



1 Groundwater impacts on surface water quality and nutrient loads in 2 lowland polder catchments: monitoring the greater Amsterdam area

3 Liang Yu^{1,2}, Joachim Rozemeijer³, Boris M. van Breukelen⁴, Maarten Ouboter², Corné van der Vlugt²,
4 Hans Peter Broers⁵

5 ¹Life and Earth Sciences, Vrije University Amsterdam, Amsterdam, 1181HV, The Netherlands

6 ²Waternet Water Authority, Amsterdam, 1096 AC, The Netherlands

7 ³Deltares, Utrecht, 3508 TC, The Netherlands

8 ⁴Delft University of Technology, Delft, 2628 CN, The Netherlands

9 ⁵TNO Geological Survey of The Netherlands, Utrecht, 3584 CB, The Netherlands

10 *Correspondence to:* Hans Peter Broers (hans-peter.broers@tno.nl)

11 **Abstract.** The Amsterdam area, a highly manipulated delta area formed by polders and reclaimed lakes, struggles with high
12 nutrient levels in its surface water system. The polders receive spatially and temporally variable amounts of water and
13 nutrients via surface runoff, groundwater seepage, sewer leakage and via water inlet from upstream polders. Diffuse
14 anthropogenic sources, such as fertilizer use and atmospheric deposition, add to the water quality problems in the polders.
15 The major nutrient sources and pathways have not yet been clarified due to the complex hydrological system in such lowland
16 catchments combined with both urban and agriculture areas. In this study, the spatial variability of the groundwater seepage
17 impact was identified by exploiting the dense groundwater and surface water monitoring networks in Amsterdam and its
18 surrounding polders. Twenty-three variables (concentrations of Total-N, Total-P, NH₄, NO₃, HCO₃, SO₄, Ca, and Cl in
19 surface water and groundwater, seepage rate, elevation, land-use, and soil type) for 144 polders were analysed statistically
20 and interpreted in relation to sources, transport mechanisms and pathways. The results imply that groundwater is a large
21 source of nutrients in these mixed urban/agricultural catchments, given the higher nutrient levels in groundwater compared
22 with surface water. The groundwater nutrient concentrations exceeded the surface water Environmental Quality Standards
23 (EQSs) in 93 % of the polders for TP and in 91 % for TN. Groundwater outflow into the polders thus adds to nutrient levels
24 in the surface water. High correlations (R^2 up to 0.88) between solutes in groundwater and surface water, together with the
25 close similarities in their spatial patterns, confirmed the large impact of groundwater on surface water chemistry, especially
26 in the polders that have high seepage rates. Our analysis indicates that the elevated nutrient and bicarbonate concentrations in
27 the groundwater seepage originate from the decomposition of organic matter in subsurface sediments coupled to sulfate
28 reduction and possibly methanogenesis. The large loads of nutrient rich groundwater seepage into the deepest polders
29 indirectly affect surface water quality in the surrounding area, because excess water from the deep polders is pumped out and
30 used to supply water to the surrounding infiltrating polders in dry periods. The study shows the importance of the connection
31 between groundwater and surface water nutrient chemistry in the greater Amsterdam area. We expect that taking account of



1 groundwater-surface water interaction is also important in other subsiding and urbanising deltas around the world, where
2 water is managed intensively in order to 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. The Netherlands is a densely populated country where surface water
6 salinization and eutrophication are common problems. It is a typical highly urbanized country, with 2/3 of its land lying
7 below mean sea level. In The Netherlands, small regulated catchments called polders have been developed over centuries by
8 diking in and draining lakes and swamps (Huisman, 1998). Over 10 million people are living in the coastal area, mainly in
9 the Western part where a Holocene layer of peat and clay covers Pleistocene fluvioglacial sands. Especially the deepest
10 polders receive large amounts of groundwater seepage. The surface water levels within the polder catchments are artificially
11 controlled by pumping water out into the regional water systems (called Boezem), which further accelerates groundwater
12 seepage. Some of the deep polders exhibit upconing of deep saline groundwater into the surface water. The salt loading
13 towards these polders is expected to increase, mainly due to the further lowering of surface water levels in response to
14 subsidence (e.g. Oude Essink et al., 2010; Delsman et al., 2014). Draining the peat polders has also led to subsidence and
15 repetitive lowering of surface water and groundwater levels. As a consequence, nutrients are released due to peat oxidation
16 (Hellmann and Vermaat, 2012). Another nutrient source is the large scale agricultural application of manure and fertilizer.
17 Although manure legislation was already enforced in 1986, surface water quality in the area still does not meet the EU Water
18 Framework Directive standards for chemical and ecological water quality (Rozemeijer et al., 2014). The local water
19 authority, called Waternet, is commissioned to improve water quality in a cost-effective mitigation program. The assessment
20 of load contributions from different pollution sources is essential to set realistic region-specific water quality targets and to
21 select appropriate mitigation options.

22 Influences of groundwater on surface water quality have recently gained more attention by hydrologists (e.g. Rozemeijer and
23 Broers, 2007; De Louw et al., 2010; Garrett et al., 2012; Delsman et al., 2015). Rozemeijer et al. (2010) found that
24 groundwater seepage has large impacts on surface water quality in a lowland agricultural catchment. A study by Holman et
25 al. (2008) in the United Kingdom and the Republic of Ireland also suggested that the groundwater contribution to surface
26 water nutrient concentrations is more important than previously thought. Furthermore, Meinikmann et al. (2015) found that
27 lacustrine groundwater discharge contributed for more than 50% of the overall external P load in their study lake.
28 Vermonden et al. (2009) concluded that upward seepage from Meuse-Waal canal delivered NO₃ and Cl to urban surface
29 water system. The impact of other landscape characteristics on surface water quality, such as soil type and land use, has also
30 been explored. For example, Van Beek et al. (2007) found that nutrient rich peat layers will remain a potential source of
31 nutrients in surface water in many peat polders in the western part of The Netherlands. Mourad et al. (2009) found that the
32 spatial patterns of nitrate and phosphate concentrations in the Ahja River catchment in Estonia were related to spatial



1 differences in urban and agricultural land use proportions. Vermaat et al. (2010) studied 13 peat polders in the Netherlands
2 and reported that agricultural land use largely determined the variability in nutrient concentrations and loads. Phosphorus
3 was observed in higher concentrations in urban areas than in rural areas by Meinikmann et al. (2015) In some studies, point
4 sources like effluent from sewage treatment plants dominated the phosphorus loads (e.g. Wade et al., 2012), but the
5 Netherlands is known to have early invested in centralised sewage treatment works, thus avoiding the many individual spills
6 that are present in some bordering countries (EU, 2017).

7 Previous water quality research in polder areas have mainly focused on the impact of land use types and topography. The
8 impact of groundwater and flow routes on spatial water quality patterns in polders has not been systematically studied. Such
9 insight is highly needed, as a cost-effective protection and regulation of water resources requires an integrated assessment of
10 water and contaminant flow routes in the water system as a whole. In general however, water and contaminant flow routes in
11 urban settings are more complex than in rural areas, due to the highly variable surface permeability and human emissions of
12 pollutants.

13 This study aimed at identifying the impact of groundwater on surface water quality in the polder catchments of the greater
14 Amsterdam city area, which is the management area of Waternet, the organisation which manages dikes, regulates water
15 levels and pumping regimes and is responsible for the clean surface water, drinking water supply and waste water treatment.
16 To achieve this, we analysed regional surface water and groundwater quality monitoring data in combination with eight
17 landscape characteristic variables for 144 polders: surface elevation, paved area percentage, surface water percentage,
18 seepage rate, and soil type represented by calcite, humus, and clay percentages. Our statistical analyses yielded insight into
19 the impact of groundwater on the surface water chemistry of the urban and rural polders of Amsterdam. The presented
20 approach contributes to realistic and effective water quality regulation in the Waternet management area and can also be
21 applied to other deltas in the world with adequate groundwater and surface water monitoring data.

22 **2 Methods**

23 **2.1 Study area**

24 This study focuses on the polder catchment landscape around the city of Amsterdam in The Netherlands. The whole study
25 area spans 700 km², from downtown Amsterdam situated in the northwest to the border of the province of Utrecht in the
26 southeast (Fig. 1). Amsterdam is a low-lying highly paved city located in the western part of the Netherlands, developed
27 around the levees of the tidal outlet of the Amstel River about 700 years ago (Vos, 2015). Nowadays, the water system in
28 Amsterdam is connected to the large fresh water body of the Lake IJ (Fig. 1). Besides Lake IJ, other important large water
29 bodies are the Amstel and Vecht rivers and the Amsterdam-Rhine canal. This regional water system, also called the
30 'Boezem', connects the Amsterdam-area water system to the Rhine River (upstream) and the Lake IJssel and the North Sea
31 (downstream). In the 19th and 20th centuries, the city expanded, and many new neighbourhoods and suburbs were built.



1 Polders and reclaimed lakes form the main landscape in the southward extensions of the city. Some of these polders are at
2 several meters below Mean Sea Level (MSL) and are influenced by groundwater seepage.

3 **2.1.1 Landscape history and hydrology**

4 **Landscape history**

5 Our study area is located in the western part of The Netherlands where large rivers and the sea have intensively interacted for
6 millions of years. The main topographic feature is a Pleistocene sandy ice pushed ridge with elevations ranging from 0 to 30
7 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
8 periglacial Pleistocene river plains of the Rhine delta. During the Holocene, these sandy river plains were covered with peat
9 and clay, which are currently found at the surface throughout the western part of the Netherlands, on top of Pleistocene
10 sands. The average thickness of the Holocene peat and clay cover is 20 m, although it increases to over 50 m in former tidal
11 inlet channels (Hijma, 2009).

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

20 The long history of marine influence stopped after closing off the estuaries and the inland sea in the 20th century (Huisman,
21 1998). In 1932, the construction of the Closure Dike (Afsluitdijk) created the fresh water Lake IJssel out of the former salt
22 water Zuiderzee (‘Southern Sea’) to protect the surroundings from floods and to enable land reclamation. The former marine
23 impact is still reflected by the presence of brackish groundwater in the shallow subsurface (Schot, 1992 b).

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

29 Mainly during the 20th century, the urban areas have been growing from the historic city-centres on river and tidal channel
30 levees into the surrounding low-lying polders. To facilitate the construction of buildings, a 1-5 meter-layer of sand was often
31 supplied on top of the original sediments. The thickness of this suppletion sand layer is extremely variable even at a small
32 scale. The sand suppletions are either calcite-poor without shell fragments or calcite rich with shell fragments that indicate



1 their (peri-) marine origin. The spatial distribution and sources of the sand suppletions probably influence groundwater and
2 surface water chemistry, but are poorly registered.

3 **Polder hydrology**

4 Within the polders, the water levels are artificially maintained between fixed boundary levels to optimize conditions for their
5 urban or agricultural land use. Boezem water levels always exceed the polder surface water levels. In the case of water
6 deficiency, water is let into the polder ditches from the boezem through pipes by gravity flow (Fig. 2a). Pumping stations are
7 situated at the boezems to regulate the water levels in the polders in times of precipitation excess. In the case of a water
8 surplus, pumping stations start pumping water out of the polder into the boezem-system (Fig. 2b).

9 The regional flow directions in wet and dry periods in the study area are depicted in Fig. 3. The Amsterdam-Rhine canal, the
10 Amstel River, and the Vecht River are the main water courses discharging surface water from the south to the north in
11 periods of water surplus (Fig. 3). In periods of water deficiency, however, the flow directions are reversed in some parts of
12 the system.

13 There are six main sources of inlet water to compensate for water shortage in dry periods (Fig. 3): (1) Amsterdam Rhine
14 Canal (ARC): water of the ARC originates from the Rhine and is supplied as inlet water for the southeast polders and
15 polders in the southeast of Amsterdam city; (2) Amstel River: the historic canals of the city of Amsterdam are mainly
16 flushed by water from the Amstel River. Via the canals, this water discharges to the downstream part of the ARC and further
17 into the North Sea; (3) Groot Mijdrecht and Horstermeer: the brackish surplus of seepage water from the deep polder Groot
18 Mijdrecht ($\sim 1000 \text{ mg Cl L}^{-1}$ on average) and Horstermeer ($\sim 500 \text{ mg Cl L}^{-1}$) is pumped into the Boezem system and is
19 redistributed towards surrounding polders (pink lines in Fig. 3); (4) Rijnland Water Authority district: polders in the far west
20 of the study area receive inlet from the neighboring Water Authority district Rijnland. The water quality of this source is
21 unknown. (5) and (6) Vecht River and Lake IJ: polders along the Vecht River receive inlet water that partly originates from
22 the Rhine and partly from Lake IJ. Polders close to Lake IJ receive large amounts of water directly from the lake. The Lake
23 IJ water is also used to flush canals in the city of Amsterdam.

