Groundwater impacts on surface water quality and nutrient loads in lowland polder catchments: monitoring the greater Amsterdam area

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Abstract. The Amsterdam area, a highly manipulated delta area formed by polders and reclaimed lakes, struggles with high nutrient levels in its surface water system. The polders receive spatially and temporally variable amounts of water and nutrients via surface runoff, groundwater seepage, sewer leakage, and via water inlet from upstream polders. Diffuse anthropogenic sources, such as manure and fertilizer use and atmospheric deposition, add to the water quality problems in the polders. The major nutrient sources and pathways have not yet been clarified due to the complex hydrological system in such lowland catchments with both urban and agricultural areas. In this study, the spatial variability of the groundwater seepage impact was identified by exploiting the dense groundwater and surface water monitoring networks in Amsterdam and its surrounding polders. Twenty-five variables (concentrations of Total-N, Total-P, NH_4, NO_3, HCO_3, SO_4, Ca, and Cl in surface water and groundwater, N and P agricultural inputs, seepage rate, elevation, land-use, and soil type) for 144 polders were analysed statistically and interpreted in relation to sources, transport mechanisms, and pathways. The results imply that groundwater is a large source of nutrients in the greater Amsterdam mixed urban/agricultural catchments. The groundwater nutrient concentrations exceeded the surface water Environmental Quality Standards (EQSs) in 93 % of the polders for TP and in 91 % for TN. Groundwater outflow into the polders thus adds to nutrient levels in the surface water. High correlations (R^2 up to 0.88) between solutes in groundwater and surface water, together with the close similarities in their spatial patterns, confirmed the large impact of groundwater on surface water chemistry, especially in the polders that have high seepage rates. Our analysis indicates that the elevated nutrient and bicarbonate concentrations in the groundwater seepage originate from the decomposition of organic matter in subsurface sediments coupled to sulfate reduction and possibly methanogenesis. The large loads of nutrient rich groundwater seepage into the deepest polders indirectly affect surface water quality in the surrounding area, because excess water from the deep polders is pumped out and used to supply water to the surrounding infiltrating polders in dry periods. The study shows the importance of the connection between groundwater and surface water nutrient chemistry in the greater Amsterdam area. We expect that taking account of groundwater-surface water interaction is

1 also important in other subsiding and urbanising deltas around the world, where water is managed intensively in order to
2 enable agricultural productivity and achieve water sustainable cities.

3 **1 Introduction**

4 The hydrology of many lowland delta areas is highly manipulated by human activities such as ditching, draining, and
5 embanking, to enable agriculture and habitation. Lowland deltas account for 2 % of the world's land, but accommodated
6 around 600 million people in 2000, and about 1400 million by 2060 as was estimated by Neumann et al. (2015). The
7 reclamation of swamps and lakes and the drainage of peat areas to enable urbanisation and agriculture severely changed the
8 hydrological, chemical, and ecological environment of these areas (Ellis et al., 2005; Yan et al., 2017). Lowland delta areas
9 are vulnerable for water quality deterioration by processes like salinization and eutrophication, which can be amplified by
10 climate change (Wu et al., 2015) and land subsidence (Minderhoud et al., 2017).
11 The Netherlands is a densely populated country where surface water salinization and eutrophication are common problems.
12 It is a typical highly urbanized country, with 2/3 of its land lying below mean sea level. In The Netherlands, small regulated
13 catchments called polders have been developed over centuries by diking in and draining lakes and swamps (Huisman, 1998).
14 Over 10 million people are living in the coastal area, mainly in the Western part where a Holocene layer of peat and clay
15 covers Pleistocene fluvioglacial sands. Especially the deepest polders receive large amounts of groundwater seepage. The
16 surface water levels within the polder catchments are artificially controlled by pumping water out into the regional water
17 systems (called Boezem), which further accelerates groundwater seepage. Some of the deep polders exhibit upconing of deep
18 saline groundwater into the surface water. The salt loading towards these polders is expected to increase, mainly due to the
19 further lowering of surface water levels in response to subsidence (e.g. Oude Essink et al., 2010; Delsman et al., 2014).
20 Draining the peat polders has also led to subsidence and repetitive lowering of surface water and groundwater levels. As a
21 consequence, nutrients are released due to peat oxidation (Hellmann and Vermaat, 2012). Another nutrient source is the large
22 scale agricultural application of manure and fertilizer. Although manure legislation was already enforced in 1986, surface
23 water quality in the area still does not meet the EU Water Framework Directive standards for chemical and ecological water
24 quality (Rozemeijer et al., 2014). The local water authority, called Waternet, is commissioned to improve water quality in a
25 cost-effective mitigation program. The assessment of load contributions from different pollution sources is essential to set
26 realistic region-specific water quality targets and to select appropriate mitigation options.
27 Influences of groundwater on surface water quality have recently gained more attention by hydrologists (e.g. Rozemeijer and
28 Broers, 2007; De Louw et al., 2010; Garrett et al., 2012; Delsman et al., 2015). Rozemeijer et al. (2010) found that
29 groundwater seepage has large impacts on surface water quality in a lowland agricultural catchment. A study by Holman et
30 al. (2008) in the United Kingdom and the Republic of Ireland also suggested that the groundwater contribution to surface
31 water nutrient concentrations is more important than previously thought. Furthermore, Meinikmann et al. (2015) found that
32 lacustrine groundwater discharge contributed for more than 50% of the overall external P load in their study lake.

1 Vermonden et al. (2009) concluded that upward seepage from Meuse-Waal canal delivered NO_3 and Cl to urban surface

2 water system. The impact of other landscape characteristics on surface water quality, such as soil type and land use, has also

3 been explored. For example, Van Beek et al. (2007) found that nutrient rich peat layers will remain a potential source of

4 nutrients in surface water in many peat polders in the western part of The Netherlands. Mourad et al. (2009) found that the

5 spatial patterns of nitrate and phosphate concentrations in the Ahja River catchment in Estonia were related to spatial

6 differences in urban and agricultural land use proportions. Vermaat et al. (2010) studied 13 peat polders in the Netherlands

7 and reported that agricultural land use largely determined the variability in nutrient concentrations and loads. Phosphorus

8 was observed in higher concentrations in urban areas than in rural areas by Meinikmann et al. (2015) In some studies, point

9 sources like effluent from sewage treatment plants dominated the phosphorus loads (e.g. Wade et al., 2012), but the

10 Netherlands is known to have early invested in centralised sewage treatment works, thus avoiding the many individual spills

11 that are present is some bordering countries (EU, 2017).

12 Previous water quality research in polder areas have mainly focused on the impact of land use types and topography. The

13 impact of groundwater and flow routes on spatial water quality patterns in polders has not been systematically studied. Such

14 insight is highly needed, as a cost-effective protection and regulation of water resources requires an integrated assessment of

15 water and contaminant flow routes in the water system as a whole. In general however, water and contaminant flow routes in

16 urban settings are more complex than in rural areas, due to the highly variable surface permeability and human emissions of

17 pollutants.

18 This study aimed at identifying the impact of groundwater on surface water quality in the polder catchments of the greater

19 Amsterdam city area, which is the management area of Waternet, the organisation which manages dikes, regulates water

20 levels and pumping regimes and is responsible for the clean surface water, drinking water supply and waste water treatment.

21 To achieve this, we analysed regional surface water and groundwater quality monitoring data in combination with ten

22 landscape characteristic variables for 144 polders: N and P agricultural inputs, surface elevation, paved area percentage,

23 surface water percentage, seepage rate, and soil type represented by calcite, humus, and clay percentages. Our statistical

24 analyses yielded insight into the impact of groundwater on the surface water chemistry of the urban and rural polders of

25 Amsterdam. The presented approach contributes to realistic and effective water quality regulation in the Waternet

26 management area and can also be applied to other deltas in the world with adequate groundwater and surface water

27 monitoring data.

28 **2 Methods**

29 **2.1 Study area**

30 This study focuses on the polder catchment landscape around the city of Amsterdam in The Netherlands. The whole study

31 area spans 700 km^2, from downtown Amsterdam situated in the northwest to the border of the province of Utrecht in the

32 southeast (Fig. 1). Amsterdam is a low-lying highly paved city located in the western part of the Netherlands, developed

around the levees of the tidal outlet of the Amstel River about 700 years ago (Vos, 2015). Nowadays, the water system in Amsterdam is connected to the large fresh water body of the Lake IJ (Fig. 1). Besides Lake IJ, other important large water bodies are the Amstel and Vecht rivers and the Amsterdam-Rhine canal. This regional water system, also called the 'Boezem', connects the Amsterdam-area water system to the Rhine River (upstream) and the Lake IJssel and the North Sea (downstream). In the 19th and 20th centuries, the city expanded, and many new neighbourhoods and suburbs were built. Polders and reclaimed lakes form the main landscape in the southward extensions of the city. Some of these polders are at several meters below Mean Sea Level (MSL) and are influenced by groundwater seepage.

2.1.1 Landscape history and hydrology

Landscape history

Our study area is located in the western part of The Netherlands where large rivers and the sea have intensively interacted for millions of years. The main topographic feature is a Pleistocene sandy ice pushed ridge with elevations ranging from 0 to 30 m, which is located on the east part of the study area (Fig. 1, Fig. S1). To the west, the ridge is bordered by the broad periglacial Pleistocene river plains of the Rhine delta. During the Holocene, these sandy river plains were covered with peat and clay, which are currently found at the surface throughout the western part of the Netherlands, on top of Pleistocene sands. The average thickness of the Holocene peat and clay cover is 20 m, although it increases to over 50 m in former tidal inlet channels (Hijma, 2009).

In 1000 AD, about 5000 years after first settlers appeared in these low lands, the inhabitants started mining peat, digging ditches, constructing dikes, reclaiming former swamps and lakes, and pumping water out into a large scale drainage system (called Boezem). Special hydrological catchments called 'polders' were formed, connected by the 'Boezem' main waterways around them. Fig. S1 and and Table S1 in the Supplementary Information show the entire system of polder catchments (indicated by numbers for reference) and boezems studied in this paper. Prominent on these maps are two deep polders Horstermeer (#79) and Groot Mijdrecht (# 80), two former lakes that were formed after peat excavations. Drainage for lake reclamation and groundwater extraction (Schot, 1992a) caused further subsidence and increased seepage of paleo-marine brackish groundwater from deep aquifers (Delsman et al., 2014).

The long history of marine influence stopped after closing off the estuaries and the inland sea in the 20th century (Huisman, 1998). In 1932, the construction of the Closure Dike (Afsluitdijk) created the fresh water Lake IJssel out of the former salt water Zuiderzee ('Southern Sea') to protect the surroundings from floods and to enable land reclamation. The former marine impact is still reflected by the presence of brackish groundwater in the shallow subsurface (Schot, 1992 b).

The construction of the Amsterdam Rhine Canal separated the study area into two parts (Fig. S1): the Central Holland in the west and the Vecht lakes area in the east. In the Central Holland polders, relatively thick peat layers and pyrite rich clays are still present in the shallow subsoil, as described by Van Wallenburg (1975). The Vecht lakes area is characterized by large open water areas and a number of wetland nature reserves. The rest of the Vecht lakes area is mainly grassland used for dairy farming. Soils in this area are generally wet and rich in organic matter and clay (Schot, 1992 b).

1 Mainly during the 20th century, the urban areas have been growing from the historic city-centres on river and tidal channel

2 levees into the surrounding low-lying polders. To facilitate the construction of buildings, a 1-5 meter-layer of sand was often

3 supplied on top of the original sediments. The thickness of this suppletion sand layer is extremely variable even at a small

4 scale. The sand suppletions are either calcite-poor without shell fragments or calcite rich with shell fragments that indicate

5 their (peri-) marine origin. The spatial distribution and sources of the sand suppletions probably influence groundwater and

6 surface water chemistry, but are poorly registered.

7 **Polder hydrology**

8 Within the polders, the water levels are artificially maintained between fixed boundary levels to optimize conditions for their

9 urban or agricultural land use. Boezem water levels always exceed the polder surface water levels. In the case of water

10 deficiency, water is let into the polder ditches from the boezem through pipes by gravity flow (Fig. 2a). Pumping stations are

11 situated at the boezems to regulate the water levels in the polders in times of precipitation excess. In the case of a water

12 surplus, pumping stations start pumping water out of the polder into the boezem-system (Fig. 2b).

13 The regional flow directions in wet and dry periods in the study area are depicted in Fig. 3. The Amsterdam-Rhine canal, the

14 Amstel River, and the Vecht River are the main water courses discharging surface water from the south to the north in

15 periods of water surplus (Fig. 3). In periods of water deficiency, however, the flow directions are reversed in some parts of

16 the system.

