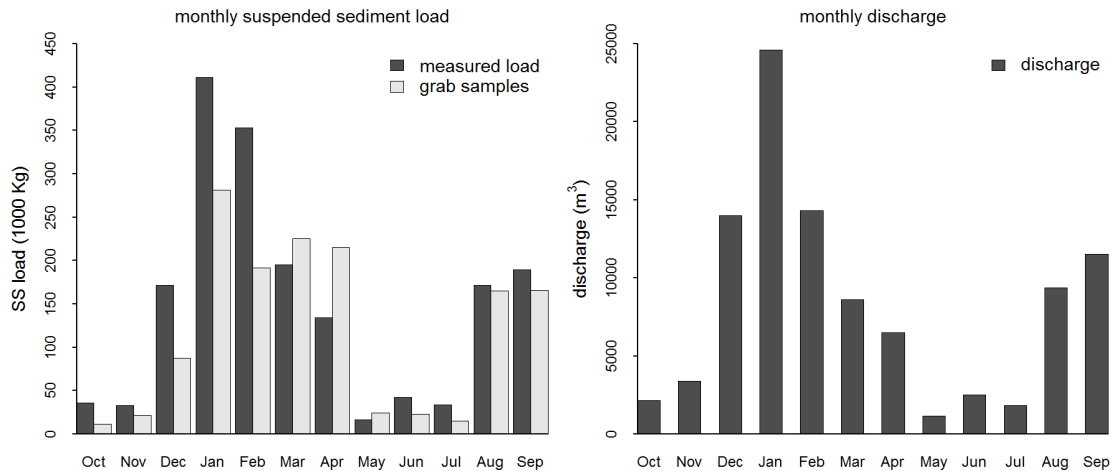
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2 Figure 2. High-frequency monitoring data for the Lage Vaart channel at the pumping station Blocq
 3 van Kuffeler: (A) discharge as generated by the pumping station and 1 day antecedent precipitation;
 4 (B) nitrate-N 5 minutes data, with NO₃-N manual sampled biweekly data; (C) total phosphorus and
 5 total reactive phosphorus 20 minutes data, with TP and DRP manual sampled biweekly data; (D)
 6 turbidity 5 minutes data, with suspended sediment manual sampled monthly data.



1

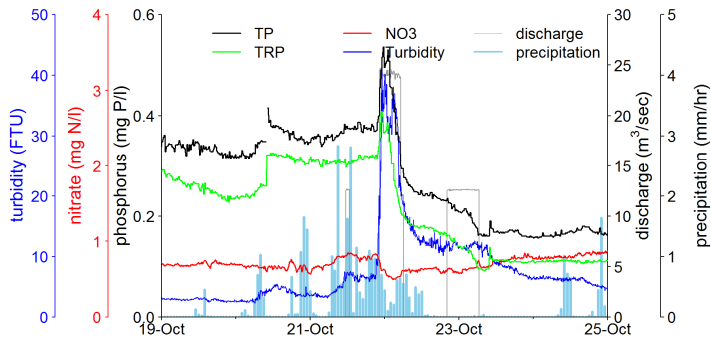
Seasonal and annual load	winter (Oct-Mar)	summer (Apr-Sep)	year	Seasonal and annual load	winter (Oct-Mar)	summer (Apr-Sep)	year
TP (kg)	10350	9150	19500	NO ₃ (1000 kg)	306.3	82.3	388.6
TP grab samples (kg)	8900	9350	18300	NO ₃ grab samples (1000 kg)	326.2	46.4	372.6
TP baseline (kg)	8600	6900	15500				



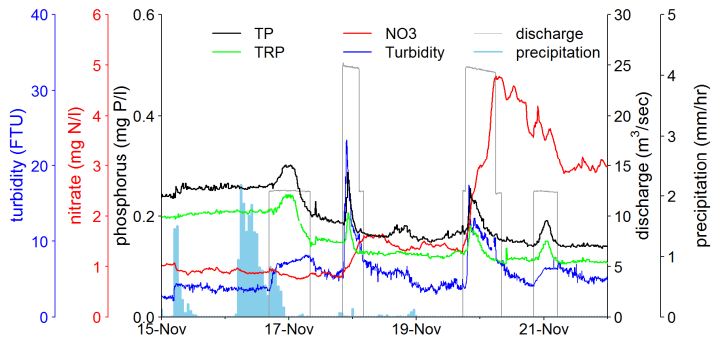
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Seasonal and annual load	winter (Oct-Mar)	summer (Apr-Sep)	year	Seasonal and annual load	winter (Oct-Mar)	summer (Apr-Sep)	year
SS (1000 kg)	1200	588	1788	Discharge (m ³)	67000	33000	100000
SS grab samples (1000 kg)	819	609	1428				