24 **2.1.2 Characterisation of regions**

25 Based on the geology and paleohydrological history as introduced in section 2.1.1, 5 regions were identified (see Fig. 4). The
26 5 regions are: (1) the Zuiderzee margin region, with shallow brackish groundwater, lies directly adjacent to the former salt
27 water Zuiderzee, which was dammed in the 1930s and transformed into the fresh water Lake IJssel (connected to Lake IJ),
28 which is now the biggest fresh water reservoir of The Netherlands; (2) the deep polders Groot-Mijdrecht and Horstermeer,
29 which are reclaimed lakes with clayey lake sediments at the surface. These polders are characterized by upconing of salt
30 groundwater from deeper layers (Oude Essink et al., 2005; Delsman et al., 2014); (3) the Central Holland system of boezems
31 and polders which are characterized by a relatively thick sequence of marine clays and intercalated peats; (4) the Vecht lakes
32 region at the western margin of the ice pushed ridge, characterized by shallow peat soils over a sandy subsoil and large
33 shallow lakes and wetlands resulting from peat excavations (van Loon, 2010); and (5) the Ice pushed ridge in the eastern part



1 of the study area, which is characterized by permeable sandy soils, recharge of freshly infiltrated water, and the mere
 2 absence of draining water courses.

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

7 **2.2 Data processing**

8 The database that was compiled and used for this study covers 144 individual polders and includes monthly surface water
 9 quality data, spatiotemporally averaged groundwater quality data (TN, NO₃, NH₄, SO₄, TP, Ca, HCO₃, and Cl), daily
 10 pumping station discharge time series, and 15 polder averages of the following statistic variables: polder seepage rates,
 11 elevations, surface water and paved area percentages, and calcite, clay, and humus percentages of the upper soil layer. More
 12 information about the data processing and the database can be found in the Supplementary information.

13 **2.2.1 Groundwater data**

14 A total of 802 observation wells of groundwater quality are available from the period 1910-2013, largely drawn from the
 15 National Groundwater Database DINO (TNO, DINOLoket). We selected analyses from the upper 50 m of the subsurface,
 16 which corresponds with the thickness of the first main Pleistocene aquifer in the area and the Holocene cover layer. For our
 17 analyses, we averaged concentrations at individual monitoring screens of each monitoring well for all sampling dates
 18 available.

19 To analyse the spatial pattern of groundwater quality, we averaged concentrations of all the monitoring wells located in the
 20 same polder (for more details, see Table S2). For 24 polders out of the polders without groundwater quality data, the
 21 concentrations were estimated by Inverse Distance Weighted interpolation, however using absolute elevation difference
 22 instead of distance. The greater the absolute elevation difference, the less influence the polder has on the output value. The
 23 equations are:

$$C_0 = \sum_{i=1}^n \lambda_i C_i \quad (1)$$

$$\lambda_i = d_{i_0}^{-p} / \sum_{i=1}^n d_{i_0}^{-p}, \quad \sum_{i=1}^n \lambda_i = 1 \quad (2)$$

24 C_0 , prediction of target polder; C_i , observed value of surrounding polders; n number of observations; p , power parameter (2
 25 in this case); d_{i_0} , absolute elevation differences of target polder with surrounding polders. Subsequently, to interpret the



1 groundwater quality patterns, the variation of concentrations in and between the 5 regions was visualized using boxplots
 2 (Helsel and Hirsch, 2002).

3 Because our dataset contains both fresh and brackish to saline water, we used the mass SO_4/Cl ratio of the samples as an
 4 indicator of sulfate reduction. SO_4/Cl ratios lower than the sea water ratio of 0.14 (Morris and Riley, 1966) point to the
 5 occurrence of sulfate reduction (Appelo and Postma, 2005; Griffioen et al., 2013). Ratios above 0.14 point to the addition of
 6 sulfate relative to diluted sea water through processes like pyrite (FeS_2) oxidation or through input via atmospheric inputs,
 7 fertilizers, manure, or leakage and overflow of sewer systems.

8 Average concentrations in groundwater for each polder were mapped to be compared with average annual surface water
 9 concentrations (See section 2.2.2). The potential relationship between the solute concentrations in groundwater (TN , NO_3 ,
 10 NH_4 , SO_4 , TP , Ca , HCO_3 , and Cl) and the landscape variables (paved area percentage, elevation, seepage rate, surface water
 11 area percentage, lutum, humus and calcite percentages of top soil) were explored using the Spearman correlation, which
 12 reduces the influence of outliers and yields a robust correlation statistic (Helsel and Hirsch, 2002).

13 To further explore the statistical relations in our data set, scatter plots were made to evaluate HCO_3 , SO_4 , Cl , and nutrient
 14 (NO_3 , NH_4 and PO_4) concentrations in groundwater. We also explored the links between alkalinity (over 99 % of our
 15 groundwater alkalinity was dominated by HCO_3 , (Stuyfzand, 2006)), Cl concentration, SO_4/Cl ratio and nutrients (TN , NH_4
 16 and TP) concentrations. For our interpretation, we also used the calculated amount of consumed or produced SO_4 in $mg L^{-1}$
 17 relative to the SO_4/Cl ratio of diluted seawater, using Eq. (3):

$$18 \quad SO_4 \text{ consumed}(-) \text{ or produced}(+) = SO_4 \text{ measured} - Cl \text{ measured} \cdot SO_4 \text{ sea} / Cl \text{ sea} \quad (3)$$

19 In order to understand the impact of cation exchange processes involving Ca and Na exchange during salinization and/or
 20 freshening of aquifers (Griffioen, 2004; Stuyfzand, 2006) we defined the amount of exchange Na_{ex} as:

$$21 \quad Na_{ex} = Na_{gw} - Cl_{gw}(Na_{gw}/Cl_{seaw}) \quad (4)$$

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

24 2.2.2 Surface water data

25 Loads represent the contribution of polders to surface water quality of the regional water system in weight per time unit. To
 26 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
 27 daily average loads of each solute divided by the polder areas using Eq. (5):

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

28 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 $m^3 d^{-1}$.
 29 ¹. Average daily loads for each year were multiplied by 365 to get average yearly loads per area. Monthly surface water



1 quality measurements for the period 2006-2013 of 144 polders were extracted from the Waternet database. The
2 measurements were converted to daily time series by stepwise interpolation between the monthly measurements. We
3 assigned a concentration of zero to measurements below the detection limits. Discharge data Q are daily measurements over
4 the same time period. An average over multiple pumps, when present, was taken for each polder. For further details about
5 the data processing we refer to Table S2.

6 The pumping discharge is regulated to respond to water surplus or deficiency conditions in the polder catchments. Using the
7 pumping frequency data, we proved that solute concentrations in pumped water are usually higher at the beginning of each
8 pumping activity (Van der Grift et al., 2016). The pumping rates may also influence water quality in the polder. To eliminate
9 differences caused by pumping rates, we used the normalized concentration calculated using Eq. (6):

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

10 In this equation, C is the normalized concentration (mg L^{-1}), Load per area is from Eq. (1), Q is the pumping discharge ($\text{m}^3 \text{y}^{-1}$)
11 1), and A is the polder area (m^2). The statistical methods that were used for groundwater quality (described in section 2.2.1)
12 were also applied to the surface water normalized concentrations.

13 Based on a national assessment on ecosystem vulnerability, Environmental Quality Standards (EQSs) were set by the Water
14 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
15 L^{-1} and 0.15 mg L^{-1} , respectively (Rozemeijer, 2014). We used these most common EQSs as reference concentration values.
16 For example, the EQSs of TN and TP were used for the legend classifications in our surface water quality maps and were
17 added as reference lines in our concentration boxplots. Percentages of polders exceeded these standards were calculated in
18 this paper.

19 **2.2.3 Surface water compared with groundwater solute concentrations**

20 We statistically analysed the groundwater and surface water quality data and landscape characteristic variables by (1)
21 calculating the correlation coefficients between averaged groundwater solutes concentrations and normalized concentrations
22 of surface water using the Spearman method, and (2) by selecting variables (based on the correlation matrix above) to be
23 integrated into multiple linear regression models for predicting surface water solute concentrations. Again, the Spearman
24 method was applied and linear regression was based on ranks in order to avoid outliers to determine the outcomes. The
25 explaining variables for surface water concentrations include groundwater solute concentrations, landscape characteristics,
26 and the SO_4/Cl ratio in groundwater. The number of selected explaining variables depends on the added value of an extra
27 component. An extra explaining variable was only added to the regression when it improved the explained variance with at
28 least 5%, and at most four variables were added. For comparison purposes, we also used the surface water EQSs as reference
29 concentration values in the groundwater quality maps and boxplots, although the EQS's have no administrative meaning for
30 groundwater itself.



1 2.2.4 Solutes redistribution in surface water

2 Loads were used to assess the impact of different polders as sources of solutes for the boezems and the receiving water
3 bodies further downstream. In general, the spatial patterns can be distinguished through maps of the surface water solute
4 loads per area if there are no other influences. However, there are exceptions such as the seepage water which is pumped out
5 of the two upcoming polders Groot Mijdrecht and Horstermeer, which is discharged into the Boezem system and used as inlet
6 water for the surrounding polders during summer. To show the impact of this inlet water on the receiving polders' water
7 quality, we analysed the inlet solute loads and the resulting surface water concentrations for polder Botshol. Polder Botshol
8 (part of polder # 104 Noorderpolder of Botshol (zuid and west)) with an area of 1.3 km² receives inlet water from the Amstel
9 boezem system that has a significant contribution of seepage water that is pumped out of the polder Groot Mijdrecht.
10 Two models were applied for simple solute concentration calculations based on inlet water quality. Model 1 calculates the
11 accumulation of solutes in the water body, with evaporation as the only output for water (leaving the solutes behind). Model
12 2 models the complete mixing and outlet of both water and solutes via other routes like the outlet weir, infiltration, and
13 leakage. In reality, water leaves Polder Botshol partly via evaporation (Model 1) and partly via other routes (Model 2):

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

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

16 where, C_{i+1} is the predicted solute concentration after getting inlet water at time i ; C_i is the predicted solute concentration in
17 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
18 polder (800.000 m³), which is assumed to be constant as water levels are tightly controlled; C_{inlet} is the estimated Cl
19 concentration in the inlet water (1000 mg L⁻¹); Q_{inlet} is estimated constant inlet water volume, 6000 m³ d⁻¹. All parameters
20 are shown in supplementary information Excel spread sheets. The models were applied in the year 2006, 2008, 2009, 2010,
21 2011 and 2012.

22 3 Results

23 3.1 Spatial pattern and statistical analysis of groundwater quality

24 Fig. 5 and Fig. 6 show the groundwater quality for the upper main aquifer under the 144 polders for Cl, Ca, HCO₃, SO₄, TN,
25 NH₄, NO₃, and TP. The relations between groundwater solutes, landscape variables, and potential hydrochemical reactions in
26 the subsurface were explored by correlation analysis of which the results are shown in Table 1 (yellow part) and Fig. 7 and
27 Fig. 8.

28 Cl, Ca, and HCO₃

29 In Fig. 5, the Zuiderzee margin, where brackish groundwater is dominant, P25 and P75 of concentrations are between 290
30 and 2100 mg L⁻¹ Cl, 100-300 mg L⁻¹ Ca, and 400-1000 mg L⁻¹ HCO₃. Relatively high concentrations of Cl, Ca and HCO₃



1 were also for the two deep polders Groot Mijdrecht (# 80) and Horstermeer (Upconing area) with known upconing of salt
2 groundwater. The Central Holland area was dominated by fresh groundwater with low Cl and Ca concentrations, but with
3 considerable amounts of HCO_3 . Polders with relatively high chloride ($>1000 \text{ mg L}^{-1}$) are distributed along the former
4 Zuiderzee margin, plus the Upconing area which is two deep polders with known upconing of brackish water. Relative to the
5 regions above, the Vecht lakes area and the Ice pushed ridge showed significantly less mineralized waters with lower HCO_3
6 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
7 350 mg L^{-1} . The groundwater HCO_3 concentrations (Fig. 6) show an east-west increasing trend with highest concentrations
8 in both the fresh and brackish areas west of the Amsterdam Rhine Canal.