17 There are six main sources of inlet water to compensate for water shortage in dry periods (Fig. 3): (1) Amsterdam Rhine

18 Canal (ARC): water of the ARC originates from the Rhine and is supplied as inlet water for the southeast polders and

19 polders in the southeast of Amsterdam city; (2) Amstel River: the historic canals of the city of Amsterdam are mainly

20 flushed by water from the Amstel River. Via the canals, this water discharges to the downstream part of the ARC and further

21 into the North Sea; (3) Groot Mijdrecht and Horstermeer: the brackish surplus of seepage water from the deep polder Groot

22 Mijdrecht (~1000 mg Cl L^{-1} on average) and Horstermeer (~500 mg Cl L^{-1}) is pumped into the Boezem system and is

23 redistributed towards surrounding polders (pink lines in Fig. 3); (4) Rijnland Water Authority district: polders in the far west

24 of the study area receive inlet from the neighboring Water Authority district Rijnland. The water quality of this source is

25 unknown. (5) and (6) Vecht River and Lake IJ: polders along the Vecht River receive inlet water that partly originates from

26 the Rhine and partly from Lake IJ. Polders close to Lake IJ receive large amounts of water directly from the lake. The Lake

27 IJ water is also used to flush canals in the city of Amsterdam.

28 **2.1.2 Characterisation of regions**

29 Based on the geology and paleohydrological history as introduced in section 2.1.1, 5 regions were identified (see Fig. 4). The

30 5 regions are: (1) the Zuiderzee margin region, with shallow brackish groundwater, lies directly adjacent to the former salt

31 water Zuiderzee, which was dammed in the 1930s and transformed into the fresh water Lake IJssel (connected to Lake IJ),

32 which is now the biggest fresh water reservoir of The Netherlands; (2) the deep polders Groot-Mijdrecht and Horstermeer,

33 which are reclaimed lakes with clayey lake sediments at the surface. These polders are characterized by upconing of salt

groundwater from deeper layers (Oude Essink et al., 2005; Delsman et al., 2014) and intensive arable farming; (3) the Central Holland region, where the polders are characterized by a relatively thick sequence of marine clays and intercalated peats; (4) the Vecht lakes region at the western margin of the ice pushed ridge, characterized by shallow peat soils over a sandy subsoil and large shallow lakes and wetlands resulting from peat excavations (van Loon, 2010) with mostly dairy farming; and (5) the Ice pushed ridge in the eastern part of the study area, which is characterized by permeable sandy soils, recharge of freshly infiltrated water, and the mere absence of draining water courses.

Our a priori expectation was that the groundwater quality of these 5 regions is significantly different, because of their specific paleohydrological situations and present day groundwater flow patterns. We therefore used the regions to evaluate the groundwater quality patterns and to give structure to our comparisons between groundwater and surface water concentrations and loads.

2.2 Data processing

The database that was compiled and used for this study covers 144 individual polders and includes monthly surface water quality data, spatiotemporally averaged groundwater quality data (TN, NO_3, NH_4, SO_4, TP, Ca, HCO_3, and Cl), daily pumping station discharge time series, and polder averages of the following statistic variables: N and P agricultural inputs, polder seepage rates, elevations, surface water and paved area percentages, and calcite, clay, and humus percentages of the upper soil layer. More information about the data processing and the database can be found in the Supplementary Information.

2.2.1 Groundwater data

A total of 802 observation wells of groundwater quality are available from the period 1910-2013 (mostly after 1980), largely drawn from the National Groundwater Database DINO (TNO, DINOLoket). We selected analyses from the upper 50 m of the subsurface, which corresponds with the thickness of the first main Pleistocene aquifer in the area and the Holocene cover layer. For our analyses, in order to use as much of the available groundwater data as possible to cover the entire region and all the polders, we averaged concentrations at individual monitoring screens of each monitoring well for all sampling dates available. The large majority of the groundwater quality data we used is from the last 30 years (for example, 85% of the chloride and 93% of the P measurements are from after 1980). In this study area, we do not expect that using some data from before 1980 creates a significant bias to the results of the study, because hydrogeochemical processes in the reactive subsurface such as sulfate reduction and methanogenesis have a stabilizing effect on the water composition in this area. Moreover, the overall flow patterns have not changed much in the past 30 to 100 years, because the flow systems are completely determined by the water levels maintained in the polder systems which have not changed much over the past 100 years. However, the interface between fresh and salt water is known to slowly move into the direction of a new equilibrium (Oude Essink et al., 2010), but the process is known to be very slow and to continue over the next 200 years.

1   To analyse the spatial pattern of groundwater quality, we averaged concentrations of all the monitoring wells located in the

2   same polder (for more details, see Table S2). For 24 polders out of the polders without groundwater quality data, the

3   concentrations were estimated by Inverse Distance Weighted interpolation, however using absolute elevation difference

4   instead of distance. The greater the absolute elevation difference, the less influence the polder has on the output value. The

5   equations are:

$$C_0 = \sum_{i=1}^{n} \lambda_i C_i \tag{1}$$

$$\lambda_i = d_{i_0}^{-p} \Big/ \sum_{i=1}^{n} d_{i_0}^{-p} \,, \qquad \sum_{i=1}^{n} \lambda_i = 1 \tag{2}$$

6   C_0, prediction of target polder; C_i, observed value of surrounding polders; n number of observations; p, power parameter (2

7   in this case); d_{i_0}, absolute elevation differences of target polder with surrounding polders. Subsequently, to interpret the

8   groundwater quality patterns, the variation of concentrations in and between the 5 regions was visualized using boxplots

9   (Helsel and Hirsch, 2002).

10   Because our dataset contains both fresh and brackish to saline water, we used the mass SO_4/Cl ratio of the samples as an

11   indicator of sulfate reduction. SO_4/Cl ratios lower than the sea water ratio of 0.14 (Morris and Riley, 1966) point to the

12   occurrence of sulfate reduction (Appelo and Postma, 2005; Griffioen et al., 2013). Ratios above 0.14 point to the addition of

13   sulfate relative to diluted sea water through processes like pyrite (FeS_2) oxidation or through input via atmospheric inputs,

14   fertilizers, manure, or leakage and overflow of sewer systems.

15   Average concentrations in groundwater for each polder were mapped to be compared with average annual surface water

16   concentrations (See section 2.2.2). The potential relationship between the solute concentrations in groundwater (TN, NO_3,

17   NH_4, SO_4, TP, Ca, HCO_3, and Cl), the N and P agricultural inputs, and the landscape variables (paved area percentage,

18   elevation, seepage rate, surface water area percentage, lutum, humus and calcite percentages of top soil) were explored using

19   the Spearman correlation, which reduces the influence of outliers and yields a robust correlation statistic (Helsel and Hirsch,

20   2002).

21   To further explore the statistical relations in our data set, scatter plots were made to evaluate HCO_3, SO_4, Cl, and nutrient

22   (NO_3, NH_4 and PO_4) concentrations in groundwater. We also explored the links between alkalinity (over 99 % of our

23   groundwater alkalinity was dominated by HCO_3, (Stuyfzand, 2006)), Cl concentration, SO_4/Cl ratio and nutrients (TN, NH_4

24   and TP) concentrations. For our interpretation, we also used the calculated amount of consumed or produced SO_4 in mg L^{-1}

25   relative to the SO_4/Cl ratio of diluted seawater, using Eq. (3):

26   $SO_4\,consumed(-)\ or\ produced(+) = SO_4\,measured - Cl\ measured \cdot SO_4\,sea/Cl\ sea \tag{3}$

1 In order to understand the impact of cation exchange processes involving Ca and Na exchange during salinization and/or

2 freshening of aquifers (Griffioen, 2004; Stuyfzand, 2006) we defined the amount of exchange Na_{ex} as:

3 $$Na_{ex} = Na_{gw} - Cl_{gw}(Na_{gw}/Cl_{seaw})$$ (4)

4 Where, Na_{ex} is the amount of Na exchange; gw, ground water; seaw, seawater. $Na_{ex} > 1$ points to freshening, $Na_{ex} < -1$ to

5 salinizing conditions.

6 **2.2.2 Surface water data**

7 Loads represent the contribution of polders to surface water quality of the regional water system in weight per time unit. To

8 eliminate the impact of the size of polders, we calculated daily load per area in kg ha^{-1} d^{-1}. This was calculated using the

9 daily average loads of each solute divided by the polder areas using Eq. (5):

$$\text{Load per area} = \frac{L}{A} = \frac{1}{A} \cdot \frac{C \cdot Q}{1000}$$ (5)

10 Where L is daily load kg d^{-1}, A is polder area (ha), C is daily solute concentration in mg L^{-1} and Q is daily discharge in m^3 d^{-}

11 ^{1}. Average daily loads for each year were multiplied by 365 to get average yearly loads per area. Monthly surface water

12 quality measurements for the period 2006-2013 of 144 polders were extracted from the Waternet database. The

13 measurements were converted to daily time series by stepwise interpolation between the monthly measurements. We

14 assigned a concentration of zero to measurements below the detection limits. Discharge data Q are daily measurements over

15 the same time period. An average over multiple pumps, when present, was taken for each polder. For further details about

16 the data processing we refer to Table S2.

17 The pumping discharge is regulated to respond to water surplus or deficiency conditions in the polder catchments. Using the

18 pumping frequency data, we proved that solute concentrations in pumped water are usually higher at the beginning of each

19 pumping activity (Van der Grift et al., 2016). The pumping rates may also influence water quality in the polder. To eliminate

20 differences caused by pumping rates, we used the normalized concentration calculated using Eq. (6):

$$C = \frac{\text{Load per area} \cdot A}{Q}$$ (6)

21 In this equation, C is the normalized concentration (mg L^{-1}), Load per area is from Eq. (1), Q is the pumping discharge (m^3 y^{-}

22 ^{1}), and A is the polder area (m^2).The statistical methods that were used for groundwater quality (described in section 2.2.1)

23 were also applied to the surface water normalized concentrations.

24 Based on a national assessment on ecosystem vulnerability, Environmental Quality Standards (EQSs) were set by the Water

25 Boards (Heinis and Evers, 2007). For most ditches and channels in the clay and peat regions, EQSs of TN and TP are 2.4 mg

26 L^{-1} and 0.15 mg L^{-1}, respectively (Rozemeijer, 2014). We used these most common EQSs as reference concentration values.

27 For example, the EQSs of TN and TP were used for the legend classifications in our surface water quality maps and were

added as reference lines in our concentration boxplots. Percentages of polders exceeded these standards were calculated in this paper.

2.2.3 Surface water compared with groundwater solute concentrations

We statistically analysed the groundwater and surface water quality data and landscape characteristic variables by (1) calculating the correlation coefficients between averaged groundwater solutes concentrations and normalized concentrations of surface water using the Spearman method, and (2) by selecting variables (based on the correlation matrix above) to be integrated into multiple linear regression models for predicting surface water solute concentrations. Again, the Spearman method was applied and linear regression was based on ranks in order to avoid outliers to determine the outcomes. The explaining variables for surface water concentrations include groundwater solute concentrations, N and P agricultural inputs, landscape characteristics, and the SO_4/Cl ratio in groundwater. We adopted the method described by Rozemeijer et al. (2010), who described a form of sequential multiple regression analysis, where variables were added to the regression depending on their effects on the coefficient of determination R^2. The regression analysis started with a singular regression using the explaining variable with the highest coefficient of determination (R^2) for explaining the surface water quality parameter under consideration. Subsequently, the best regression models were searched with two and three explaining variables, where we accepted an additional variable only when the coefficient of determination R^2 increased with at least 0.03. In this method, dependent variables can still add to the resulting R^2 as the coefficient of determination R^2 of the individual dependent variable pair is seldom larger than 0.7, pointing to some explaining power may still be present in the uncorrelated part (0.3). For comparison purposes, we also used the surface water EQSs as reference concentration values in the groundwater quality maps and boxplots, although the EQS's have no administrative meaning for groundwater itself.

2.2.4 Solutes redistribution in surface water

Loads were used to assess the impact of different polders as sources of solutes for the boezems and the receiving water bodies further downstream. In general, the spatial patterns can be distinguished through maps of the surface water solute loads per area if there are no other influences. However, there are exceptions such as the seepage water which is pumped out of the two upconing polders Groot Mijdrecht and Horstermeer, which is discharged into the Boezem system and used as inlet water for the surrounding polders during summer. To show the impact of this inlet water on the receiving polders' water quality, we analysed the inlet solute loads and the resulting surface water concentrations for polder Botshol. Polder Botshol (part of polder # 104 Noorderpolder of Botshol (zuid and west)) with an area of 1.3 km^2 receives inlet water from the Amstel boezem system that has a significant contribution of seepage water that is pumped out of the polder Groot Mijdrecht.

Two models were applied for simple solute concentration calculations based on inlet water quality. Model 1 calculates the accumulation of solutes in the water body, with evaporation as the only output for water (leaving the solutes behind). Model 2 models the complete mixing and outlet of both water and solutes via other routes like the outlet weir, infiltration, and leakage. In reality, water leaves Polder Botshol partly via evaporation (Model 1) and partly via other routes (Model 2):

1   Model 1 (evaporation): $\qquad C_{i+1} = (C_i \cdot V_0 + C_{inlet} \cdot Q_{inlet})/V_0$ (7)

2   Model 2 (infiltration/outlet): $\qquad C_{i+1} = (C_i \cdot V_0 + C_{inlet} \cdot Q_{inlet})/(V_0 + Q_{inlet})$ (8)

3   where, C_{i+1} is the predicted solute concentration after getting inlet water at time i; C_i is the predicted solute concentration in

4   the polder at time i, the outlet measurements in the beginning of wet period were taken as C_0; V_0 is the water volume in the

5   polder (800.000 m^3), which is assumed to be constant as water levels are tightly controlled; C_{inlet} is the estimated Cl

6   concentration in the inlet water (1000 mg L^{-1}); Q_{inlet} is estimated constant inlet water volume, 6000 m^3 d^{-1}. All parameters

7   are shown in supplementary information Excel spread sheets. The models were applied in the year 2006, 2008, 2009, 2010,

8   2011 and 2012.