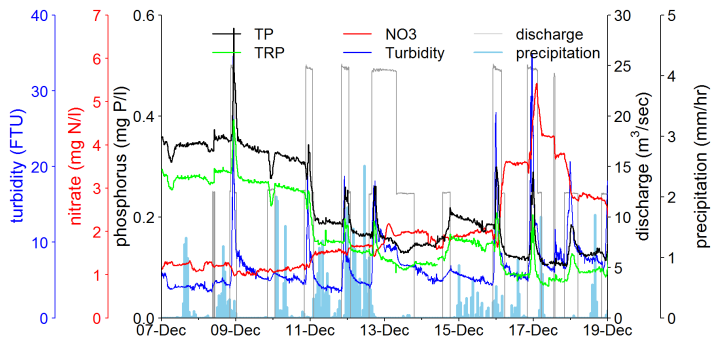
3 Figure 3: TP, NO₃ and SS export loads and discharge at the pumping station Blocq van Kuffeler. The
 4 measured load is calculated from the high-frequency data, the grab sample load is calculated from
 5 interpolation of the low-frequency data, the TP baseline load was calculated with the high-frequency
 6 TP data after separation of the short-scale concentration peaks generated by the pumping station.



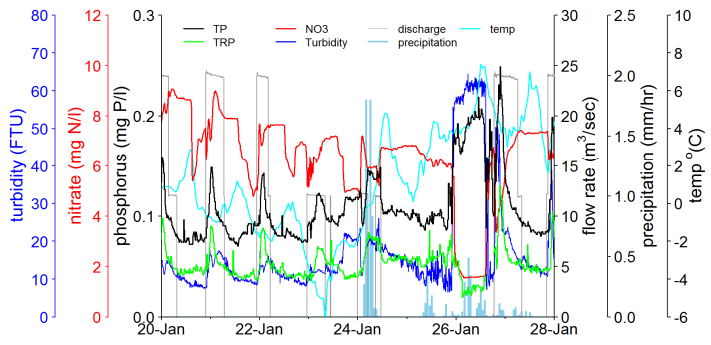
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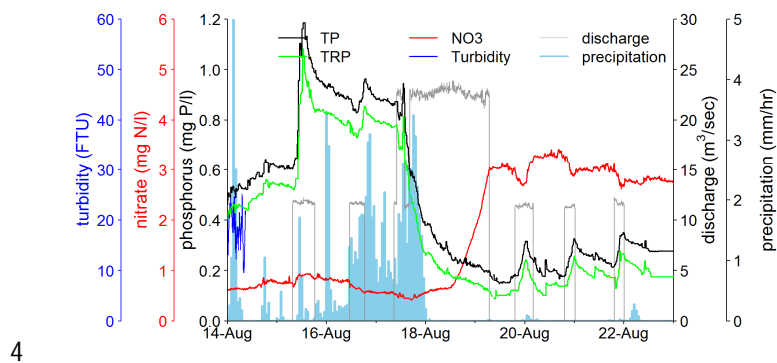
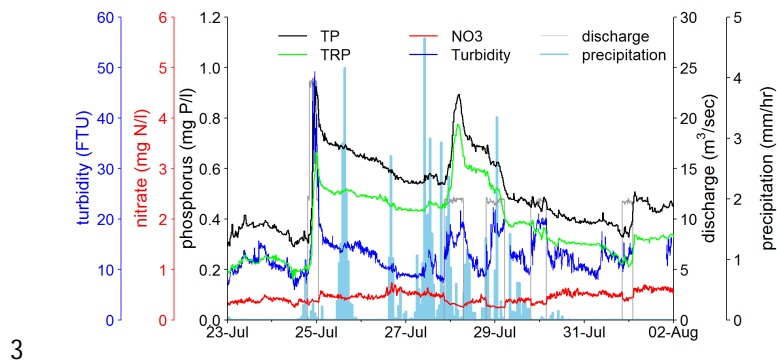
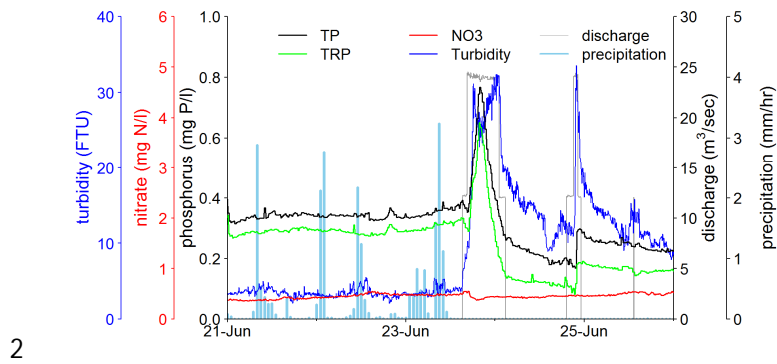
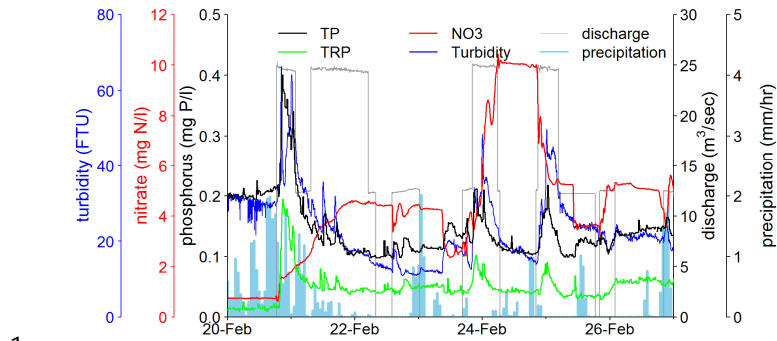
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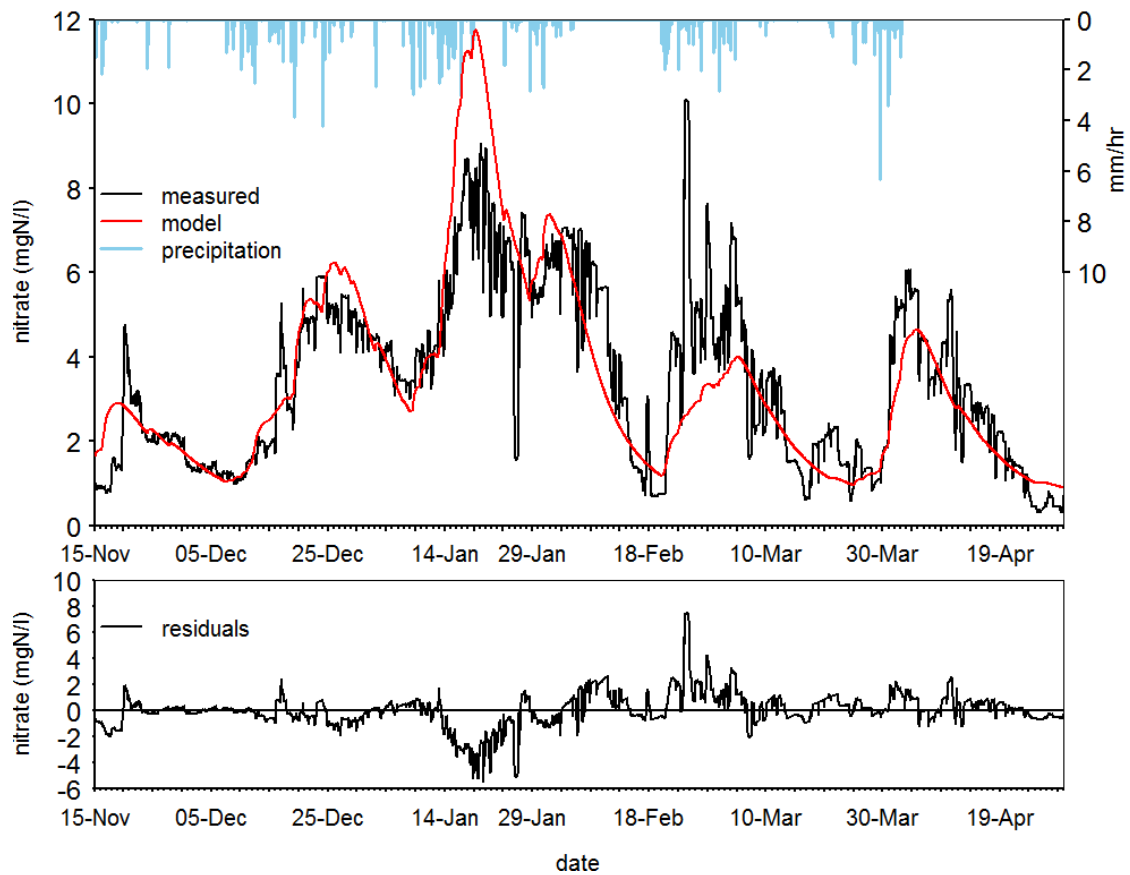