9 **SO_4 and SO_4/Cl**

10 The Zuiderzee margin and the Upconing area showed large ranges of SO_4 concentrations (P25 and P75: $7\text{-}125 \text{ mg L}^{-1}$ and 7-
11 250 mg L^{-1} , respectively) with the SO_4/Cl mass ratios generally lower than the 0.14 ratio for diluted seawater. The polders in
12 the eastern Zuiderzee margin showed the highest average SO_4 levels (Fig. 6). The Central Holland area exhibited the lowest
13 SO_4 concentrations with the smallest variability, with SO_4/Cl P75 typically lower than 0.14. However, some outliers in this
14 region reached quite high sulfate concentration levels ($>200 \text{ mg L}^{-1}$). The Vecht lakes and the Ice pushed ridge showed
15 intermediate sulfate concentrations and typically have a SO_4/Cl ratio clearly above 0.14.

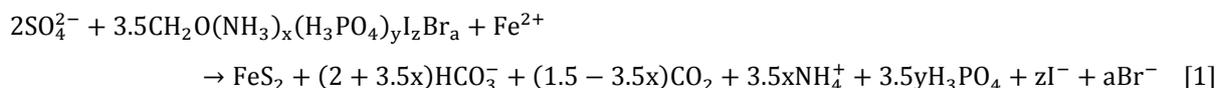
16 **NH_4 , TN, NO_3 , and TP**

17 The higher groundwater NH_4 and TP concentrations generally locate in the western part of the study area (Zuiderzee margin,
18 Upconing area, and Central Holland regions). Median NH_4 concentrations in the Zuiderzee margin (6.4 mg L^{-1}) and Central
19 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
20 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
21 (medians $5.7 \text{ mg NH}_4 \text{ L}^{-1}$ and 0.14 mg P L^{-1}) were relatively low compared with the groundwater in the Zuiderzee margin
22 and Central Holland areas, although we consider the NH_4 concentration levels to be substantial given the surface water EQS
23 of 2.4 mg N L^{-1} . TN showed the highest median concentration levels in the Zuiderzee margin and Central Holland regions, as
24 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
25 region, nitrate is the main component of TN, while NH_4 is the main component in the other regions.

26 Groundwater quality varied from fresh, low mineralized in the eastern parts (Vecht lakes and Ice pushed ridge, Figure 4)
27 towards brackish, highly mineralized and nutrient rich groundwater in the northwest (Zuiderzee margin and Central Holland,
28 Fig. 4). This relationship was further indicated by the strong correlations between Ca and Cl (Spearman R^2 0.77) and
29 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
30 pattern (Fig. 6), showing higher Ca concentrations in the brackish waters, which is related to the high Ca concentrations in
31 (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,
32 except in the suboxic groundwaters under the Ice pushed ridge where nitrate dominates TN. HCO_3 , TP and NH_4 were all
33 weakly negatively correlated with elevation, indicating that higher concentrations exist in the deeper polders which are more
34 affected by brackish groundwater seepage.



1 In the more mineralized groundwater systems, sulfate reduction is a potential cause of the significant relationship between
 2 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.
 3 3), it appears that most of the brackish groundwater showed signs of sulfate reduction. Figure 7 shows that the amount of
 4 SO_4 consumed in the sulfate reduction process increased with the chloride concentration of the groundwater, and that sulfate
 5 reduction was complete only in part of the groundwaters. Note that groundwater below polders with excess SO_4 are all in
 6 water with $\text{Cl} < 1000 \text{ mg L}^{-1}$. It follows from Figure 8 that high HCO_3^- , TP, and NH_4^+ concentrations mostly occurred in
 7 groundwater with a SO_4/Cl ratio lower than 0.14, indicating sulfate reduction which induces the release of N and P from the
 8 mineralized organic matter in the subsurface and the production of alkalinity during that process. Therefore, these waters
 9 typically have increased HCO_3^- concentrations above 480 mg L^{-1} (Fig. 8A and 8B) and are often associated with brackish
 10 groundwater that once contained sulfate (Fig. 8C: $\text{Cl} > 300 \text{ mg L}^{-1}$). The hypothetical chemical relation between sulfate
 11 reduction (SO_4 consumed) and $\text{HCO}_3^-/\text{NH}_4^+/\text{H}_3\text{PO}_4$ production from the mineralisation of organic matter can be found in the
 12 reaction equation below (Stuyfzand, 2006):



13 3.2 Spatial patterns and statistical analysis of surface water quality

14 Fig. 9 and Fig. 10 show the solute concentrations in the four regions: Zuiderzee margin, Upconing area, and Central Holland,
 15 and Vecht lakes. Due to insufficient surface water quality data, no results are shown for several polders in the Amsterdam
 16 city area (see Fig. 4) and the Ice pushed ridge region. The first is related to the monitoring priorities of the Waternet water
 17 board, the latter is related to the almost absence of surface water in this region.

18 Cl, Ca, and HCO_3^-

19 Highest chloride levels ($>300 \text{ mg L}^{-1}$) were found in the Upconing polders with brackish seepage and in a minority of the
 20 polders in the Zuiderzee margin and Central Holland regions (Fig. 9 and 10). The high Ca and HCO_3^- concentrations in these
 21 polders are also related to the occurrence of brackish water. However, most of the surface water in the Zuiderzee margin and
 22 the Central Holland area is fresh with relatively low Cl concentrations (Fig. 10). The Vecht lakes area exhibits the most fresh
 23 and least mineralized surface water.

24 SO_4 and SO_4/Cl

25 The highest SO_4 concentration levels and SO_4/Cl mass ratios mostly occurred in the Central Holland area, especially the
 26 western part. The elevated SO_4 and SO_4/Cl ratios indicate the presence of sulfate sources other than (relict) seawater in this
 27 area, probably atmospheric deposition, agriculture and/or oxidation of pyrite exposed in the upper soils which developed in
 28 marine clay deposits and are denoted as “cat clays” (Wallenberg, 1975). In the Zuiderzee margin and the two upconing
 29 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
 30 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.



1 TN, NH₄, NO₃, and TP

2 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
3 polders of the study area. The outliers with even higher nutrient concentrations are mainly located in the west of the Central
4 Holland region. P25 and P75 of TP and TN in the Zuiderzee margin and in Central Holland regions all significantly
5 exceeded EQSs for surface water. In the two upcoming polders, polder Groot Mijdrecht showed higher concentrations of TP
6 and TN than polder Horstermeer (medians of 0.28 vs. 0.11 mg P L⁻¹ and 5.4 vs. 1.8 mg N L⁻¹). Polders with concentrations
7 below the EQS's were mainly situated in the Vecht lakes area where large open water areas exist. In this region, TP slightly
8 exceeded 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
9 below the EQS. The concentrations of NO₃ and NH₄ in the Vecht lakes area were relatively low as well.

10 Similar to the results of groundwater, higher nutrient levels also exist in higher mineralized surface waters, which is also
11 indicated by the correlation results (Table 1, blue part): Ca and HCO₃ are both correlated with NH₄ (Spearman R² are 0.64
12 and 0.67), TP (R² 0.55, 0.62), and TN (R² 0.57, 0.47). In surface water, Ca and HCO₃ had a significant correlation (R² 0.88).
13 This indicates that groundwater is the probable source of the water and nutrients in the surface water of the polders. This
14 groundwater impact was further supported by the correlations between the following pairs of solutes in surface water: Cl
15 with Ca (R² 0.55), HCO₃ (R² 0.52), SO₄ (R² 0.49) and NH₄ (R² 0.51), as well as SO₄ with TN (R² 0.57) and NO₃ (R² 0.50). A
16 more direct indication for the groundwater impact is that NH₄, HCO₃ and Ca concentrations in surface water were positively
17 related to the seepage rate. In a similar way, the groundwater impact is suggested by the negative correlations between
18 elevation and the concentration levels of most surface water solutes (TN: R² -0.67, NH₄: R² -0.59, NO₃: R² -0.40, HCO₃: R² -
19 0.48, SO₄: R² -0.47 and Ca: R² -0.57).

20 For the soil variables (lutum, humus and calcite), only humus showed correlations with TN, NH₄, Ca, and Cl in surface water
21 (Table 1). Paved area percentage, surface water area percentage, calcite and clay percentages did not show correlation
22 coefficients above 0.4 with surface water quality. Surface water TN correlated more closely to NH₄ (0.77) than to NO₃
23 (0.57), which reflects that NH₄ is generally the main form of TN in the study area.

24 3.3 Groundwater and surface water quality comparison

25 A common spatial pattern in surface and groundwater chemistry is that polders in the Zuiderzee margin area, the two
26 upcoming polders, and the Central Holland area suffer from a worse water quality situation than the polders in the Vecht
27 lakes and Ice pushed ridge areas. However, compared with the underlying groundwater quality, surface water in the whole
28 area has much lower chloride, bicarbonate, and nutrient levels, but higher SO₄ concentrations (Fig. 5 and Fig. 9). The polders
29 generally have much higher TP and TN concentrations in groundwater than in surface water. The groundwater nutrient
30 concentrations exceeded the surface water EQS's in 93 % of the polders for TP, and in 91 % for TN. Polders with
31 groundwater nutrient levels below the EQS's were mainly found near Lake IJssel. Especially the groundwater TN
32 concentrations in the Ice pushed ridge severely exceeded surface water EQSs, which can be mainly attributed to the elevated



1 NO₃ concentrations. For TP in groundwater, the Zuiderzee margin and Central Holland areas show more significant EQS
2 exceedances compared to the Upconing area, Ice pushed ridge and the Vecht lakes area.

3 Table 1 shows that TP, NH₄, HCO₃, and Cl concentrations in groundwater correlate with the same components in surface
4 water (R² 0.53, 0.43, 0.66, and 0.72). In addition, HCO₃ in groundwater showed moderate correlations with nutrient
5 concentrations in surface water (TP (R² 0.64), TN (R² 0.50), and NH₄ (R² 0.46)). HCO₃ concentrations in surface water also
6 correlated with nutrient concentrations in surface water (TP (R² 0.60), TN (R² 0.49), and NH₄ (R² 0.59)). Surface water SO₄
7 weakly correlated to groundwater Cl (R² 0.47).

8 Based on these correlations, we selected groundwater parameters and landscape characteristics to be integrated in multiple
9 linear regression models to predict concentrations of surface water components. For most solutes (TP, NH₄, TN, HCO₃, and
10 Cl, the R² of the regression models is around 0.5, which indicates that around 40 ~ 50% of the spatial variance in surface
11 water can be explained by specific groundwater chemistry parameters, seepage, and elevation. For NO₃ and SO₄, the R² of
12 the regression models (inverse with Elevation) are very low, 0.18 and 0.21, respectively. For all other parameters, the
13 groundwater HCO₃ concentration was the best explaining variable for the surface water concentrations. The spatial variation
14 in HCO₃_{SW} and Ca_{SW} were relatively well explained by only HCO₃_{GW} combined with Seepage, respectively (Eq. 13 and Eq.
15 15).

16 The regression models were significantly improved by including groundwater concentrations of TP, NH₄, and Cl (Eq. 9, 11
17 and 16). In regression models Eq. 9, 10, 11, 12, 14, and 15, the elevation of the polders also explained part of the spatial
18 variation in surface water concentrations. When only including polders with net groundwater seepage, the R² improved
19 significantly for TP, NH₄ and HCO₃.

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

22 3.4 Surface water solute redistribution

23 Figure 11 showed that the solute loads of polders to the boezem are relatively high in the Zuiderzee margin, the Upconing
24 polders, and the Central Holland regions. The Vecht lakes area has large open water areas and showed the lowest loads to the
25 boezem system.

26 A clear similarity between the spatial patterns of the solute loads and the average seepage rate patterns was observed in Fig.
27 3 and Fig. 11. In general, polders with high seepage rates also discharge relatively high loads to the Boezem system. Some
28 examples of polders with relatively high seepage rates are polder #119 (Bethunepolder, 13 mm d⁻¹), #79 (Horstermeer, 8.7
29 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
30 mm d⁻¹), #80 (Polder Groot Mijdrecht en Polder de Eerste Bedijking (oost), 5.0 mm d⁻¹), #74 (Polder de Nieuwe Bullewijk
31 en Holendrecht- en Bullewijker Polder noord, 1.8 mm d⁻¹) and #75 (Bijlmer, 2.0 mm d⁻¹). The highest loads are discharged
32 from the two upconing polders: Groot Mijdrecht (#80) and Horstermeer (#79).