9   **3 Results**

10   **3.1 Spatial pattern and statistical analysis of groundwater quality**

11   Fig. 5 and Fig. 6 show the groundwater quality for the upper main aquifer under the 144 polders for Cl, Ca, HCO_3, SO_4, TN,

12   NH_4, NO_3, and TP. The relations between groundwater solutes, landscape variables, and potential hydrochemical reactions in

13   the subsurface were explored by correlation analysis of which the results are shown in Table 1 (yellow part) and Fig. 7 and

14   Fig. 8.

15   **Cl, Ca, and HCO_3**

16   In Fig. 5, the Zuiderzee margin, where brackish groundwater is dominant, P25 and P75 of concentrations are between 290

17   and 2100 mg L^{-1} Cl, 100-300 mg L^{-1} Ca, and 400-1000 mg L^{-1} HCO_3. Relatively high concentrations of Cl, Ca and HCO_3

18   were also for the two deep polders Groot Mijdrecht (# 80) and Horstermeer (Upconing area) with known upconing of salt

19   groundwater. The Central Holland area was dominated by fresh groundwater with low Cl and Ca concentrations, but with

20   considerable amounts of HCO_3. Polders with relatively high chloride (>1000 mg L^{-1}) are distributed along the former

21   Zuiderzee margin, plus the Upconing area which is two deep polders with known upconing of brackish water. Relative to the

22   regions above, the Vecht lakes area and the Ice pushed ridge showed significantly less mineralized waters with lower HCO_3

23   and Cl concentrations. For example, the P75s of Cl in these two regions are below 150 mg L^{-1} and the P75s of HCO_3 below

24   350 mg L^{-1}. The groundwater HCO_3 concentrations (Fig. 6) show an east-west increasing trend with highest concentrations

25   in both the fresh and brackish areas west of the Amsterdam Rhine Canal.

26   **SO_4 and SO_4/Cl**

27   The Zuiderzee margin and the Upconing area showed large ranges of SO_4 concentrations (P25 and P75: 7-125 mg L^{-1} and 7-

28   250 mg L^{-1}, respectively) with the SO_4/Cl mass ratios generally lower than the 0.14 ratio for diluted seawater. The polders in

29   the eastern Zuiderzee margin showed the highest average SO_4 levels (Fig. 6). The Central Holland area exhibited the lowest

30   SO_4 concentrations with the smallest variability, with SO_4/Cl P75 typically lower than 0.14. However, some outliers in this

1 region reached quite high sulfate concentration levels (>200 mg L^{-1}). The Vecht lakes and the Ice pushed ridge showed

2 intermediate sulfate concentrations and typically have a SO$_4$/Cl ratio clearly above 0.14.

3 **NH$_4$, TN, NO$_3$, and TP**

4 The higher groundwater NH$_4$ and TP concentrations generally locate in the western part of the study area (Zuiderzee margin,

5 Upconing area, and Central Holland regions). Median NH$_4$ concentrations in the Zuiderzee margin (6.4 mg L^{-1}) and Central

6 Holland (10.6 mg L^{-1}) were far higher than in the Vecht lakes (2.1 mg L^{-1}) and Ice pushed ridge regions (0.07 mg L^{-1}). The

7 same was observed for TP (0.7, 1.6, 0.2 and 0.06 mg P L^{-1}, respectively). Nutrient concentrations in the Upconing area

8 (medians 5.7 mg NH$_4$ L^{-1} and 0.14 mg P L^{-1}) were relatively low compared with the groundwater in the Zuiderzee margin

9 and Central Holland areas, although we consider the NH$_4$ concentration levels to be substantial given the surface water EQS

10 of 2.4 mg N L^{-1}. TN showed the highest median concentration levels in the Zuiderzee margin and Central Holland regions, as

11 well as in the Ice pushed ridge (7.3 mg N L^{-1}). The Ice pushed ridge region also showed the highest level of NO$_3$. In the latter

12 region, nitrate is the main component of TN, while NH$_4$ is the main component in the other regions.

13 Groundwater quality varied from fresh, low mineralized in the eastern parts (Vecht lakes and Ice pushed ridge, Figure 4)

14 towards brackish, highly mineralized and nutrient rich groundwater in the northwest (Zuiderzee margin and Central Holland,

15 Fig. 4). This relationship was further indicated by the strong correlations between Ca and Cl (Spearman R^2 0.77) and

16 between HCO$_3$, TP and NH$_4$ (R^2 0.68-0.82) (Table 1, yellow part). The spatial Ca pattern corresponds largely with the Cl

17 pattern (Fig. 6), showing higher Ca concentrations in the brackish waters, which is related to the high Ca concentrations in

18 (diluted) seawater (Section 4.1). The strong correlation between TN and NH$_4$ (R^2 0.81) showed the dominance of NH$_4$ in TN,

19 except in the suboxic groundwaters under the Ice pushed ridge where nitrate dominates TN. HCO$_3$, TP and NH$_4$ were all

20 weakly negatively correlated with elevation, indicating that higher concentrations exist in the deeper polders which are more

21 affected by brackish groundwater seepage. No significant correlation was found with agricultural N and P inputs, except for

22 a negative correlation between groundwater TN concentrations and N input (Table S2, absolute value lower than 0.4). This

23 suggests that non-agriculture sources of N dominate in most areas.

24 In the more mineralized groundwater systems, sulfate reduction is a potential cause of the significant relationship between

25 HCO$_3$, TP, and NH$_4$. From using the SO$_4$/Cl ratio of the samples and comparing them with the SO$_4$/Cl ratio in seawater (Eq.

26 3), it appears that most of the brackish groundwater showed signs of sulfate reduction. Figure 7 shows that the amount of

27 SO$_4$ consumed in the sulfate reduction process increased with the chloride concentration of the groundwater, and that sulfate

28 reduction was complete only in part of the groundwaters. Note that groundwater below polders with excess SO$_4$ are all in

29 water with Cl<1000 mg L^{-1}. It follows from Figure 8 that high HCO$_3$, TP, and NH$_4$ concentrations mostly occurred in

30 groundwater with a SO$_4$/Cl ratio lower than 0.14, indicating sulfate reduction which induces the release of N and P from the

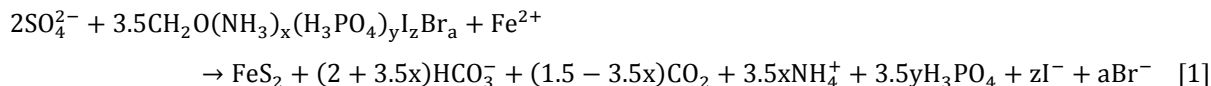
31 mineralized organic matter in the subsurface and the production of alkalinity during that process. Therefore, these waters

32 typically have increased HCO$_3$ concentrations above 480 mg L^{-1} (Fig. 8A and 8B) and are often associated with brackish

33 groundwater that once contained sulfate (Fig. 8C: Cl>300 mg L^{-1}). The hypothetical chemical relation between sulfate

1 reduction (SO_4 consumed) and $HCO_3/NH_4/H_3PO_4$ production from the mineralisation of organic matter can be found in the

2 reaction equation below (Stuyfzand, 2006):

$$2SO_4^{2-} + 3.5CH_2O(NH_3)_x(H_3PO_4)_yI_zBr_a + Fe^{2+}$$
$$\rightarrow FeS_2 + (2 + 3.5x)HCO_3^- + (1.5 - 3.5x)CO_2 + 3.5xNH_4^+ + 3.5yH_3PO_4 + zI^- + aBr^- \quad [1]$$

3 **3.2 Spatial patterns and statistical analysis of surface water quality**

4 Fig. 9 and Fig. 10 show the solute concentrations in the four regions: Zuiderzee margin, Upconing area, and Central Holland,

5 and Vecht lakes. Due to insufficient surface water quality data, no results are shown for several polders in the Amsterdam

6 city area (see Fig. 4) and the Ice pushed ridge region. The first is related to the monitoring priorities of the Waternet water

7 board, the latter is related to the almost absence of surface water in this region.

8 **Cl, Ca, and HCO_3**

9 Highest chloride levels (>300 mg L^{-1}) were found in the Upconing polders with brackish seepage and in a minority of the

10 polders in the Zuiderzee margin and Central Holland regions (Fig. 9 and 10). The high Ca and HCO_3 concentrations in these

11 polders are also related to the occurrence of brackish water. However, most of the surface water in the Zuiderzee margin and

12 the Central Holland area is fresh with relatively low Cl concentrations (Fig. 10). The Vecht lakes area exhibits the most fresh

13 and least mineralized surface water.

14 **SO_4 and SO_4/Cl**

15 The highest SO_4 concentration levels and SO_4/Cl mass ratios mostly occurred in the Central Holland area, especially the

16 western part. The elevated SO_4 and SO_4/Cl ratios indicate the presence of sulfate sources other than (relict) seawater in this

17 area, probably atmospheric deposition, agriculture and/or oxidation of pyrite exposed in the upper soils which developed in

18 marine clay deposits and are denoted as "cat clays" (Wallenberg, 1975). In the Zuiderzee margin and the two upconing

19 polders, the median SO_4 levels are 64 and 62 mg L^{-1}, respectively, and SO_4/Cl mass ratios of the two upconing polders are

20 below 0.14. A generally lower SO_4 with SO_4/Cl ratios far exceeding the 0.14 were found in the Vecht lakes region.

21 **TN, NH_4, NO_3, and TP**

22 According to Fig. 9 and Fig. 10, surface water EQSs of TN (2.4 mg N L^{-1}) and TP (0.15 mg P L^{-1}) were exceeded in most

23 polders of the study area. The outliers with even higher nutrient concentrations are mainly located in the west of the Central

24 Holland region. P25 and P75 of TP and TN in the Zuiderzee margin and in Central Holland regions all significantly

25 exceeded EQSs for surface water. In the two upconing polders, polder Groot Mijdrecht showed higher concentrations of TP

26 and TN than polder Horstermeer (0.28 vs. 0.11 mg P L^{-1} and 5.4 vs. 1.8 mg N L^{-1}). Polders with concentrations below the

27 EQSs were mainly situated in the Vecht lakes area where large open water areas exist. In this region, TP slightly exceeded

28 the EQS with a median concentration of 0.22 mg L^{-1}, while the median TN concentration of 2.26 mg L^{-1} was just below the

29 EQS. The concentrations of NO_3 and NH_4 in the Vecht lakes area were relatively low as well.

1   Similar to the results of groundwater, higher nutrient levels also exist in higher mineralized surface waters, which is also
2   indicated by the correlation results (Table 1, blue part): Ca and HCO_3 are both correlated with NH_4 (Spearman R^2 are 0.64
3   and 0.67), TP (R^2 0.55, 0.62), and TN (R^2 0.57, 0.47). In surface water, Ca and HCO_3 had a significant correlation (R^2 0.88).
4   This indicates that groundwater is the probable source of the water and nutrients in the surface water of the polders. This
5   groundwater impact was further supported by the correlations between the following pairs of solutes in surface water: Cl
6   with Ca (R^2 0.55), HCO_3 (R^2 0.52), SO_4 (R^2 0.49) and NH_4 (R^2 0.51), as well as SO_4 with TN (R^2 0.57) and NO_3 (R^2 0.50). A
7   more direct indication for the groundwater impact is that NH_4, HCO_3 and Ca concentrations in surface water were positively
8   related to the seepage rate. In a similar way, the groundwater impact is suggested by the negative correlations between
9   elevation and the concentration levels of most surface water solutes (TN: R^2 -0.67, NH_4: R^2 -0.59, NO_3: R^2 -0.40, HCO_3: R^2 -
10   0.48, SO_4: R^2 -0.47 and Ca: R^2 -0.57).
11   For the soil variables (lutum, humus and calcite), only humus showed correlations with TN, NH_4, Ca, and Cl in surface water
12   (Table 1). Paved area percentage, surface water area percentage, calcite and clay percentages, and agricultural N and P inputs
13   did not show absolute values of correlation coefficients above 0.4 with surface water quality, but a slight negative correlation
14   was found between the agricultural N input and the normalized concentrations of HCO_3 in surface water (Table S2).
15   Surface water TN correlated more closely to NH_4 (0.77) than to NO_3 (0.57), which reflects that NH_4 is generally the main
16   form of TN in the study area. This is especially true for the Zuiderzee margin, the Upconing area and the Central Holland
17   area (Fig.9). The NO_3 and NH_4 contributions to TN are about equal in the Vecht lakes area. For the Ice pushed ridge (not
18   shown in Fig.9 due to insufficient data), a dominance of NO_3 in surface water was expected as was the case in groundwater
19   of this area. However, there is only limited amount of surface water that is draining the Ice pushed ridge directly.