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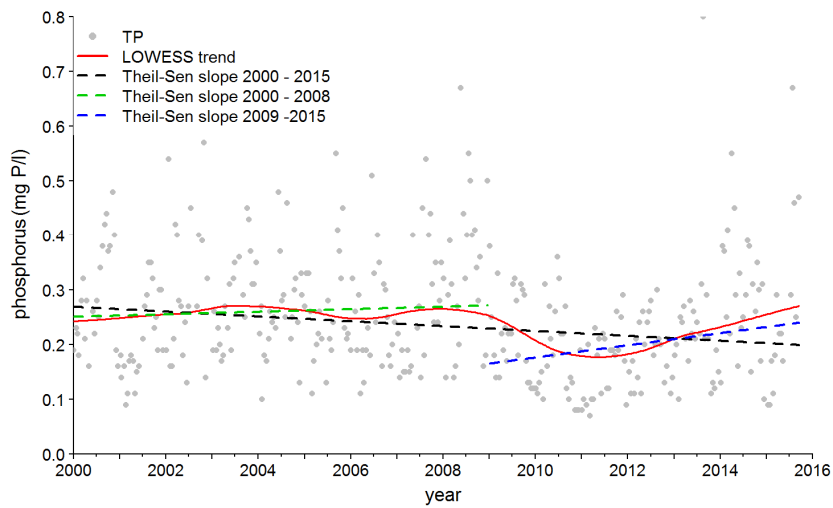
5 Figure 4. Examples of surface water NO_3 , TP and turbidity dynamics at the pumping station Blocq van
 6 Kuffeler during meteorological events between October 2014 and August 2015 together with the
 7 pumping regime and precipitation (in mm hr^{-1}). The January event demonstrates the effect of freeze-

- 1 thaw on the nutrient concentrations while the other events show the nutrient dynamics upon
- 2 rainfall events.

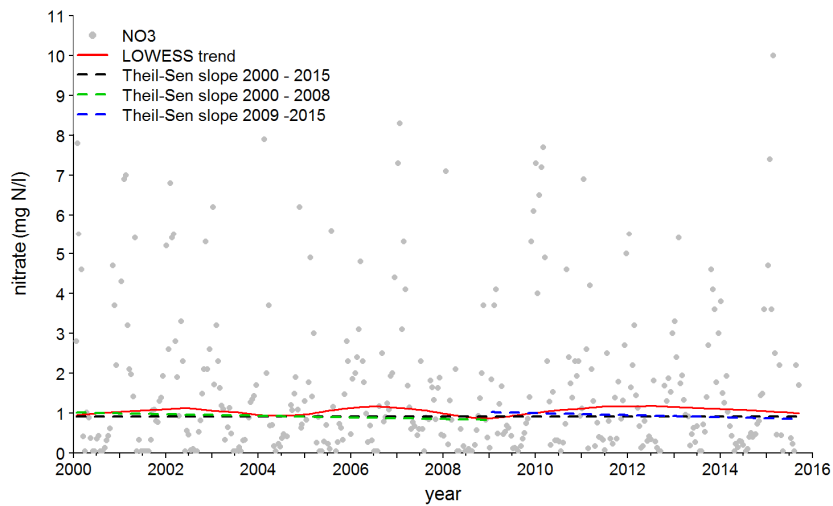


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- 4 Figure 5. Measured and simulated NO_3 concentrations and rainfall data (top); and residual NO_3 series
- 5 (bottom).

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- 7
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3 Figure 6: Trends in TP and NO₃ concentrations over the period 2000-2015 at location 1 (Blocq van
4 Kuffeler).

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