1 The influence of the redistribution of the large water volumes and loads from deep polders was also observed in Fig. 3 and
2 Fig. 11. Polders that receive inlet water from Groot Mijdrecht and Horstermeer (see section 2.1.1, Fig. 3) showed relatively
3 high solute loads, independent of their own seepage or infiltration fluxes. This especially holds for polders downstream of
4 Groot Mijdrecht and Horstermeer, like polder #73 (Holendrecht- en Bullewijker Polder (zuid en west), -0.05), #74 (Polder
5 de Nieuwe Bullewijk en Holendrecht- en Bullewijker Polder noord, 1.8 mm d^{-1}), #104 (Noorderpolder of Botshol (zuid en
6 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}),
7 and polder #107 (Polder Waardassacker en Holendrecht, -0.15 mm d^{-1}).

8 The impact of this redistributed water on polder water chemistry is demonstrated by a simple water and solute mass balance
9 calculation for the receiving polder Botshol (see paragraph 2.2.4). Fig. 12 gives the chloride concentration results of both the
10 ‘evaporation’ and the ‘infiltration/outlet’ models. Figure 12 shows that a very simple model can easily explain the peak Cl
11 concentrations in the Polder Botshol to be the result of the inlet of water from the boezem and Groot Mijdrecht. The
12 ‘evaporation’ model performs better in 2006 and 2008 and the ‘infiltration/outlet’ model in 2011 and 2012. Most of the time,
13 the measured concentrations are between the calculated concentrations from both models. This aligns with the understanding
14 that water leaves Botshol via a combination of evapotranspiration and other outflow routes, such as infiltration, leakage, and
15 outlet.

16 **4 Discussion**

17 This study aimed at identifying the impact of groundwater on surface water quality in the polder catchments of the greater
18 Amsterdam city area. According to the statistical analysis of data over five regions in the study area, a clear influence was
19 identified. Solute concentrations in groundwater and surface water correlated well, although groundwater solute
20 concentrations were generally much higher than normalized concentrations in surface water. The latter seems logical given
21 the dilution of surface water by the precipitation surplus on an annual basis, with the annually discharged surface water being
22 a mixture of seeping groundwater and precipitation. Moreover, similar spatial patterns in solute concentrations were found in
23 groundwater and surface water. Polders that are influenced by groundwater seepage or by redistributed seepage water from
24 nearby deep polders are at risk of non-compliance, as groundwater concentrations exceeded the TN and TP EQSs for surface
25 water in more than 90% of the polders. Consequently, the groundwater nutrients input hinders achieving water quality
26 targets in the surface water in those lowland landscapes.

27 **4.1 Key hydro chemical processes**

28 In general, the groundwater chemistry corresponds with the geological history of the study area. In the peat land polder
29 catchments within the Dutch delta system of marine, peri-marine and fluvial unconsolidated deposits, abundant organic
30 matter is present in the subsurface (e.g. Hijma, 2009). The presence of reactive organic matter in the shallow subsurface



1 depletes the infiltrating groundwater from oxygen and nitrate, leading to an overall low redox potential in groundwater,
2 which enables the further decomposition of organic matter downstream.

3 Our data strongly suggests that sulfate reduction, sometimes in combination with methanogenesis, is the main process
4 releasing nutrients (N, P) and HCO_3 from the organic rich subsurface in the study area, especially in both the fresh and
5 brackish groundwater of the Zuiderzee margin, the Upconing polders, and Central Holland that are characterized by low
6 SO_4/Cl ratios (Table 1, Fig. 8). The Holocene marine transgression undoubtedly influenced the chemistry of groundwater by
7 salinizing processes that also increased sulfate availability derived from diluted sea water. Refreshing of the aquifers by
8 infiltration of fresh water from rivers and rain in more elevated polders and lakes further influenced part of the groundwater.
9 We examined the amount of freshening and salinization using the exchange Na (Na_{ex}) and investigated how this process may
10 have influenced the release of P as was suggested by Griffioen et al. (2004). Figure S2 shows that high P (and HCO_3 , not
11 shown) does occur in both refreshing water ($\text{Na}_{\text{ex}} > 1$) and in salinizing water ($\text{Na}_{\text{ex}} < -1$), but mainly when the SO_4/Cl ratio is
12 below 0.14. Therefore, we infer that sulfate reduction/organic matter decomposition is the prime process in releasing P, and
13 is more discriminating high P than cation exchange processes. There is a high probability for sulfate reduction dominated
14 polder catchments to have very high HCO_3 concentration in groundwater according to Eq. [1]. In our study area, high HCO_3
15 concentration levels in both groundwater and surface water were mainly present in areas with marine sediments that contain
16 shell fragments and organic matter. The base level groundwater alkalinity from the dissolution of shell fragments and
17 carbonate minerals is further increased by the organic matter decomposition in the subsurface. This observation confirms the
18 earlier findings of Griffioen et al. (2013) who highlighted the relation between the nutrient concentrations and pCO_2 in these
19 marine sediments. The main chemical reactions involved are listed in Table 3.

20 The seepage of the alkalized groundwater increases alkalinity of the surface water, which is indicated by the high correlation
21 between groundwater and surface water HCO_3 , and with Ca in surface water (Table 1). Subsurface organic matter
22 mineralization by processes like sulfate reduction and methanogenesis (Chapelle et al., 1987; Griffioen et al., 2013) (Table 3
23 [2], [6]), is a probable major reason for enhanced surface water HCO_3 in polders with brackish groundwater, like the
24 polders in the Zuiderzee margin and the Upconing polders (Fig. 8).

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

29 Sulfate concentrations are higher in the receiving surface water than in the groundwater. We ascribe the sulfate surpluses
30 (Fig. 7) to additional sources affecting the surface water, including atmospheric deposition, agricultural inputs, sewer
31 leakage (Ellis, et al., 2005), storm runoff, and/or the oxidation of pyrite (FeS_2). Pyrite is ubiquitously present in this area
32 (Griffioen et al., 2013) and oxidizes in the topsoil, where either O_2 or NO_3 can act as electron acceptor (Wallenburg, 1975).
33 We suggest that sulfate concentrations are especially high in polders where shallow groundwater flow is enhanced by the
34 presence of tile drains in clay rich polders that needed this drainage system to prevent water tables rising into the root zone in



1 wet periods. Tile drain flow can bring the released SO_4 to the surface water. For urban polders with high SO_4 concentrations,
2 like the Zuiderzee margin region polders, sewer system leakage may be an additional source of SO_4 . Aging and faulty
3 connections of pipes may result in a leakage of water with high SO_4 and nutrient concentrations.

4 **4.2 Groundwater contribution to surface water composition**

5 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
6 surface waters (Delsman, 2015). Brackish groundwater especially seeps up into the polders of the Zuiderzee margin region
7 and into the Upconing area. The seepage of paleo-marine, brackish groundwater is driven by the low surface water levels
8 after the lake reclamation and the drainage via pumping stations. De Louw et al. (2010) reported that this groundwater
9 seepage predominantly takes place via concentrated boils through the clay and peat cover layer.

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

15 **4.3 Other sources of nutrients**

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

24 In the study area, the most intensively urbanized polders are mainly infiltrating and are more affected by inlet water
25 containing high Cl and HCO_3 concentrations than by groundwater. For deep urban polders, the situation is different. In these
26 polders, the influences of typical urbanization related water quality issues are masked by the large impact of brackish,
27 nutrient rich groundwater exfiltration. Although the paved area percentage in this paper was used as a variable representing
28 urban land cover influences, it seems not be the dominant landscape characteristic that governs the spatial patterns in polder
29 surface water quality. Urban water quality is determined by multiple factors, as was also concluded by several other studies
30 (Göbel et al., 2007; Vermonden et al., 2009). However, a better measurement method or classification of paved area
31 percentage may improve the explanatory power of this variable (Brabec et al., 2002).



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

7 **4.4 Uncertainties and perspectives**

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

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

22 In future studies, urban lowland catchments with and without seepage could be studied separately and more detailed land use
23 or paved area categories could be included. The drainage and/or leakage from sewage systems and the drainage via tube
24 drains should be taken into consideration. Drainage systems can provide a short-cut for solute transport towards surface
25 water (Rozemeijer and Broers, 2007), leading to higher solute concentrations in surface water. High groundwater levels may
26 induce groundwater discharge via the sewage or drainage systems (Ellis, 2005). In addition, studying the temporal variation
27 of surface water quality will give more insights into how the groundwater impact on surface water quality functions, as well
28 as on solutes transport and pathways in urban hydrological systems. A detailed monitoring network in several urban polder
29 catchments, which is anticipated as further work, could yield a more complete insight into water and contaminant flow routes
30 and their effects on surface water solute concentrations and loads.



1 **5 Conclusion**

2 In this paper, a clear groundwater impact on surface water quality was identified for the greater Amsterdam area. It was
3 concluded that this groundwater seepage significantly impacts surface water quality in the polder catchments by introducing
4 brackish, alkaline, and nutrient rich water. In general, nutrient concentrations in groundwater were much higher than in
5 surface water and often exceeded surface water Environmental Quality Standards (EQSs) (in 93 % of the polders with
6 available data for TP and in 91 % for TN) which indicates that groundwater is a large potential source of nutrients in surface
7 water. Our results strongly suggest that organic matter mineralization is a major source of nutrients in the subsurface of
8 coastal peat land areas. High correlations (R^2 up to 0.88) between solutes in groundwater and surface water confirmed the
9 effects of surface water-groundwater interaction on surface water quality. Especially in seepage polders, groundwater is a
10 major source of Cl, HCO_3 , Ca and the nutrients N and P, leading to general exceedances of EQS's for N and P in surface
11 waters. Redistribution of these high nutrient seepage waters in dry periods seems to lead to EQS exceedances in adjacent
12 boezem systems and in the receiving polders. Surface water quality in the Amsterdam urban area is also influenced by
13 groundwater seepage, but other anthropogenic sources, such as leaking and overflowing sewers might amplify the
14 eutrophication problems.

15 **Acknowledgements**

16 This work was funded through a CSC scholarship (No.201309110088) and supported by the Strategic Research Funding of
17 TNO and Deltares. We would like to thank the Waternet organization for making available their regional data on surface
18 water quality and appreciate the contributions by Jos Beemster, Jan Willem Voort and Jasper Stroom.

19 **References**

- 20 Appelo, C. A. J., Postma, D.: Geochemistry, groundwater and pollution, Second Edition, A.A. Balkema Publishers, Leiden, The
21 Netherlands, 2005.
- 22 Brabec, E., Schulte, S., Richards, P. L.: Impervious Surfaces and Water Quality: A Review of Current Literature and Its Implications for
23 Watershed Planning, Journal of Planning Literature, 16, 499-513, 2002.
- 24 Chapelle, F. H., Zelibor, J. L., Grimes, D. J., Knobel, L. L.: Bacteria in deep coastal plain sediments of Maryland: a possible source of CO_2
25 to groundwater. Water Resour Res, 23, 1625-1632, 1987.
- 26 De Louw, P. G. B., Oude Essink, G. H. P., Stuyfzand, P. J., van der Zee, S. E. A. T. M.: Upward groundwater flow in boils as the
27 dominant mechanism of salinization in deep polders, The Netherlands. J Hydrol, 394, 494-506, 2010.
- 28 Delsman, J. R.: Saline Groundwater - Surface Water Interaction in Coastal Lowlands. Ph. D. thesis, VU University Amsterdam,
29 Amsterdam, The Netherlands, 2015.