20   **3.3 Groundwater and surface water quality comparison**

21   A common spatial pattern in surface and groundwater chemistry is that polders in the Zuiderzee margin area, the two
22   upconing polders, and the Central Holland area suffer from a worse water quality situation than the polders in the Vecht
23   lakes and Ice pushed ridge areas. However, compared with the underlying groundwater quality, surface water in the whole
24   area has much lower chloride, bicarbonate, and nutrient levels, but higher SO_4 concentrations (Fig. 5 and Fig. 9). The polders
25   generally have much higher TP and TN concentrations in groundwater than in surface water. The groundwater nutrient
26   concentrations exceeded the surface water EQSs in 93 % of the polders for TP, and in 91 % for TN. Polders with
27   groundwater nutrient levels below the EQSs were mainly found near Lake IJssel. Especially the groundwater TN
28   concentrations in the Ice pushed ridge severely exceeded surface water EQSs, which can be mainly attributed to the elevated
29   NO_3 concentrations. For TP in groundwater, the Zuiderzee margin and Central Holland areas show more significant EQS
30   exceedances compared to the Upconing area, Ice pushed ridge and the Vecht lakes area.
31   Table 1 shows that TP, NH_4, HCO_3, and Cl concentrations in groundwater correlate with the same components in surface
32   water (R^2 0.49, 0.44, 0.68, and 0.69). In addition, HCO_3 in groundwater showed moderate correlations with nutrient
33   concentrations in surface water (TP (R^2 0.64), TN (R^2 0.52), and NH_4 (R^2 0.51)). HCO_3 concentrations in surface water also

correlated with nutrient concentrations in surface water (TP (R^2 0.62), TN (R^2 0.47), and NH_4 (R^2 0.67)). Based on these correlations, we selected groundwater parameters and landscape characteristics to be integrated in multiple linear regression models to predict concentrations of surface water components (Table 2). For most solutes (TP, NH_4, TN, HCO_3, and Cl, the R^2 of the regression models is around 0.5, which indicates that around 40 ~ 50% of the spatial variance in surface water can be explained by specific groundwater chemistry parameters, N agricultural input, seepage, and elevation and humus. For NO_3 and SO_4, the R^2 of the regression models (inverse with Elevation) are very low, 0.18 and 0.25, respectively. For all other parameters, the groundwater HCO_3 concentration was the best explaining variable for the surface water concentrations. The spatial variation in $HCO_{3\,SW}$ and Ca_{SW} were relatively well explained by only $HCO_{3\,GW}$ combined with Seepage/Elevation, respectively (Eq. 13 and Eq. 15).

The regression models were significantly improved by including groundwater concentrations of TP, NH_4, and Cl (Eq. 9, 11 and 16). For TN and NO_3, the R^2 also improved after adding N agricultural input. In regression models Eq. 10, 11, 12, 14, and 15, the elevation of the polders also explained part of the spatial variation in surface water concentrations. When only including polders with net groundwater seepage, the R^2 improved significantly for TP, NH_4 and HCO_3.

The results above strongly suggest that the groundwater composition puts limitations to the compliance of the receiving surface water towards the EQSs defined for N and P.

3.4 Surface water solute redistribution

Figure 11 shows that the solute loads of polders to the boezem are relatively high in the Zuiderzee margin, the Upconing polders, and the Central Holland regions. The Vecht lakes area has large open water areas and showed the lowest loads to the boezem system. A clear similarity between the spatial patterns of the solute loads and the average seepage rate patterns was observed in Fig. 3 and Fig. 11. In general, polders with high seepage rates also discharge relatively high loads to the Boezem system. Some examples of polders with relatively high seepage rates are polder #119 (Bethunepolder, 13 mm d^{-1}), #79 (Horstermeer, 8.7 mm d^{-1}), #50 (Polder De Toekomst, 2.4 mm d^{-1}), #131 (Hilversumse Meent, 2.4 mm d^{-1}), #98 (Polder Wilnis-Veldzijde, 3.7 mm d^{-1}), #80 (Polder Groot Mijdrecht en Polder de Eerste Bedijking (oost), 5.0 mm d^{-1}), #74 (Polder de Nieuwe Bullewijk en Holendrechter- en Bullewijker Polder noord, 1.8 mm d^{-1}) and #75 (Bijlmer, 2.0 mm d^{-1}). The highest loads are discharged from the two upconing polders: Groot Mijdrecht (#80) and Horstermeer (#79).

The influence of the redistribution of the large water volumes and loads from deep polders was also observed in Fig. 3 and Fig. 11. Polders that receive inlet water from Groot Mijdrecht and Horstermeer (see section 2.1.1, Fig. 3) showed relatively high solute loads, independent of their own seepage or infiltration fluxes. This especially holds for polders downstream of Groot Mijdrecht and Horstermeer, like polder #73 (Holendrechter- en Bullewijker Polder (zuid en west), -0.05), #74 (Polder de Nieuwe Bullewijk en Holendrechter- en Bullewijker Polder noord, 1.8 mm d^{-1}), #104 (Noorderpolder of Botshol (zuid en west), -1.4 mm d^{-1}), #105 (Noorderpolder of Botshol (Nellestein), -0.7 mm d^{-1}), #106 (Polder de Rondehoep, -1.1 mm d^{-1}), and polder #107 (Polder Waardassacker en Holendrecht, -0.15 mm d^{-1}).

1 The impact of this redistributed water on polder water chemistry is demonstrated by a simple water and solute mass balance

2 calculation for the receiving polder Botshol (see paragraph 2.2.4). Fig. 12 gives the chloride concentration results of both the

3 'evaporation' and the 'infiltration/outlet' models. Figure 12 shows that a very simple model can easily explain the peak Cl

4 concentrations in the Polder Botshol to be the result of the inlet of water from the boezem and Groot Mijdrecht. The

5 'evaporation' model performs better in 2006 and 2008 and the 'infiltration/outlet' model in 2011 and 2012. Most of the time,

6 the measured concentrations are between the calculated concentrations from both models. This aligns with the understanding

7 that water leaves Botshol via a combination of evapotranspiration and other outflow routes, such as infiltration, leakage, and

8 outlet.

9 **4 Discussion**

10 This study aimed at identifying the impact of groundwater on surface water quality in the polder catchments of the greater

11 Amsterdam city area. According to the statistical analysis of data over five regions in the study area, a clear influence was

12 identified. Solute concentrations in groundwater and surface water correlated well, although groundwater solute

13 concentrations were generally much higher than normalized concentrations in surface water. The latter seems logical given

14 the dilution of surface water by the precipitation surplus on an annual basis, with the annually discharged surface water being

15 a mixture of seeping groundwater and precipitation. Moreover, similar spatial patterns in solute concentrations were found in

16 groundwater and surface water. The findings on the dominance of groundwater inputs is also supported by the poor

17 correlation with agricultural nutrients inputs, which are usually assumed to be a large source of N and P in surface water.

18 Polders that are influenced by groundwater seepage or by redistributed seepage water from nearby deep polders are at risk of

19 non-compliance, as groundwater concentrations exceeded the TN and TP EQSs for surface water in more than 90% of the

20 polders. Consequently, the groundwater nutrients input hinders achieving water quality targets in the surface water in those

21 lowland landscapes.

22 **4.1 Key hydro chemical processes**

23 In general, the groundwater chemistry corresponds with the geological history of the study area. In the peat land polder

24 catchments within the Dutch delta system of marine, peri-marine and fluvial unconsolidated deposits, abundant organic

25 matter is present in the subsurface (e.g. Hijma, 2009). The presence of reactive organic matter in the shallow subsurface

26 depletes the infiltrating groundwater from oxygen and nitrate, leading to an overall low redox potential in groundwater,

27 which enables the further decomposition of organic matter downstream.

28 Our data strongly suggests that sulfate reduction, sometimes in combination with methanogenesis, is the main process

29 releasing nutrients (N, P) and HCO_3 from the organic rich subsurface in the study area, especially in both the fresh and

30 brackish groundwater of the Zuiderzee margin, the Upconing polders, and the Central Holland that are charactreized by low

31 SO_4/Cl ratios (Table 1, Fig. 8). The Holocene marine transgression undoubtedly influenced the chemistry of groundwater by

salinizing processes that also increased sulfate availability derived from diluted sea water. Refreshing of the aquifers by infiltration of fresh water from rivers and rain in more elevated polders and lakes further influenced part of the groundwater. We examined the amount of freshening and salinization using the exchange Na (Na_{ex}) and investigated how this process may have influenced the release of P as was suggested by Griffioen et al. (2004). Figure S2 shows that high P (and HCO_3, not shown) does occur in both refreshing water ($Na_{ex} > 1$) and in salinizing water ($Na_{ex} < -1$), but mainly when the SO_4/Cl ratio is below 0.14. Therefore, we infer that sulfate reduction/organic matter decomposition is the prime process in releasing P, and is more discriminating high P than cation exchange processes. There is a high probability for sulfate reduction dominated polder catchments to have very high HCO_3 concentration in groundwater according to Eq. [1]. In our study area, high HCO_3 concentration levels in both groundwater and surface water were mainly present in areas with marine sediments that contain shell fragments and organic matter. The base level groundwater alkalinity from the dissolution of shell fragments and carbonate minerals is further increased by the organic matter decomposition in the subsurface. This observation confirms the earlier findings of Griffioen et al. (2013) who highlighted the relation between the nutrient concentrations and pCO_2 in these marine sediments. The main chemical reactions involved are listed in Table 3.

The seepage of the alkalized groundwater increases alkalinity of the surface water, which is indicated by the high correlation between groundwater and surface water HCO_3, and with Ca in surface water (Table 1). Subsurface organic matter mineralization by processes like sulfate reduction and methanogenesis (Chapelle et al., 1987; Griffioen et al., 2013) (Table 3 [2], [6]), is a probable major reason for enhanced surface water HCO_3 in polders with brackish groundwater, like the polders in the Zuiderzee margin and the Upconing polders (Fig. 8).

In the urban area of Amsterdam sand suppletion, which varies greatly in thickness and chemical composition, is another source of alkalinity. Some of the sands contain shell fragments because of their marine origin. However, little is known about the distribution of these calcite-rich sands. The poorly registered spatial distribution and sources of the supplied calcite-rich sands might complicate the assessment of their impact on urban polder water quality.

Sulfate concentrations are higher in the receiving surface water than in the groundwater. We ascribe the sulfate surpluses (Fig. 7) to additional sources affecting the surface water, including atmospheric deposition, agricultural inputs, sewer leakage (Ellis, et al., 2005), storm runoff, and/or the oxidation of pyrite (FeS_2). Pyrite is ubiquitously present in this area (Griffioen et al., 2013) and oxidizes in the topsoil, where either O_2 or NO_3 can act as electron acceptor (Wallenburg, 1975). We suggest that sulfate concentrations are especially high in polders where shallow groundwater flow is enhanced by the presence of tile drains in clay rich polders that needed this drainage system to prevent water tables rising into the root zone in wet periods. Tile drain flow can bring the released SO_4 to the surface water. For urban polders with high SO_4 concentrations, like the Zuiderzee margin region polders, sewer system leakage may be an additional source of SO_4. Aging and faulty connections of pipes may result in a leakage of water with high SO_4 and nutrient concentrations.

4.2 Groundwater contribution to surface water composition

The groundwater in the upper 50 m of the subsurface of the study area is an important source of nutrients in the study area's surface waters (Delsman, 2015). Brackish groundwater especially seeps up into the polders of the Zuiderzee margin region and into the Upconing area. The seepage of paleo-marine, brackish groundwater is driven by the low surface water levels after the lake reclamation and the drainage via pumping stations. De Louw et al. (2010) reported that this groundwater seepage predominantly takes place via concentrated boils through the clay and peat cover layer.

The excess water in the Upconing area is re-used as inlet water for several downstream polder catchments, which extends the impact of the brackish, alkaline, and nutrient rich groundwater to a larger scale. The water redistribution disturbs the 'natural' surface water quality patterns and local groundwater impact in the receiving polders, such as polder Botshol. The redistributed water largely infiltrates and returns with variable travel times via the groundwater system back towards the deep upconing polders.

Groundwater seepage in our study area leads to eutrophication and redistributing the discharge from some deep polders further spreads the nutrients into the whole water system. Similar patterns are expected to exist in other lowland areas, which are highly manipulated by human activities. Typical delta areas where subsurface processes are expected to release nutrients from reactive organic matter and peat in the subsurface are the Mekong delta (Minderhoud et al., 2017), the Mississippi delta (Törnqvist et al., 2008) and the Sacramento-San Joaquin delta (Drexler et al., 2009). In many of these areas the water management shows resemblance to the Dutch situation. However, the large amount of groundwater quality and surface water quality data that was available in our study area is unique. Still, signals of groundwater influence on nutrient concentrations were reported from eastern England (pers. comm. M.E. Stuart, British Geological Survey) and from the lowland parts of Denmark (Kronvang et al. 2013).

4.3 Other sources of nutrients

Besides the contribution from nutrient rich groundwater seepage, this study indicated that there are other possible sources of nutrients in the study area. In agricultural lands, a part of the applied nutrients is typically lost towards the surface water via drainage and runoff. The high groundwater NO_3 concentrations in the Ice pushed ridge are caused by the infiltration of agricultural water (Schot et al., 1992b). The high nitrate loads and concentrations in surface water and groundwater of the polders in the southeast (e.g. # 122 (Muyeveld), # 140 ('t Gooi)) originate from agricultural activities in surrounding polders. In the urban polders within the Amsterdam city that have no significant seepage (average seepage ≤ 0), TP and TN EQSs are frequently exceeded because of intensive human activities such as application of fertilizer, feeding ducks and fish, and point emissions like sewer overflow leakage from the sewer system (pers. Comm. Waternet).

In the study area, the most intensively urbanized polders are mainly infiltrating and are more affected by inlet water containing high Cl and HCO_3 concentrations than by groundwater. For deep urban polders, the situation is different. In these polders, the influences of typical urbanization related water quality issues are masked by the large impact of brackish,

nutrient rich groundwater exfiltration. Although land use was incorporated in variables like paved area percentage and N and P inputs, (as well as agricultural land percentage, shown in Supplement Information), land use seems not be the dominant landscape characteristic that governs the spatial patterns in polder surface water quality. Urban water quality is determined by multiple factors, as was also concluded by several other studies (Göbel et al., 2007; Vermonden et al., 2009). However, a better measurement method or classification of paved area percentage may improve the explanatory power of this variable (Brabec et al., 2002).

The Vecht lakes polders with high surface water area percentages, representing lakes that are mainly used for recreation purposes, showed relatively low solute concentrations and loads in surface water (Fig. 10 and Fig. 11). In our study area, many lakes and polders with large surface water areas show large infiltration rates due to their elevation relative to other polders (Vermaat et al., 2010). Moreover, some of these lakes are replenished by inlet water that has passed a phosphate purification unit. In addition, the large open water area retains nutrient transport due to long residence times and ample opportunities for chemical and biological transformation processes like denitrification, adsorption, and plant uptake.

4.4 Uncertainties

Due to the disturbance of urban constructions, combined with redistribution of water through artificial drainage corridors, water flow in lowland urban areas is more complex than in rural or non-low-lying and freely draining catchments. Natural patterns of water chemistry might be significantly disturbed and hydrochemical processes are masked. The understanding of urban water quality patterns might improve if the monitoring program would be extended with tracers that are typical for specific sources, such as sewage leakage or urban runoff. Most solutes that are currently measured can originate from various anthropogenic and natural sources.

In the statistical analysis, for each pair of variables, only polders with complete data were taken into account, which could result in a loss of information. Seepage data was simulated by a group of models of which the results may deviate from the hard to measure actual seepage. We used averages of groundwater concentrations and soil properties, which caused a loss of information on the spatial variation within the polders. The interpolation of groundwater quality data also added uncertainty, for example hidden correlations for groundwater parameters. The calculation of the agricultural N and P inputs may also differ from the actual inputs due to errors in the nutrient book keeping and model uncertainties. In addition, differences in sampling methods and analytical procedures between groundwater and surface water quality monitoring programs may add uncertainties. These uncertainties may all have influenced the data characteristics apart from the uncertainties in the concentration measurements caused by the sampling, transport, and analytical procedures.

4.5 Perspectives

In future studies, urban lowland catchments with and without seepage could be studied separately and more detailed land use or paved area categories could be included. The drainage and/or leakage from sewage systems and the drainage via tube drains should be taken into consideration. Drainage systems can provide a short-cut for solute transport towards surface

water (Rozemeijer and Broers, 2007), leading to higher solute concentrations in surface water. High groundwater levels may induce groundwater discharge via the sewage or drainage systems (Ellis, 2005). In addition, studying the temporal variation of surface water quality will give more insights into how the groundwater impact on surface water quality functions, as well as on solutes transport and pathways in urban hydrological systems. A detailed monitoring network in several urban polder catchments, which is anticipated as further work, could yield a more complete insight into water and contaminant flow routes and their effects on surface water solute concentrations and loads.

To the water management scenarios, as our study showed that the groundwater nutrient loading towards surface water dominates, reducing the amounts of agricultural nutrient inputs might not contribute enough in improving the water quality. This certainly holds for urban areas where agricultural inputs are absent (see Fig. S3). Given the large loads of N and P that originate from one large polder with upconing brackish groundwater - the Groot Mijdrecht polder - one of the solutions proposed in The Netherlands was to turn this area back into a fresh water lake. By doing so, the seepage of nutrient rich groundwater would stop as the higher water levels would lead to neutral or even infiltrating conditions. However, this proposal led to a lot of protest among the municipalities and farming communities in the polder and was not considered feasible given the economic values that were involved. This example shows that the reclamation of swamps and lakes for urbanisation or agriculture can lead increased nutrient loads to surface waters in the surroundings which are hard to mitigate. This scenario has wider implications for water management in other urbanising lowland areas around the world.

5 Conclusion

In this paper, a clear groundwater impact on surface water quality was identified for the greater Amsterdam area. It was concluded that this groundwater seepage significantly impacts surface water quality in the polder catchments by introducing brackish, alkaline, and nutrient rich water. In general, nutrient concentrations in groundwater were much higher than in surface water and often exceeded surface water Environmental Quality Standards (EQSs) (in 93 % of the polders with available data for TP and in 91 % for TN) which indicates that groundwater is a large potential source of nutrients in surface water. Our results strongly suggest that organic matter mineralization is a major source of nutrients in lowland deltas where water levels are lowered to enable urbanisation and agricultural land use. High correlations (R^2 up to 0.88) between solutes in groundwater and surface water confirmed the effects of surface water-groundwater interaction on surface water quality. Especially in seepage polders, groundwater is a major source of Cl, HCO_3, Ca and the nutrients N and P, leading to general exceedances of EQSs for N and P in surface waters. The discharge and redistribution of nutrient rich water from reclaimed lakes and swamps enhances eutrophication in downstream water resources and is hard to mitigate. Surface water quality in the Amsterdam urban area is also influenced by groundwater seepage, but other anthropogenic sources, such as leaking and overflowing sewers might amplify the eutrophication problems.

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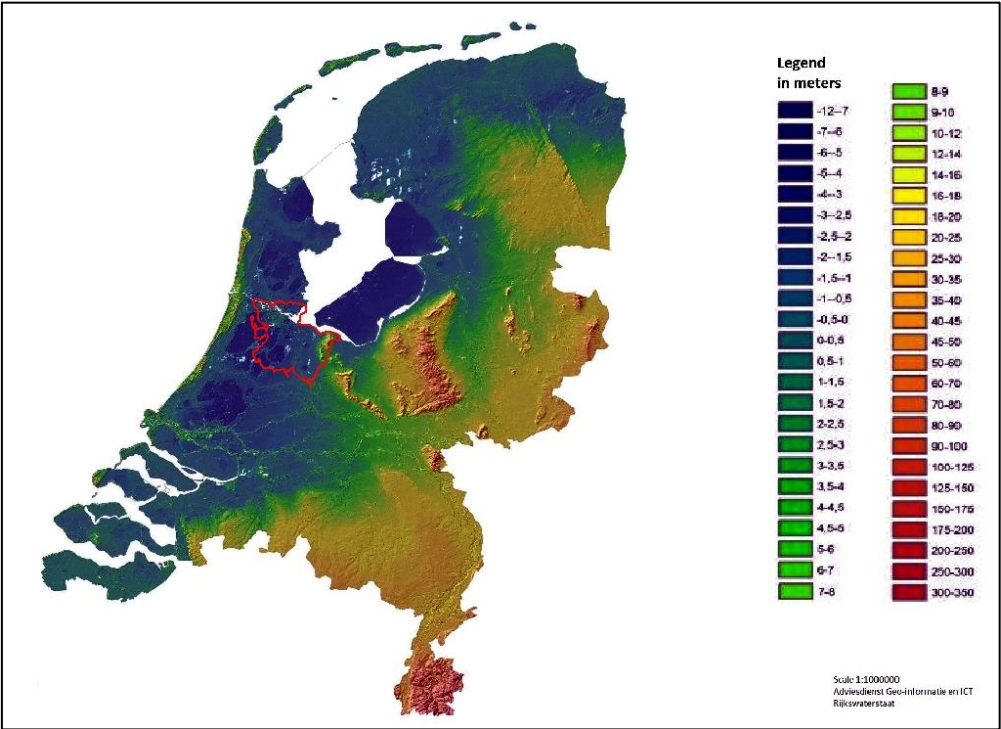


Figure 1: Location of the research area (red) projected on the elevation map of The Netherlands (elevations in meters above mean sea level (MSL))

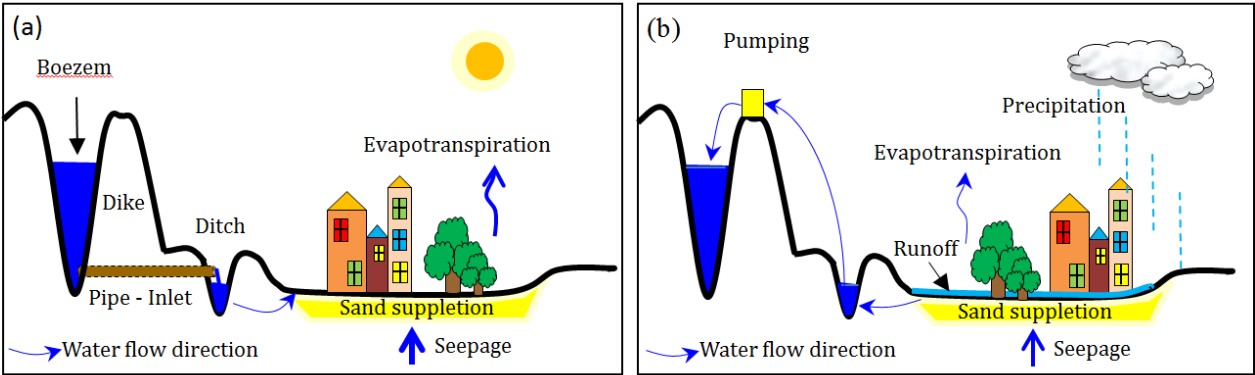



Figure 2: Conceptual model of water fluxes in a polder system in times of water deficiency (a) and surplus (b).

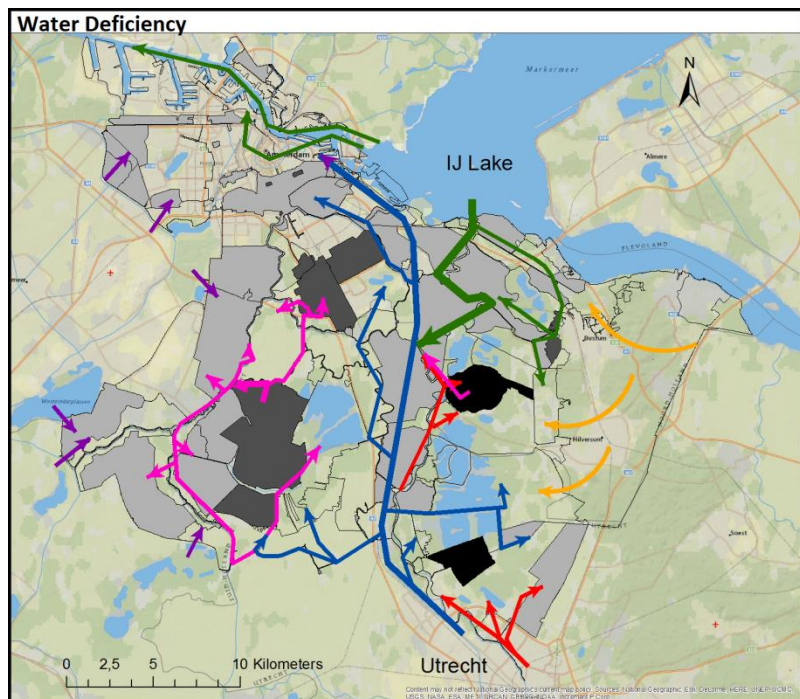
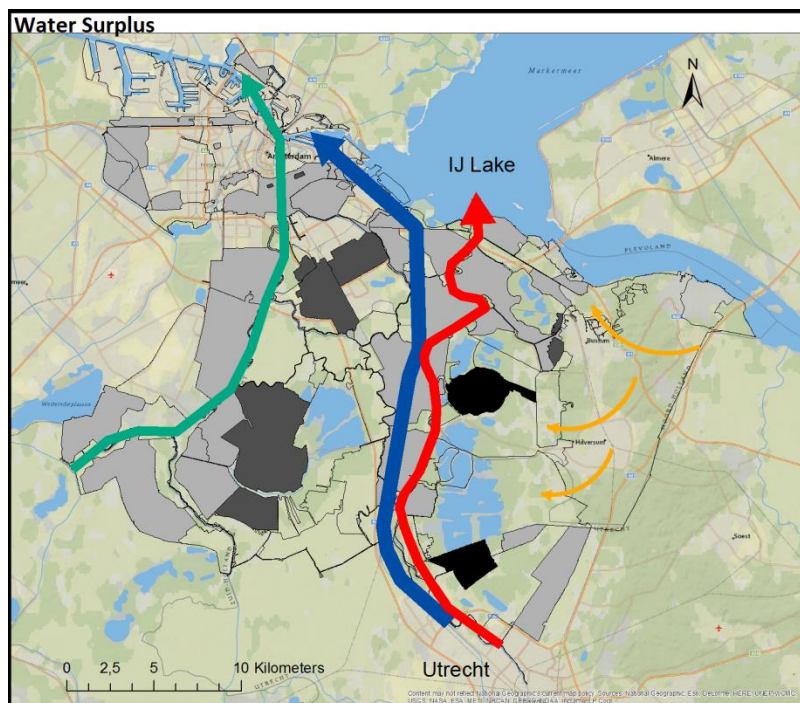
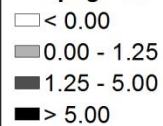