- 1 Delsman, J. R., Huang, K. R. M., Vos, P. C., De Louw, P. G. B., Oude Essink, G. H. P., Stuyfzand, P. J., Bierkens, M. F. P.: Paleo-
2 modeling of coastal saltwater intrusion during the Holocene: an application to the Netherlands, *Hydrol Earth Syst Sc*, 18, 10, 3891-
3 3905, 2014.
- 4 Dinoloket: <https://www.dinoloket.nl/>, last access: date October, 14, 2016.
- 5 Ellis, J. B., Marsalek, J., Chocat, B.: *Encyclopedia of Hydrological Sciences, Urban Water Quality*, 1st edition, M G Anderson, John Wiley
6 & Sons, Ltd, United States, 8, 97, 2005.
- 7 EU (2017) Commission Staff Working Document; the EU Environmental Implementation Review. Country Report – The Netherlands.
8 The EU Environmental Implementation Review: Common Challenges and how to combine efforts to deliver better results.
9 COM(2017) 63 final, http://ec.europa.eu/environment/eir/pdf/report_nl_en.pdf
- 10 Garrett, C. G., Vulava, V. M., Callahan, T. J., Jones, M. L.: Groundwater-surface water interactions in a lowland watershed: source
11 contribution to stream flow. *Hydrol Process*, 26, 3195-3206, 2012.
- 12 Göbel, P., Dierkes, C., Coldewey, W. G.: Storm water runoff concentration matrix for urban areas, *J Contam Hydrol*. 91, 26-42, 2007.
- 13 Grift, B. van der, Broers, H. P., Berendrecht, W., Rozemeijer, J. R., Osté, L., and Griffioen, J.: High-frequency monitoring reveals nutrient
14 sources and transport processes in an agriculture-dominated lowland water system, *Hydrol. Earth Syst. Sci.*, 20, 1851-1868,
15 doi:10.5194/hess-20-1851-2016, 2016.
- 16 Griffioen, J.: Uptake of phosphate by iron hydroxides during seepage in relation to development of groundwater composition in coastal
17 areas. *Environmental science & technology*, 28, 675-681, 1994.
- 18 Griffioen, J., Vermooten, S., Janssen, G.: Geochemical and palaeohydrological controls on the composition of shallow groundwater in the
19 Netherlands. *Appl geochem*, 39, 129 -149, 2013.
- 20 Heinis, F. and C. H. M. Evers: *Toelichting op ecologische doelen voor nutriënten in oppervlaktewateren*. STOWA-report (in Dutch),
21 Utrecht, The Netherlands, 2007.
- 22 Helsel, D. R. and Hirsch, R. M.: *Statistical Methods in Water Resources, Techniques of Water Resources Investigations*, 2nd edition, U. S.
23 Geological Survey, U. S. A, Book 4, chapter A3, 2002.
- 24 Hellmann, F. and Vermaat, J. E.: Impact of climate change on water management in Dutch peat polders. *Ecol Model*, 240, 74-83, 2012.
- 25 Holman, I. P., Whelan, M. J., Howden, N. J. K., Bellamy, P. H., Willby, N. J., Rivas-Casado, M., McConvey, P.: Phosphorus in
26 groundwater - an overlooked contributor to eutrophication, *HYDROL PROCESS*, 22, 5121-5127, 2008.
- 27 Huisman, P., Cramer, W., van Ee, G., Hooghart, J. C., Salz, H. Zuidema, F. C.: *Water in the Netherlands*. Netherlands Hydrological
28 Society, Rotterdam, the Netherlands, 1998.
- 29 Hijma, M. P.: *From river valley to estuary: the early-mid Holocene transgression of the Rhine-Meuse valley*, Ph. D. thesis, Utrecht
30 University, Utrecht, The Netherlands, 2009.
- 31 Meinikmann, K., Hupfer, M., Lewandowski, J.: Phosphorus in groundwater discharge - A potential source for lake eutrophication, *J*
32 *Hydrol*, 524, 214 - 226, 2015.
- 33 Morris, A. W. and Riley, J. P.: The bromide/chlorinity and sulphate/chlorinity ratio in sea water, *Deep Sea Research and Oceanographic*
34 *Abstracts*, [http://dx.doi.org/10.1016/0011-7471\(66\)90601-2](http://dx.doi.org/10.1016/0011-7471(66)90601-2), 13, 699-705, 1966.
- 35 Mourad, D. S. J. and van der Perk, M.: Spatio-temporal patterns of nutrient concentrations and export in a north-eastern European lowland
36 catchment. *Hydrol. Process*, 23: 1821- 1833, 2009.
- 37 Oude Essink, G. H. P., Houtman, H., Goes, B. J. M.: Chloride concentration at the bottom of the Holocene aquitard in the Netherlands (in
38 Dutch), Rep. NITG 05-056-A, 17 pp., TNO, Utrecht, Netherlands, 2005.



- 1 Oude Essink, G. H. P., Van Baaren, E. S., De Louw, P. G. B.: Effects of climate change on coastal groundwater systems: a modeling
2 study in the Netherlands, *Water Resour Res*, 46, 10, 2010.
- 3 Rozemeijer, J. C. and Broers, H. P.: The groundwater contribution to surface water contamination in a region with intensive agricultural
4 land use (Noord-Brabant, The Netherlands). *Environ Pollut*, 148, 695-706, 2007.
- 5 Rozemeijer, J. C., Van der Velde, Y., Van Geer, F. C., Bierkens, M. F. P., Broers, H. P.: Direct measurements of the tile drain and
6 groundwater flow route contributions to surface water contamination: From field-scale concentration patterns in groundwater to
7 catchment-scale surface water quality, *Environ Pollut*, 158, 3571-3579, 2010.
- 8 Rozemeijer, J. C., Klein, J., Broers, H. P., van Tol-Leenders, T. P., van der Grift, B.: Water quality status and trends in agriculture-
9 dominated headwaters; a national monitoring network for assessing the effectiveness of national and European manure legislation
10 in The Netherlands, *Environ Monit Assess*, 186, 8981-8995, 2014.
- 11 Schot, P. P. and Molenaar, A.: Regional changes in groundwater flow patterns and effects on groundwater composition, *J Hydrol*, 130,
12 151-170, 1992 a.
- 13 Schot, P. P. and van der Wal, J.: Human impact on regional groundwater composition through intervention in natural flow patterns and
14 changes in landuse. *J Hydrol*, 134, 297-313, 1992 b.
- 15 Stuyfzand, P. J. and Stuurman, R. J.: Origin, distribution and chemical mass balances of non-anthropogenic, brackish and (hyper) saline
16 groundwaters in the Netherlands, 1st SWIM-SWICA Joint Saltwater Intrusion Conference, Cagliari-Chia Laguna, Italy, 2006.
- 17 Van Loon, A. H.: Unravelling hydrological mechanisms behind fen deterioration in order to design restoration strategies, Ph. D. thesis,
18 Utrecht University, Utrecht, The Netherlands, 2010.
- 19 Van Beek, C. L., Droogers, P., van Harveldt, H. A., van den Eertwegh, G. A. P. H., Velthof, G. L., Oenema, O.: Leaching of solutes
20 from an intensively managed peat soil to surface water, *Water Air Soil Poll*, 182, 291-301, 2007.
- 21 Van Wallenburg, C.: Kattekleigronden en potentiële kateklee in droogmakerijen in het Westen van Nederland. *Boor en Spade: verspreide*
22 *bijdragen tot de kennis van de bodem van Nederland*, 19, 116-133, 1975.
- 23 Vermaat, J. E., Hellmann, F.: Covariance in water- and nutrient budgets of Dutch peat polders: what governs nutrient retention?
24 *Biogeochemistry*, 99, 109-126, 2010.
- 25 Vermonden, K., Hermus, M. A. A., van Weperen, M., Leuven, R. S. E. W., van der Velde, G., Smolders, A. J. P., Roelofs, J. G. M.,
26 Hendriks, A. J.: Does upward seepage of River water and storm water runoff determine water quality of urban drainage system in
27 lowland areas? A case study for the Rhine-Meuse delta, *Hydrol. Process*, 23, 3110-3120, 2009.
- 28 Vos, P.: Origin of the dutch coastal landscape: long-term landscape evolution of the Netherlands during the Holocene, described and
29 visualized in national, regional and local palaeogeographical map series, Ph. D. thesis, Utrecht University, Utrecht, The
30 Netherlands, 2015.
- 31 Wade, A. J., Palmer-Felgate, E. J., Halliday, S. J., Skeffington, R. A., Loewenthal, M., Jarvie, H. P., Bowes, M. J., Greenway, G. M.,
32 Haswell, S. J., Bell, I. M., Joly, E., Fallatah, A., Neal, C., Williams, R. J., Gozzard, E., Newman, J. R.: Hydrochemical processes in
33 lowland rivers: insights from in situ, high-resolution monitoring, *Hydrol Earth Syst Sc*, 16, 4323-4342, 2012.
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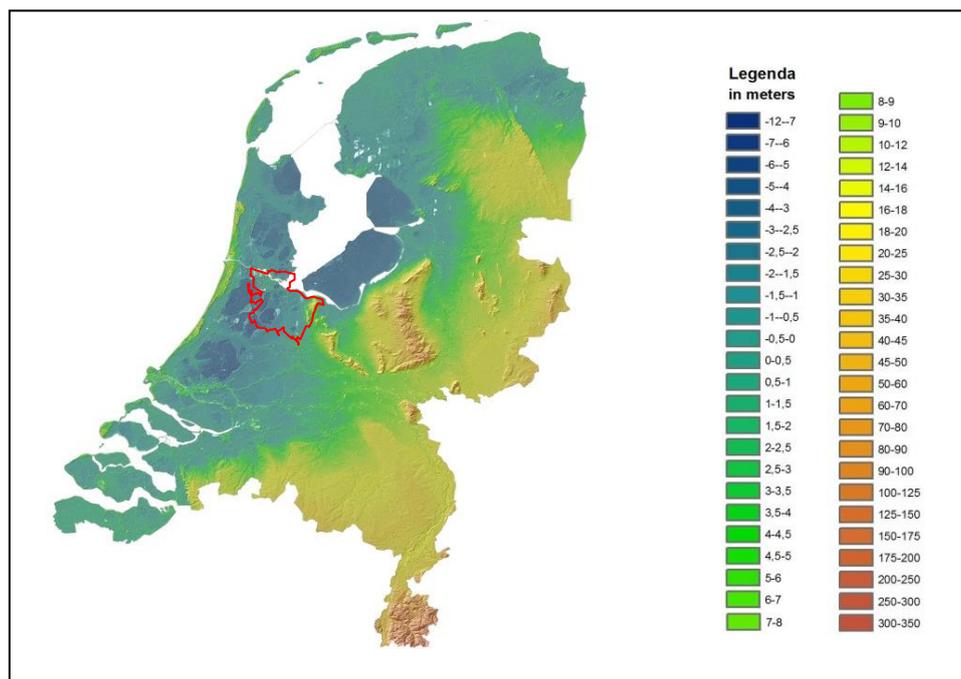


Figure 1: Location of the research area (red) projected on the elevation map of The Netherlands (elevations in meters above mean sea level (MSL))

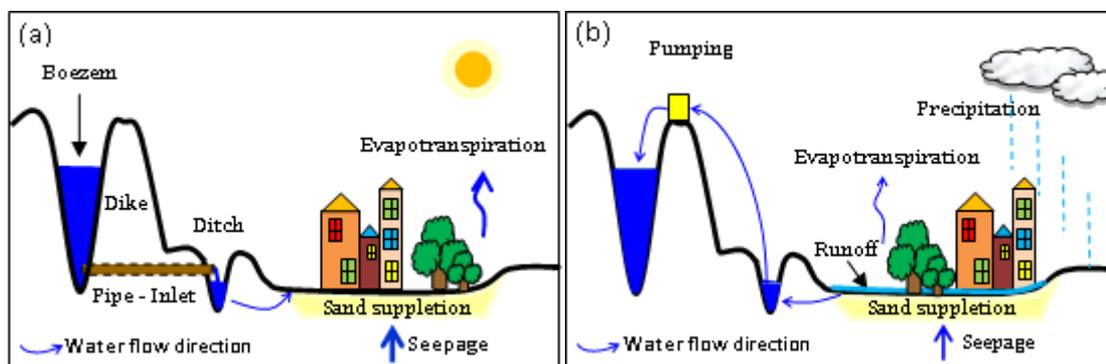
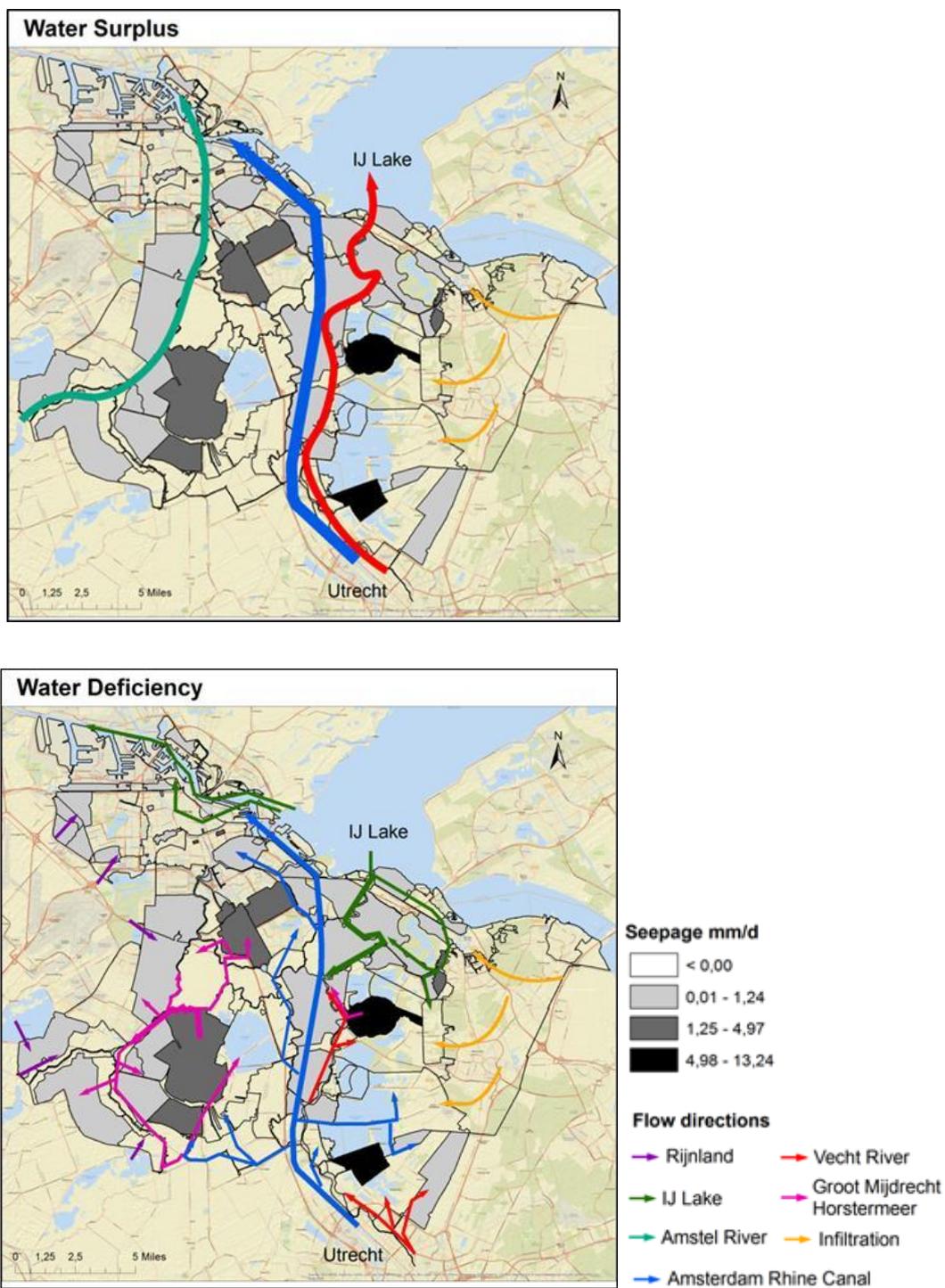


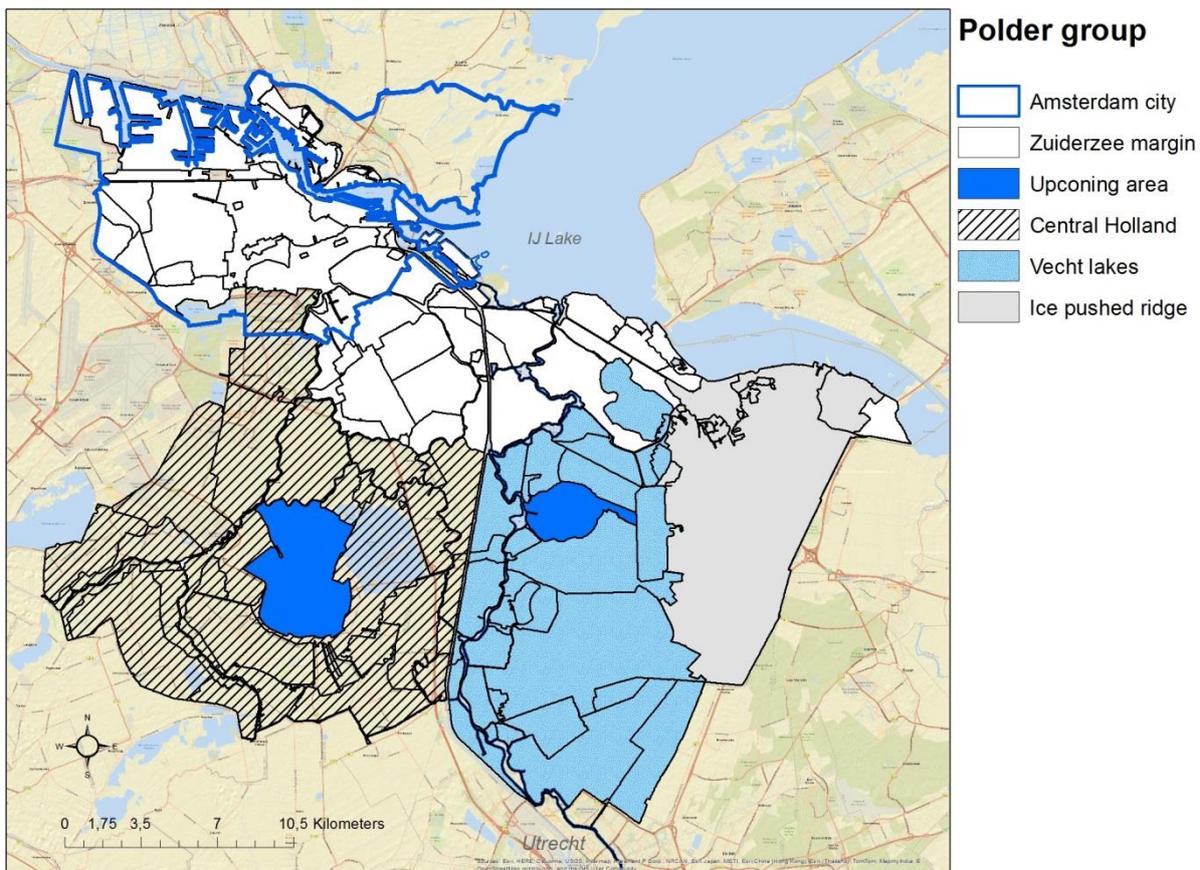
Figure 2: Conceptual model of water fluxes in a polder system in times of water deficiency (a) and surplus (b).



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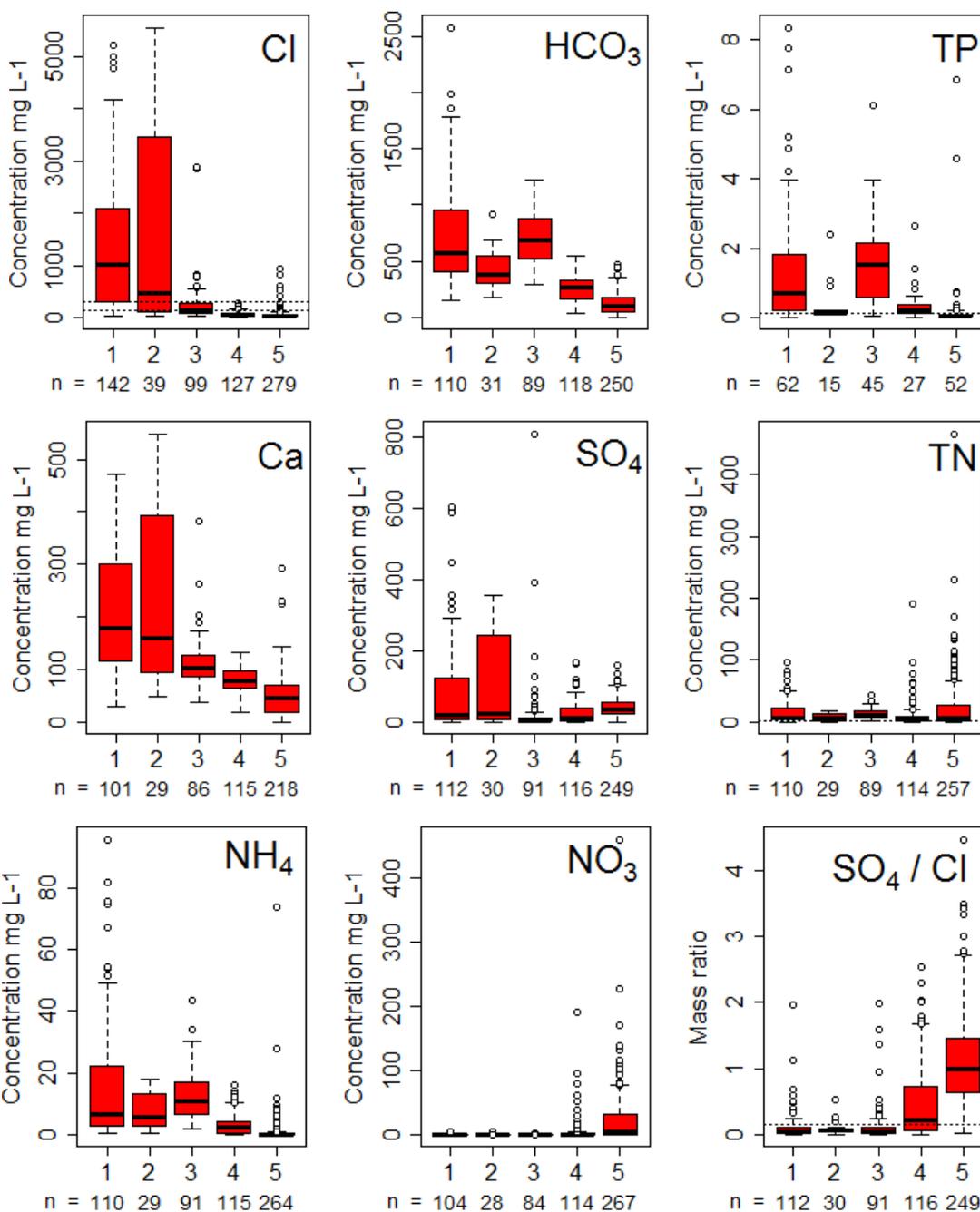


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Figure 4: Regions of the study area: (1) Zuiderzee margin, (2) Upconing area (deep brackish seepage polders Groot Mijdrecht and Horstermeer), (3) Central Holland, (4) Vecht lakes and (5) Ice pushed ridge. The Amsterdam city area is circled by the blue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



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5 **Figure 5: Spatial variation of groundwater quality. 1-Zuiderzee margin, 2-Upconing area (Groot Mijdrecht and Horstermeer), 3-**
 6 **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**
 7 **distribution of solutes in the five regions. The two horizontal dashed lines for Cl indicate fresh water (<150 mg L⁻¹) and brackish**
 8 **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**
 9 **SO₄/Cl plot indicates the mass ratio of 0.14 in seawater (<0.14 indicates sulfate reduction; >0.14 indicates additional sources of**
 10 **sulfate besides (diluted) seawater)**