Figure 3: Flow directions of surface water in water surplus and water deficiency period

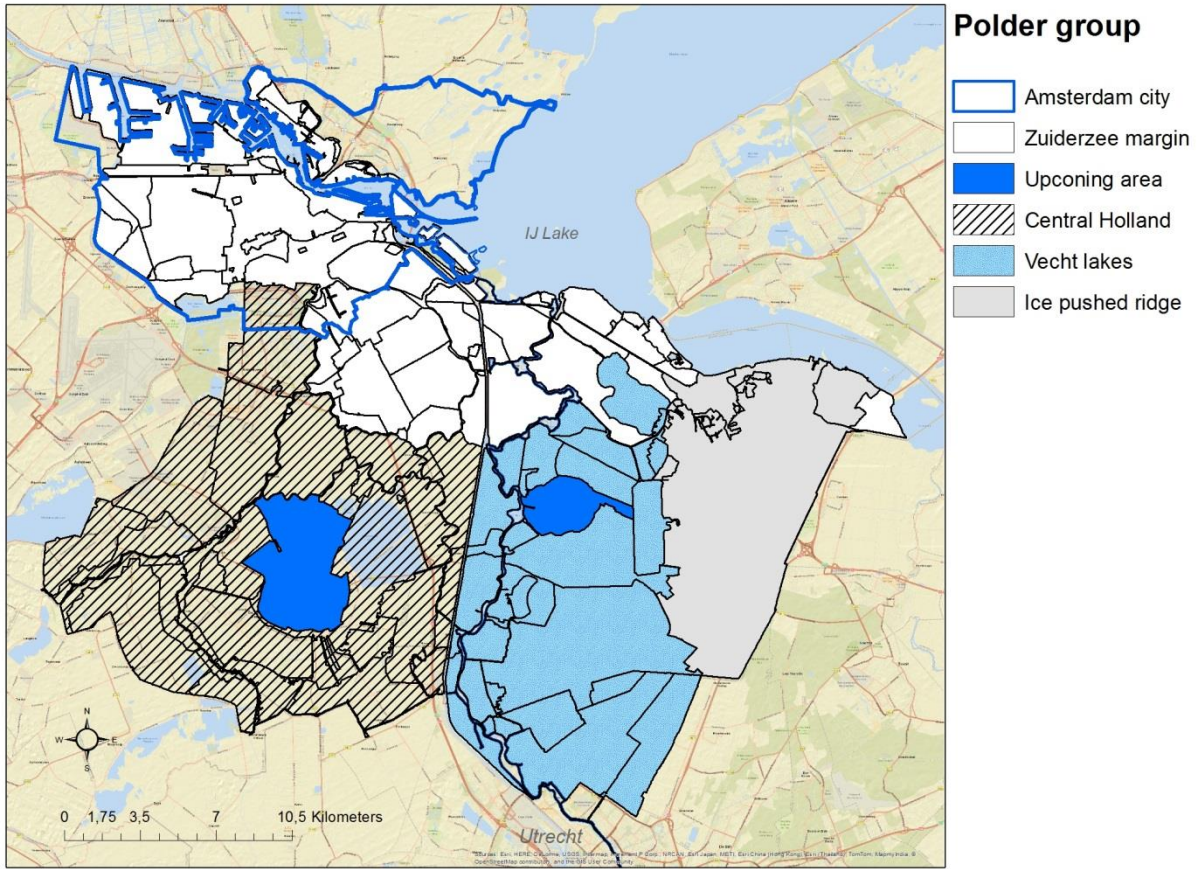



Figure 4: Regions of the study area: (1) Zuiderzee margin, (2) Upconing area (deep brackish seepage polders Groot Mijdrecht and Horstermeer), (3) Central Holland, (4) Vecht lakes and 5) Ice pushed ridge. The Amsterdam city area is circled by the blue line.

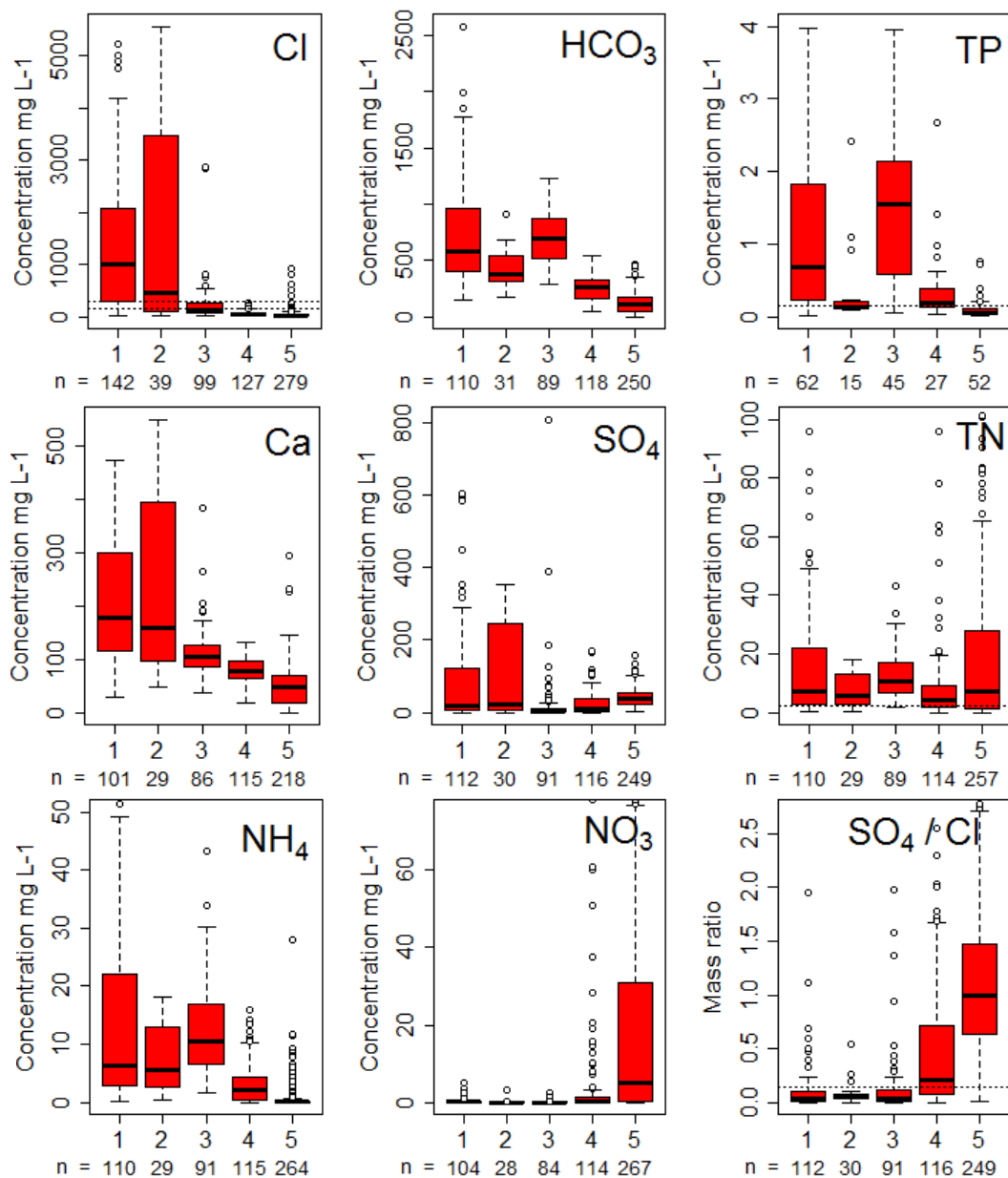



Figure 5: Spatial variation of groundwater quality. 1-Zuiderzee margin, 2-Upconing area (Groot Mijdrecht and Horstermeer), 3-Central Holland, 4-Vecht lakes, 5-Ice pushed ridge (see Fig. 4). n is the amount of available data of each group. Boxplots show the distribution of solutes in the five regions. The two horizontal dashed lines for Cl indicate fresh water (<150 mg L^{-1}) and brackish water (>300 mg L^{-1}), respectively. Dashed lines represent EQSs for TN (2.4 mg L^{-1}) and TP (0.15 mg L^{-1}). The dashed line in the SO_4/Cl plot indicates the mass ratio of 0.14 in seawater (<0.14 indicates sulfate reduction; >0.14 indicates additional sources of sulfate besides (diluted) seawater). Part of the outliers of TP, TN, NH_4 NO_3 and SO_4/Cl fell out of the ranges in the figures.

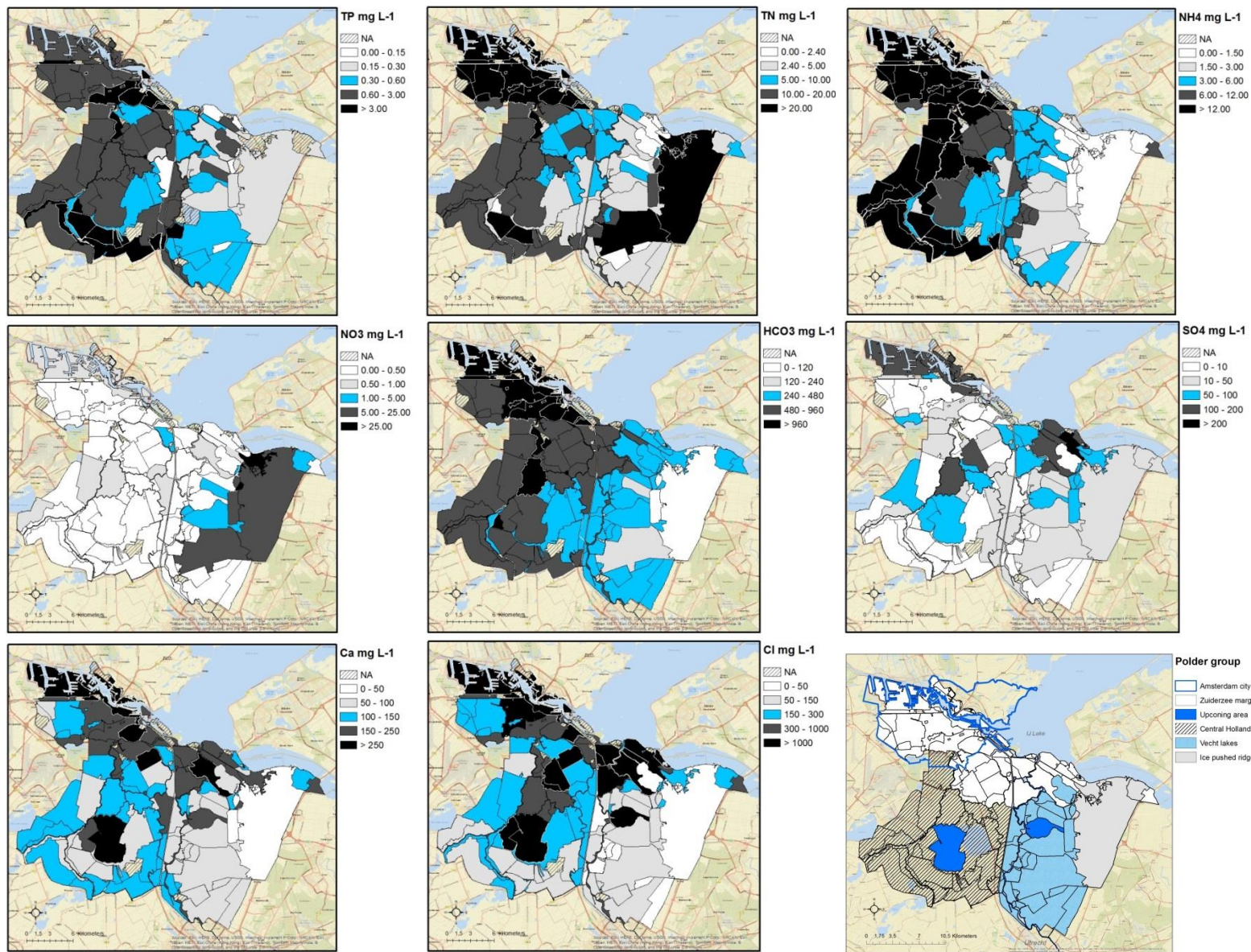



Figure 6: Average groundwater concentrations (mg L^{-1}) per polder.

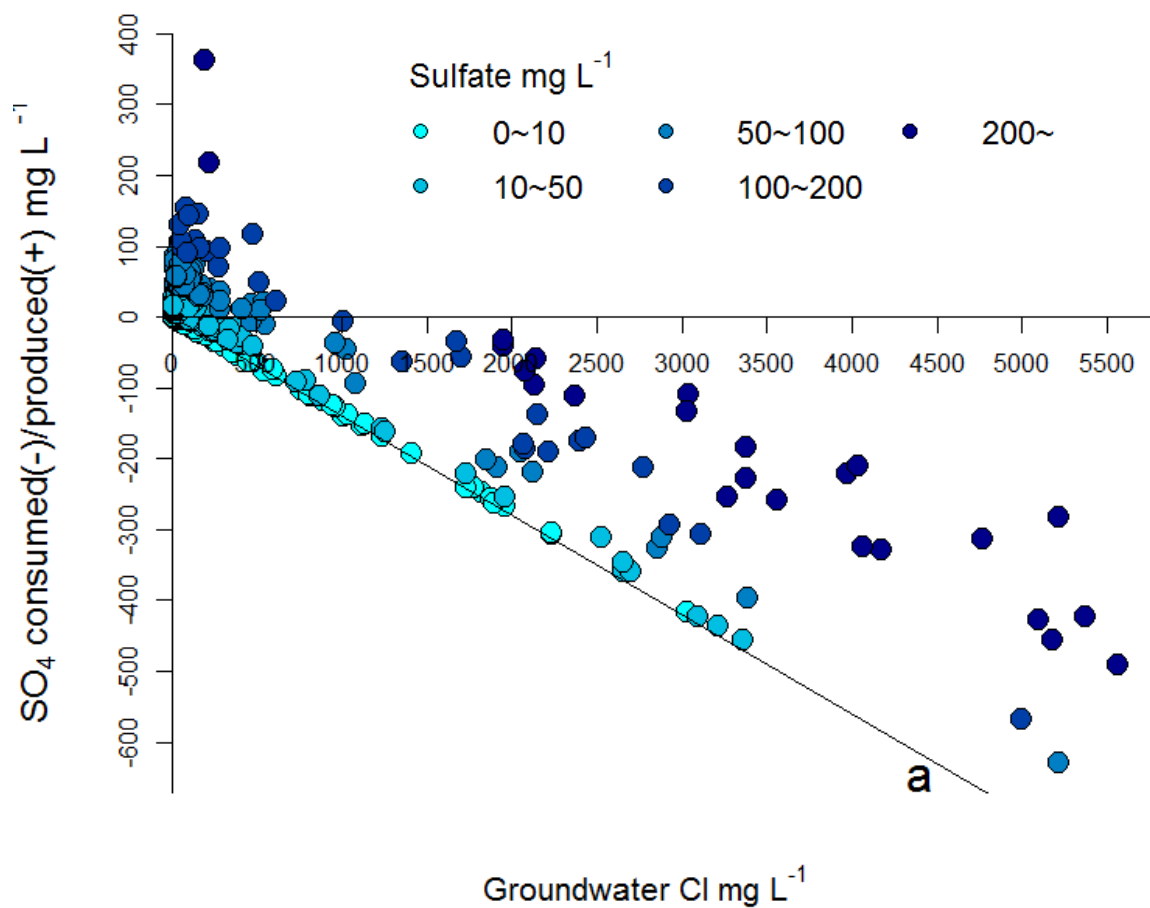



Figure 7: Calculated concentration of sulfate reacted versus groundwater chloride concentration. The black line indicates the fresh water – seawater mixing line where sulfate-reduction is complete.

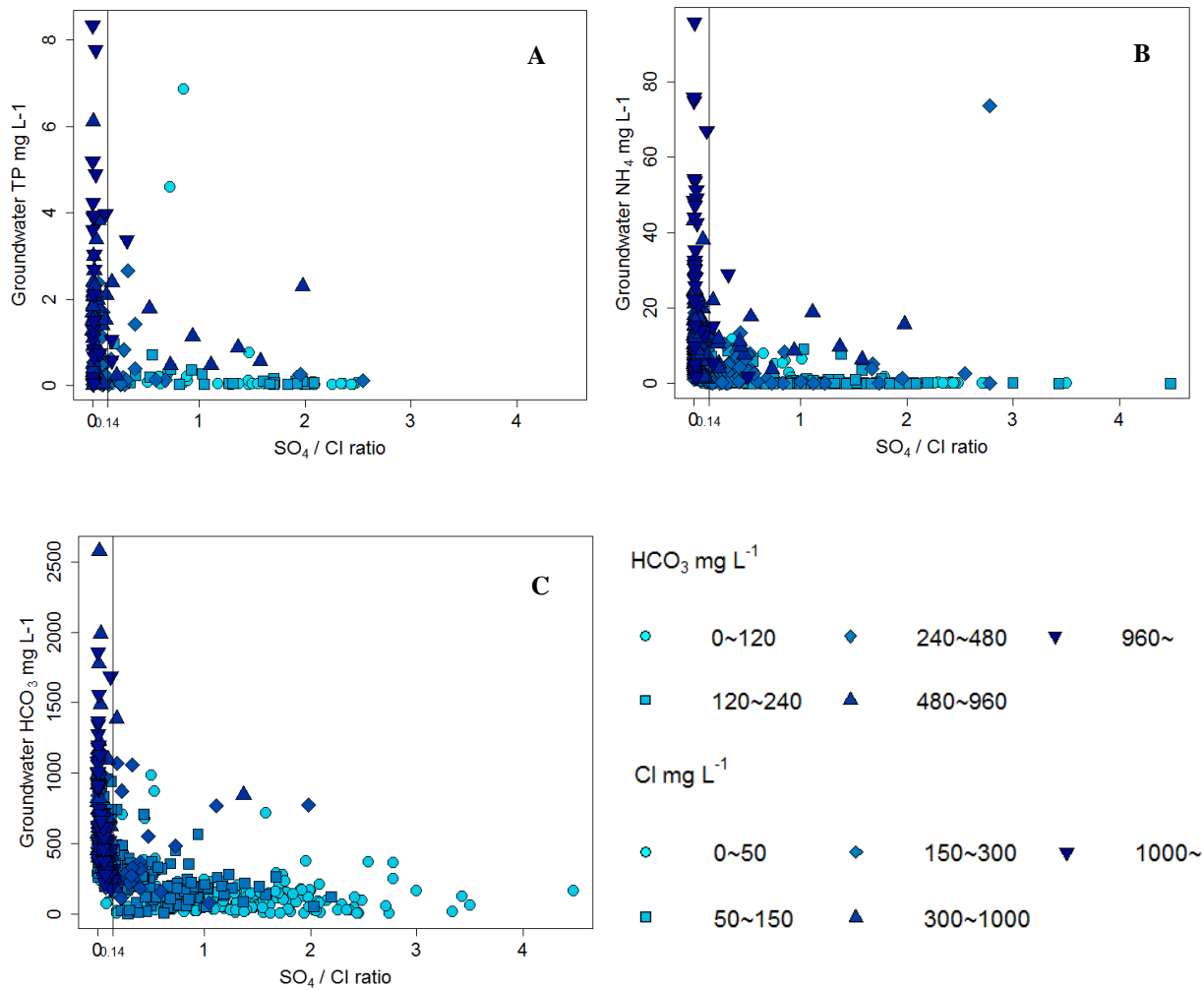



Figure 8: Groundwater nutrient (TP and NH₄) concentrations with sulfate reduction (mass ratio SO₄/Cl, samples with value below 0.14 are considered to be affected by sulfate reduction and above 0.14 indicates sulfate production by natural or artificial processes). The symbols in (A) and (B) are colored by HCO₃ concentration and in (C) by Cl concentration.

6

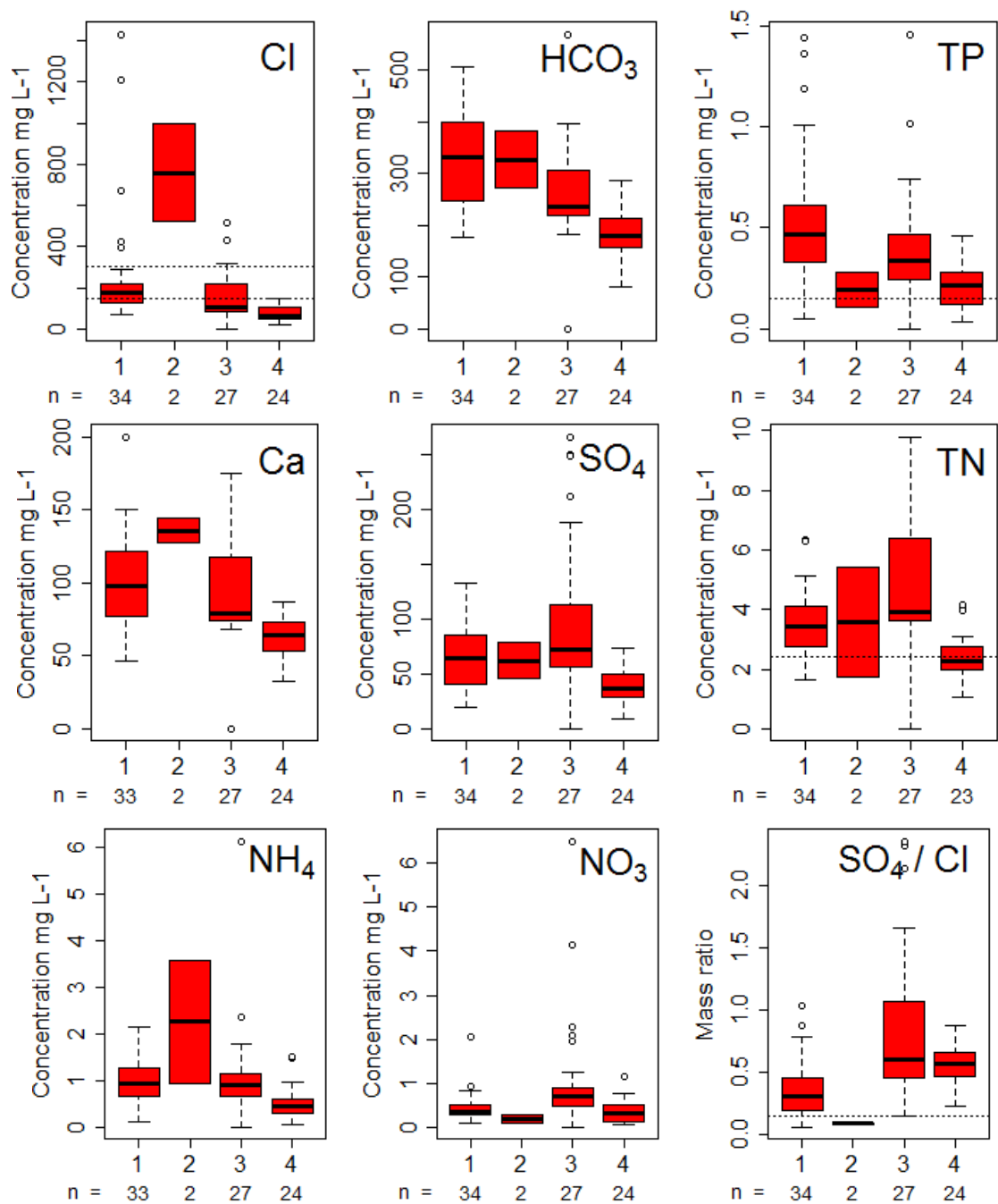
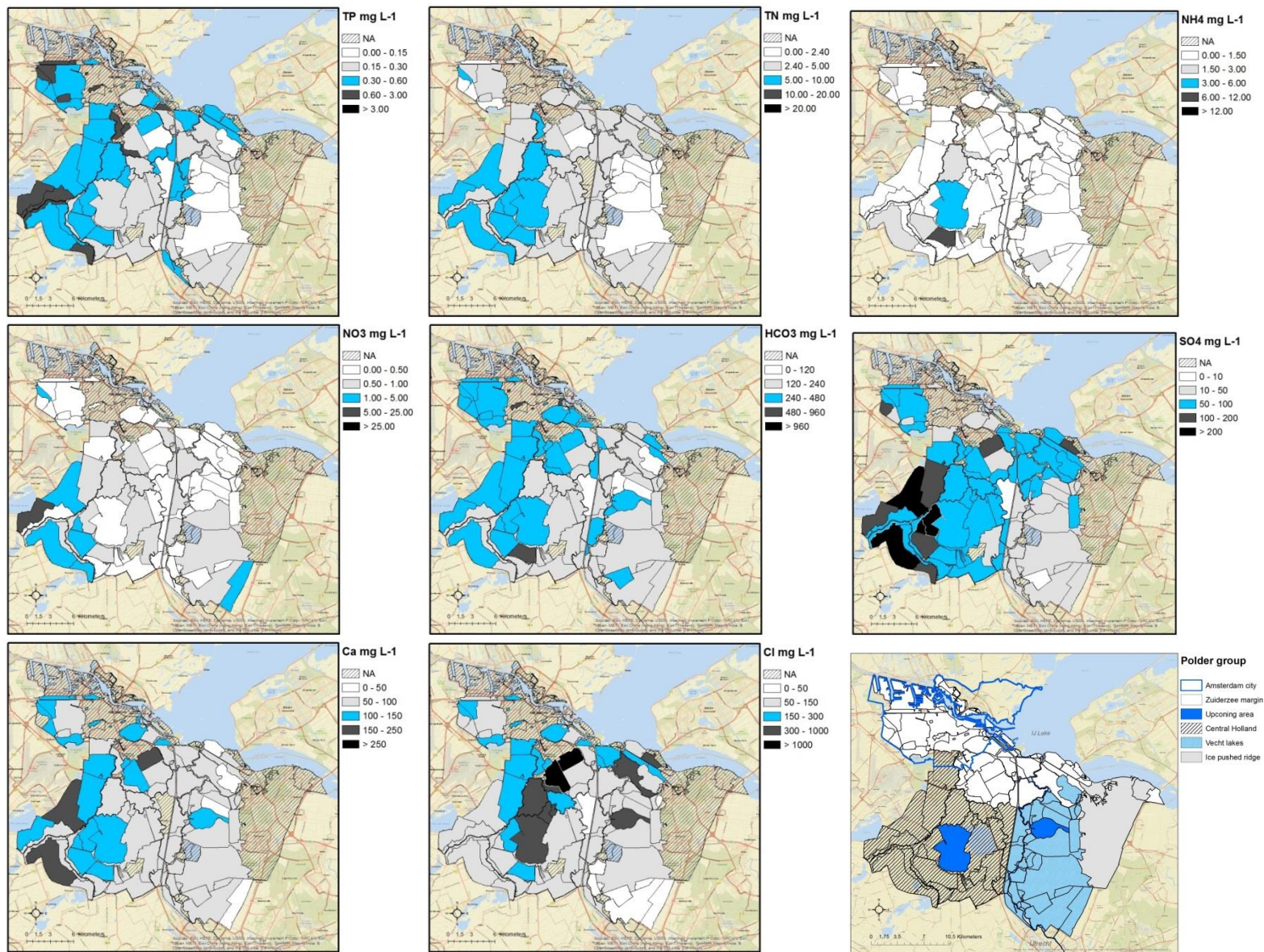