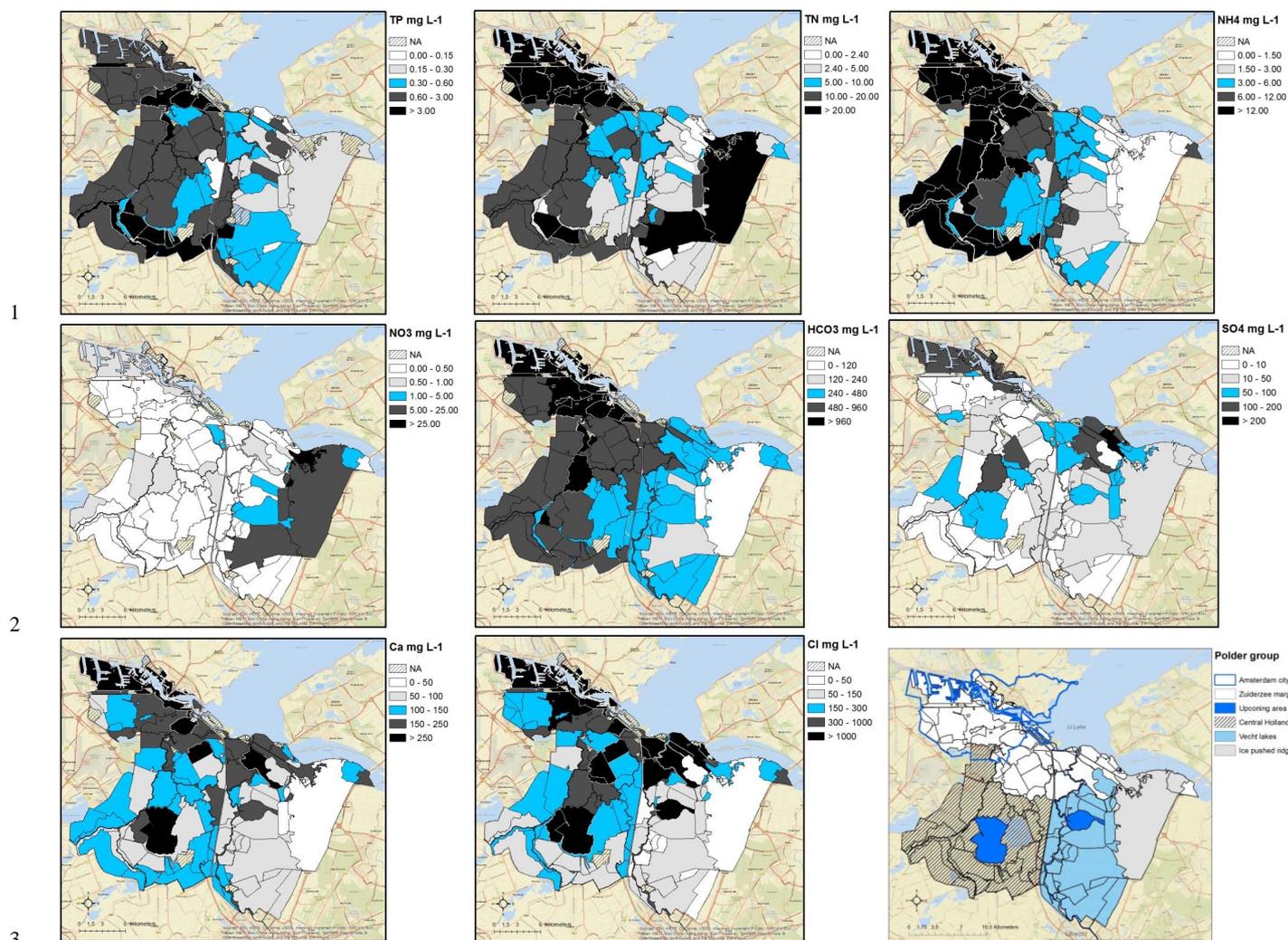
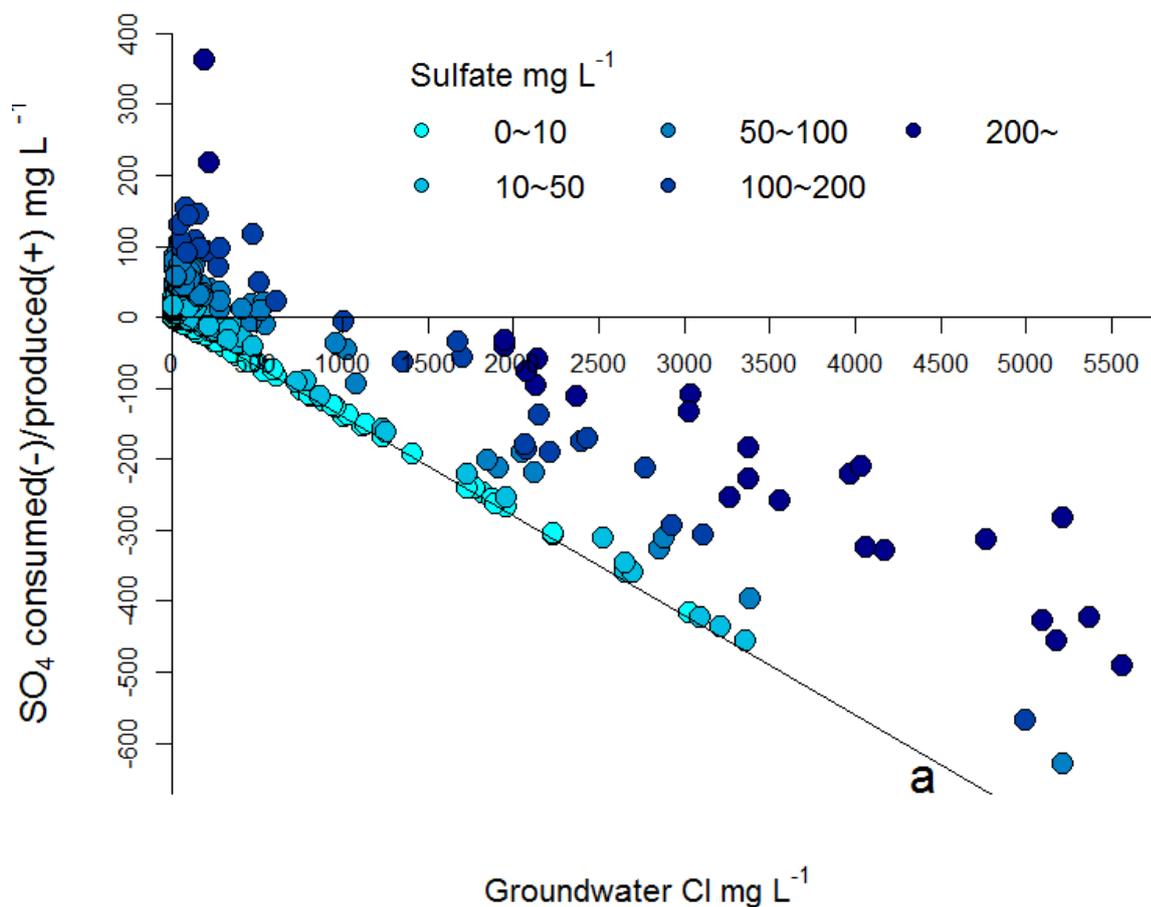


Figure 6: Average groundwater concentrations (mg L⁻¹) per polder.

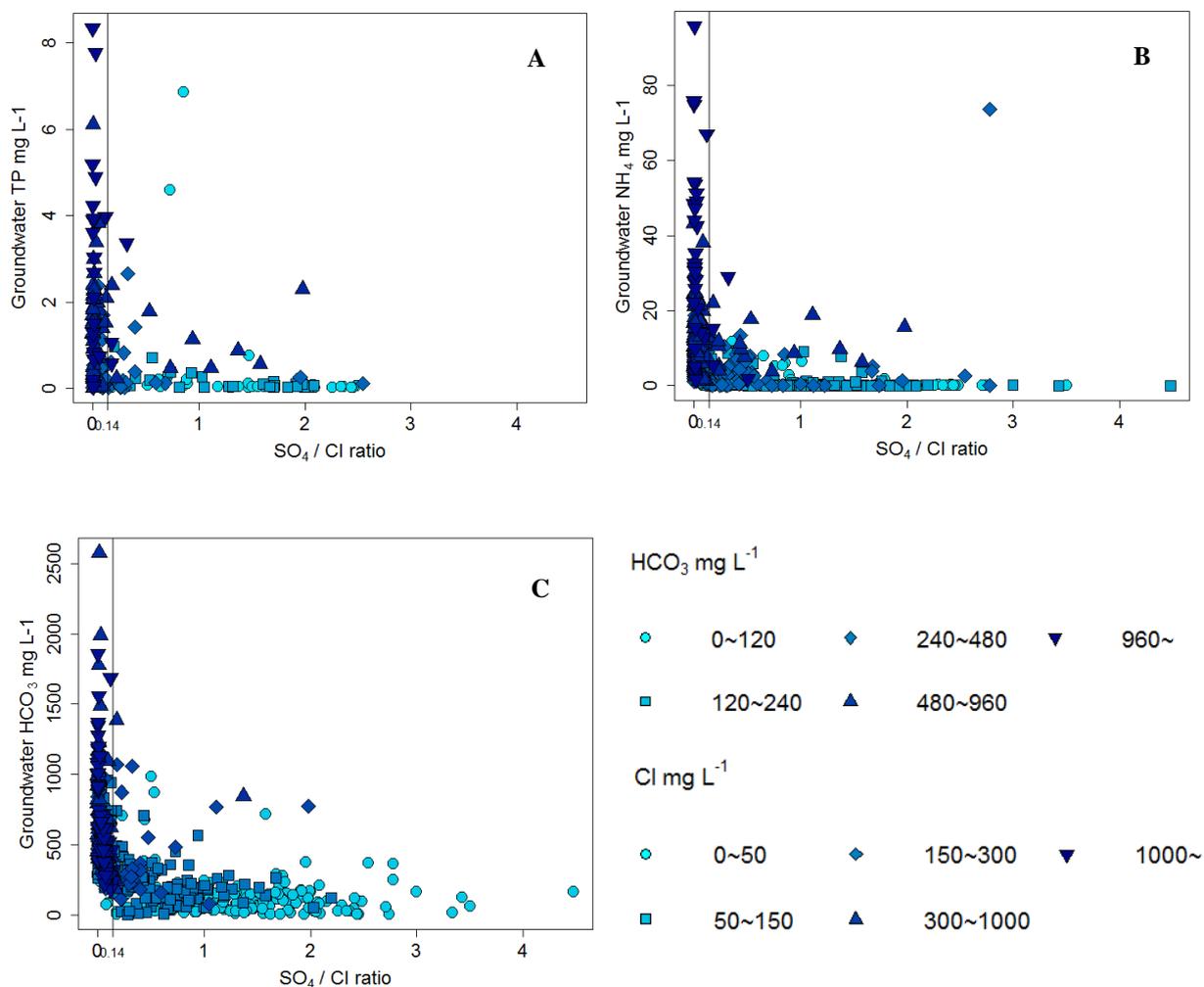


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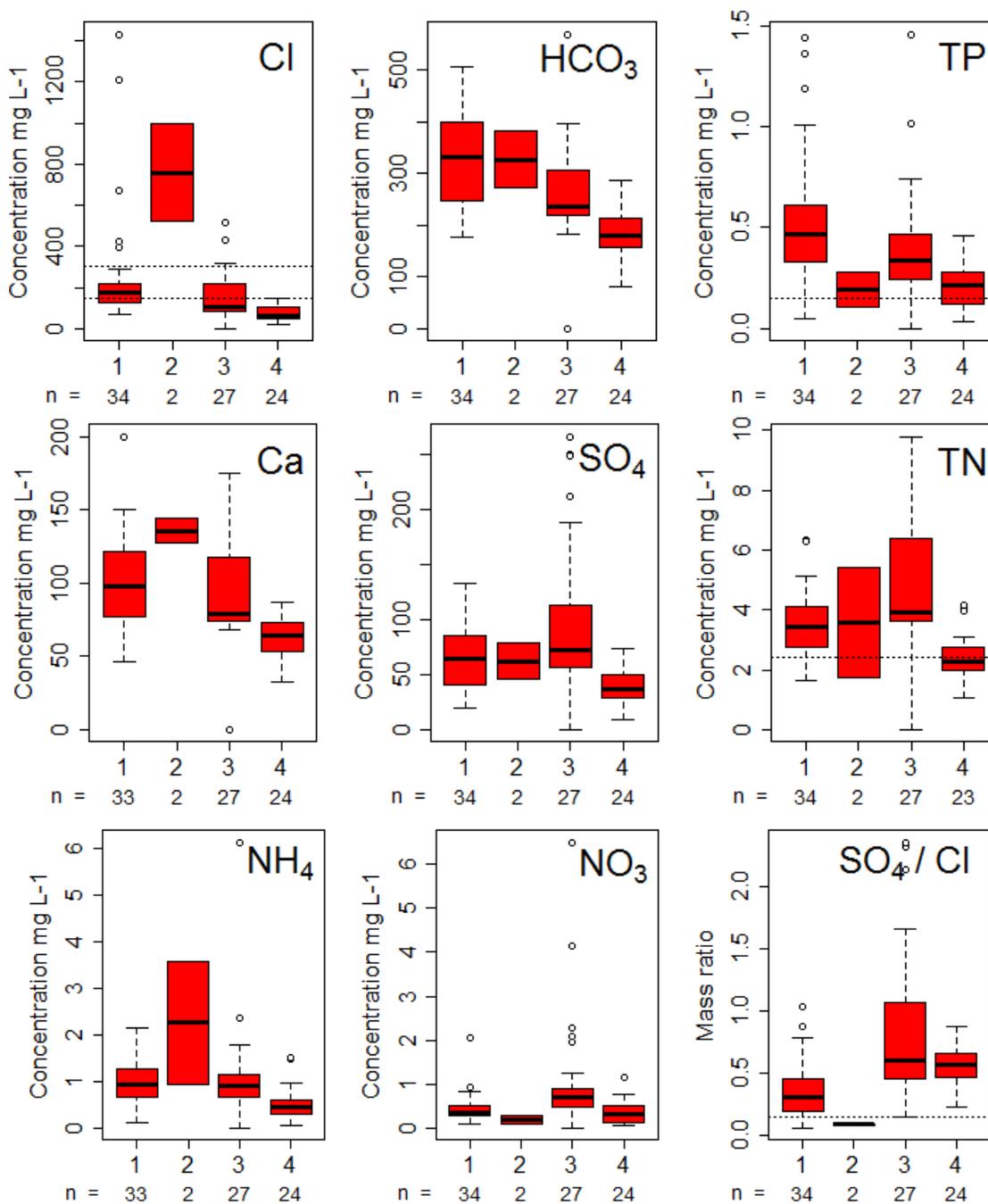
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Figure 7: Calculated concentration of sulfate reacted versus groundwater chloride concentration. The black line indicates the fresh water – seawater mixing line where sulfate-reduction is complete.