Figure 9: Spatial variation of surface water quality. 1-Zuiderzee margin, 2-Upconing area, 3-Central Holland, 4-Vecht lakes (5-Ice pushed ridge not shown due to insufficient data). n is the observation number of each group. The two horizontal dashed lines for Cl indicate fresh water (<150 mg L^{-1}) and brackish water (>300 mg L^{-1}), respectively. Dashed lines in TP and TN represent EQSs for TN (2.4 mg L^{-1}) and TP (0.15 mg L^{-1}). The dashed line in the SO$_4$/Cl plot indicates the mass ratio of 0.14 in seawater (<0.14 indicates sulfate reduction; >0.14 indicates additional sources of sulfate besides (diluted) seawater).

4 **Figure 10: Discharge-normalized average concentrations (mg L⁻¹) per polder**

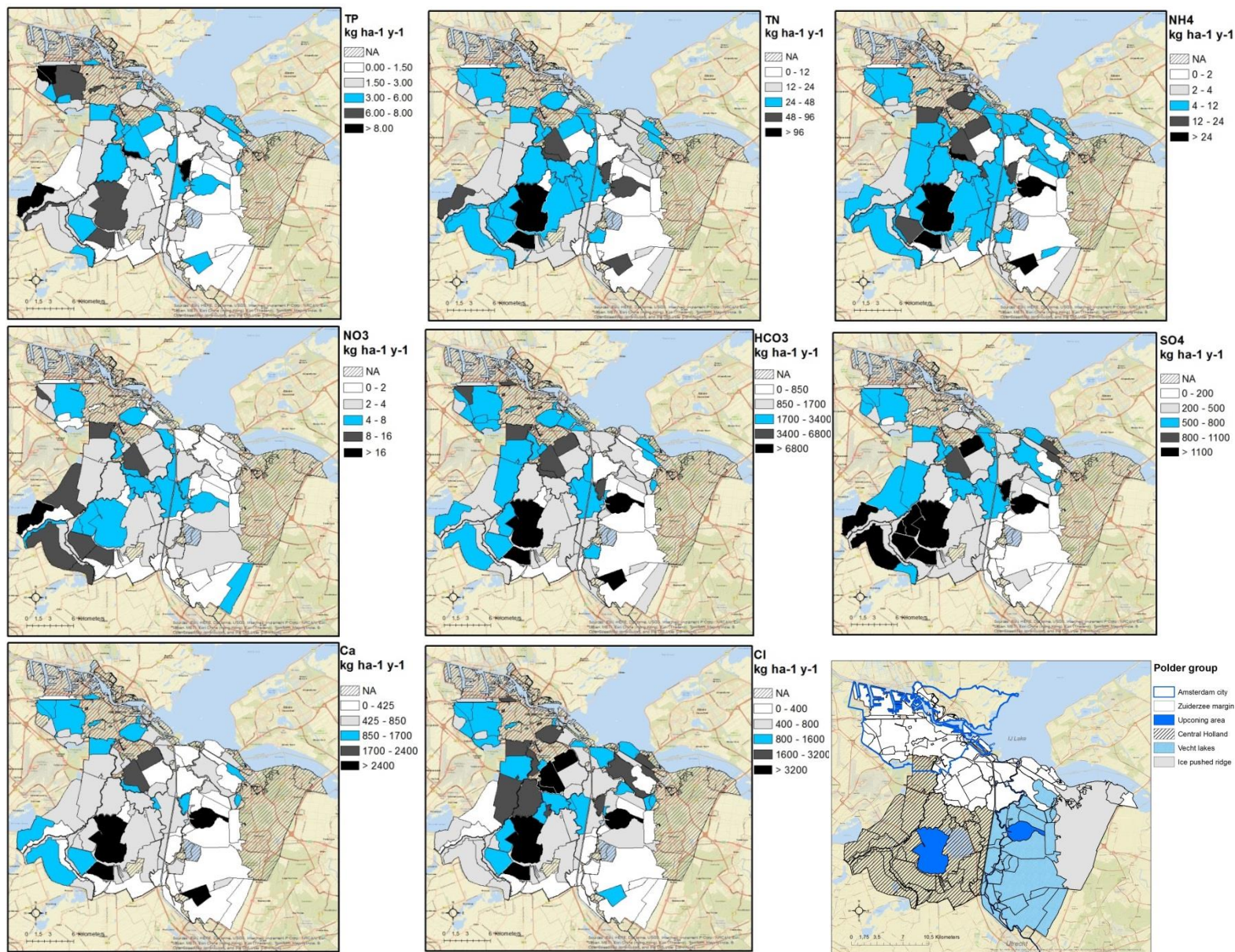



Figure 11: Surface water solute loads (average of 2010 to 2013) distribution maps in kg ha⁻¹y⁻¹

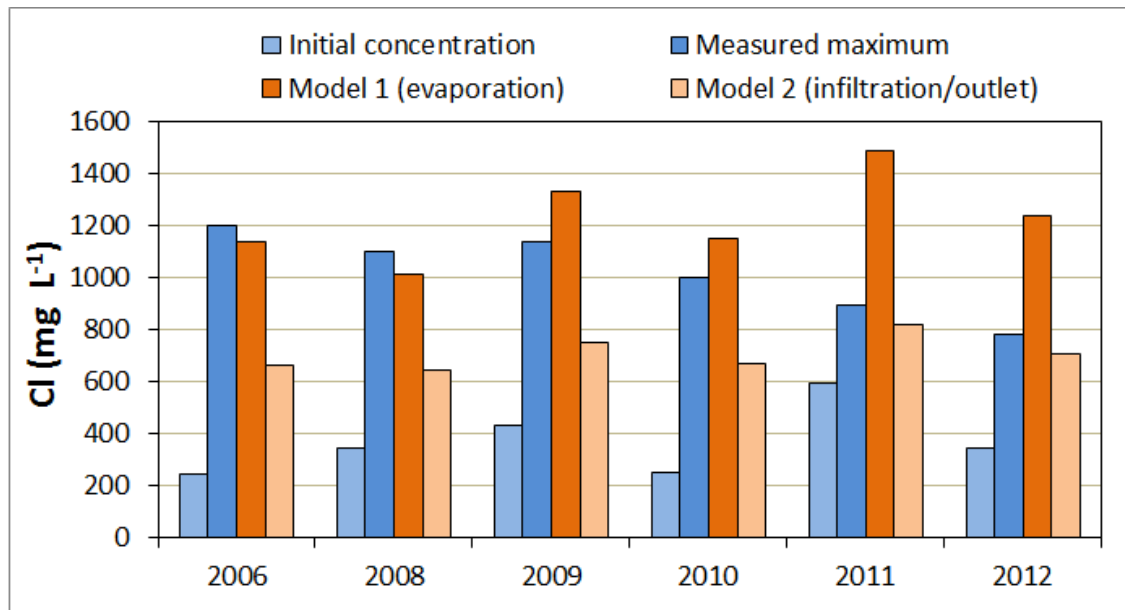



Figure 12: Summary of the water and chloride balance for polder Botshol; the graph shows (1) the initial Cl before the water inlet
season (light blue), (2) the resulting Cl peak in Botshol after some months of inlet (dark blue), and (3) the results of the two models
(model 1 dark orange, model 2 light orange).

Table 1 Coefficients of determination between groundwater quality and surface water quality

	TP GW	TN GW	NH$_4$ GW	NO$_3$ GW	HCO$_3$ GW	SO$_4$ GW	Ca GW	Cl GW	TP SW	TN SW	NH$_4$ SW	NO$_3$ SW	HCO$_3$ SW	SO$_4$ SW	Ca SW	Cl SW
TP $_{GW}$	1															
TN $_{GW}$	0,66	1														
NH$_4$ $_{GW}$	0,77	0,84	1													
NO$_3$ $_{GW}$				1												
HCO$_3$ $_{GW}$	0,68	0,63	0,82		1											
SO$_4$ $_{GW}$	-0,46			0,41		1										
Ca $_{GW}$					0,50		1									
Cl $_{GW}$					0,48	0,40	0,77	1								
TP $_{SW}$	0,49	0,51	0,60		0,64				1							
TN $_{SW}$	0,45		0,44		0,52				0,59	1						
NH$_4$ $_{SW}$			0,44		0,51				0,49	0,77	1					
NO$_3$ $_{SW}$										0,57		1				
HCO$_3$ $_{SW}$	0,57	0,55	0,64		0,68			0,41	0,63	0,47	0,67		1			
SO$_4$ $_{SW}$										0,57		0,50		1		
Ca $_{SW}$	0,59	0,54	0,63		0,71			0,41	0,55	0,56	0,64		0,88		1	
Cl $_{SW}$					0,47	0,47		0,69		0,47	0,51		0,52	0,49	0,55	1
N input kg ha^{-1} y^{-1}																
P input kg ha^{-1} y^{-1}																
Paved area %																
Elevation									-0,67	-0,59	-0,40	-0,48	-0,47	-0,57		
Seepage rate										0,48			0,45		0,46	
Surface water %																
Lutum %																
Humus %					0,50				0,46	0,40					0,41	0,48
Calcite %																

* Only absolute value of coefficients higher than or equal to 0.40 were shown in the table

TP sw: surface water TP concentration in mg L^{-1}

TP gw: groundwater TP concentration in mg L^{-1}

Table 2 Linear regression results of each surface water solute (Spearman)

	n_1	n_2	n_3	R^2	R^2 *with only seeping polders*	
TP_{SW}	+ $HCO_{3\,GW}$	+ NH_{4GW}		0.43	0.49	(9)
TN_{SW}	- Elevation	+ $HCO_{3\,GW}$	+ N_{input}	0.57	0.48	(10)
$NH_{4\,SW}$	- Elevation	+ $HCO_{3\,GW}$	+ Seepage	0.50	0.61	(11)
$NO_{3\,SW}$	- Elevation	+ N_{input}		0.18	0.23	(12)
$HCO_{3\,SW}$	+ $HCO_{3\,GW}$	+ Seepage	+ $NH4_{GW}$	0.57	0.70	(13)
$SO_{4\,SW}$	- Elevation	+ SO_{4GW}		0.25	0.22	(14)
Ca_{SW}	+ $HCO_{3\,GW}$	- Elevation	+ Seepage	0.65	0.63	(15)
Cl_{SW}	+ Cl_{GW}	+ $HCO_{3\,GW}$	+ P_{Humus}	0.57	0.51	(16)

* '+' positive relation, '-' negative relation

n_1: first variable, the most significant variable

$HCO_{3\,SW}$: surface water HCO_3 concentration in mg L^{-1}

$HCO_{3\,GW}$: groundwater HCO_3 concentration in mg L^{-1}

Elevation: average polder elevation in m N.A.P

Seepage: seepage rate in mm y^{-1}

P_{Humus}: percentage of humus in the soil profile sample

N_{input}: manure and fertilizer N input in kg ha^{-1} y^{-1}

Table 3 Main hydrogeochemical reactions in the study area

Process		Reactions	No
Organic matter decomposition		$CH_2O\,N_xP_y \rightarrow xN + yP + HCO_3^- +$ other components	[2]
		$CH_2O\,N_xP_y + O_2 \rightarrow CO_2 + H_2O + xN + yP$	[3]
		$5CH_2O\,N_xP_y + 4NO_3^- \rightarrow 2N_2 + CO_2 + 4HCO_3^- + 3H_2O + 5xN + 5yP$	[4]
		$2CH_2O\,N_xP_y + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- + 2xN + 2yP$	[5]
Pyrite oxidation		$2CH_2O\,N_xP_y \rightarrow CH_4 + CO_2 + 2xN + 2yP$	[6]
		$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$	[7]
		$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 10SO_4^{2-} + 7N_2 + 2H_2O$	[8]
Calcite dissolution	Closed system	$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^-$	[9]
	Open system	$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$	[10]