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 2 **Figure 8: Groundwater nutrient (TP and NH₄) concentrations with sulfate reduction (mass ratio SO₄/Cl, samples with value below**
 3 **0.14 are considered to be affected by sulfate reduction and above 0.14 indicates sulfate production by natural or artificial**
 4 **processes). The symbols in (A) and (B) are colored by HCO₃ concentration and in (C) by Cl concentration.**

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4 **Figure 9: Spatial variation of surface water quality. 1-Zuiderzee margin, 2-Upcoming area, 3-Central Holland, 4-Vecht lakes (5-Ice**
 5 **pushed ridge not shown due to insufficient data). n is the observation number of each group. The two horizontal dashed lines for**
 6 **Cl indicate fresh water (<150 mg L⁻¹) and brackish water (>300 mg L⁻¹), respectively. Dashed lines in TP and TN represent EQSs**
 7 **for TN (2.4 mg L⁻¹) and TP (0.15 mg L⁻¹). The dashed line in the SO₄/Cl plot indicates the mass ratio of 0.14 in seawater (<0.14**
 8 **indicates sulfate reduction; >0.14 indicates additional sources of sulfate besides (diluted) seawater).**

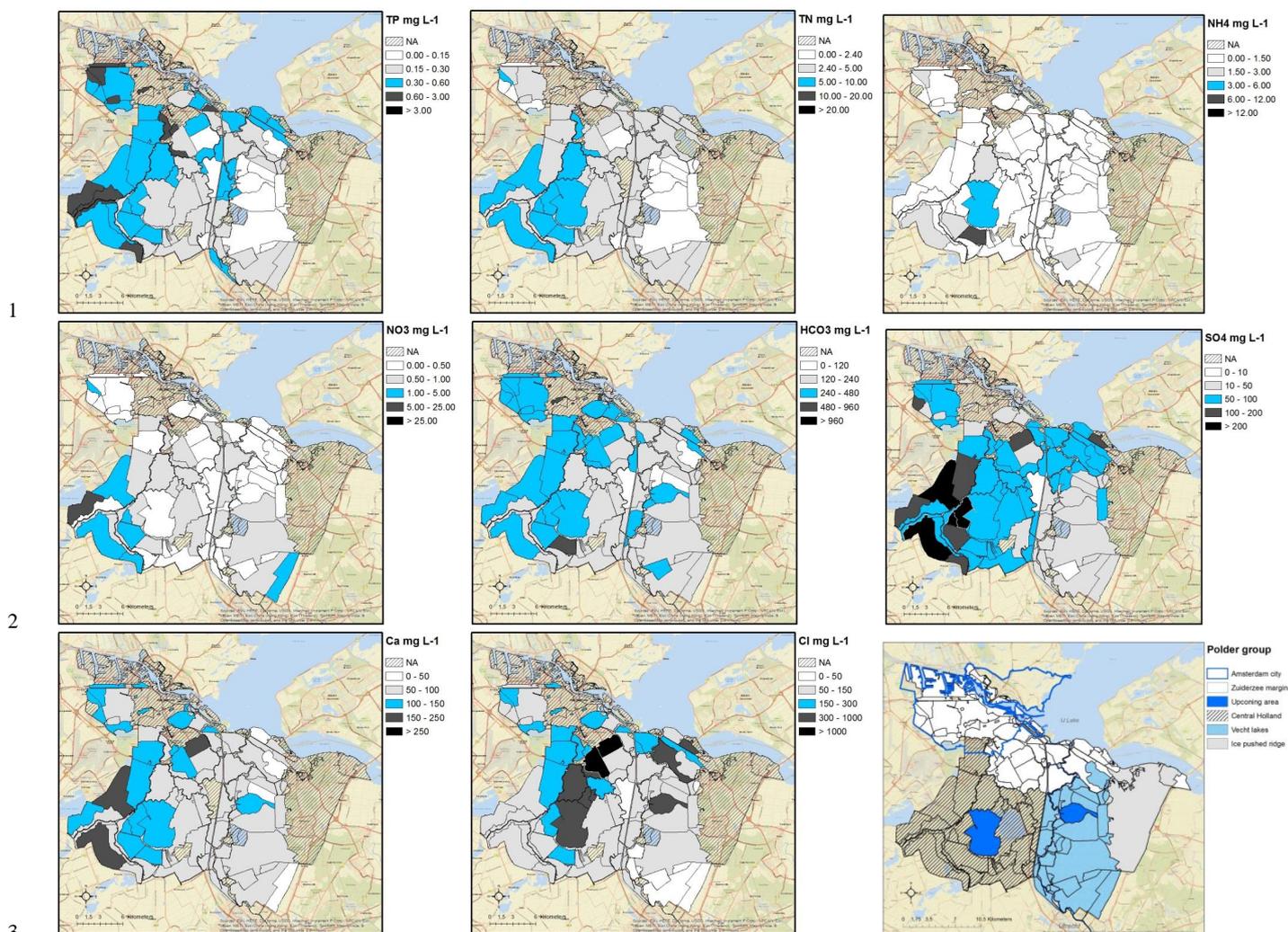


Figure 10: Discharge-normalized average concentrations (mg L⁻¹) per polder

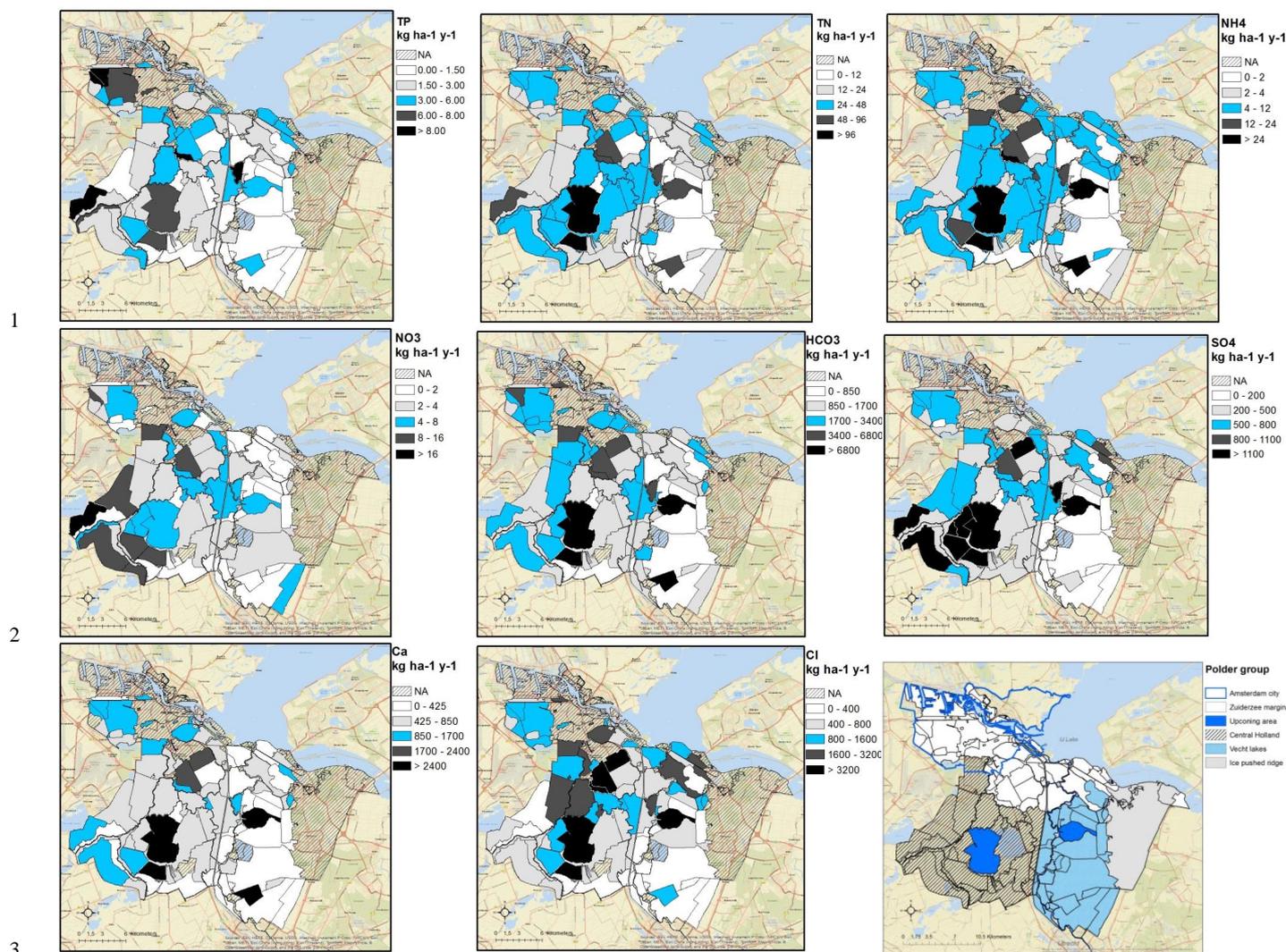
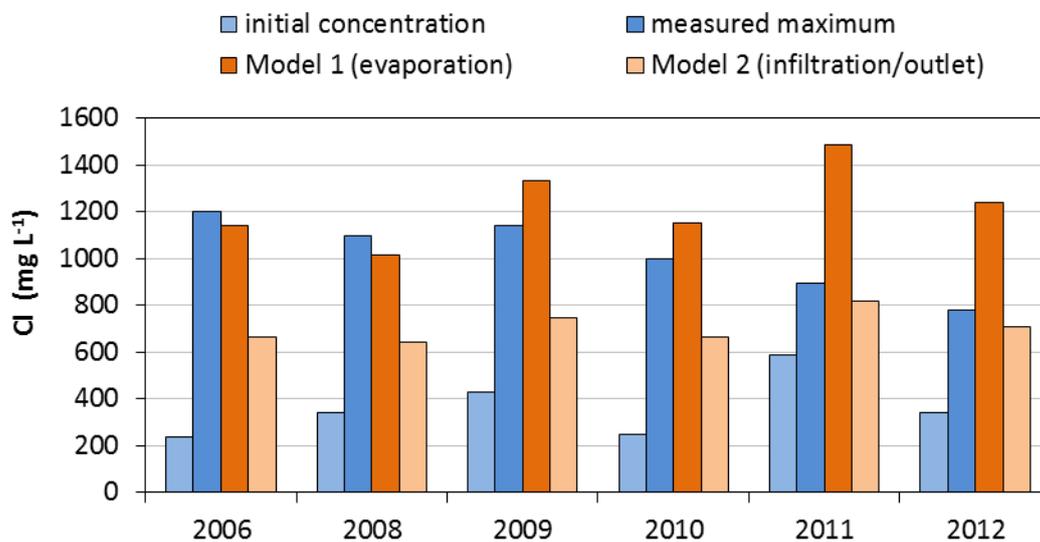


Figure 11: Surface water solute loads (average of 2010 to 2013) distribution maps in $\text{kg ha}^{-1}\text{y}^{-1}$



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10 **Figure 12: Summary of the water and chloride balance for polder Botshol; the graph shows (1) the initial Cl before the water inlet**
11 **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**
12 **(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}																
TN _{GW}	0.65															
NH ₄ _{GW}	0.77	0.84														
NO ₃ _{GW}																
HCO ₃ _{GW}	0.68	0.63	0.82													
SO ₄ _{GW}	-0.46			0.41												
Ca _{GW}					0.50											
Cl _{GW}					0.48	0.40	0.77									
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 %																
TP _{SW}	0.49	0.51	0.60		0.64											
TN _{SW}	0.45		0.44		0.52				0.58							
NH ₄ _{SW}			0.44		0.51				0.49	0.77						
NO ₃ _{SW}										0.57						
HCO ₃ _{SW}	0.57	0.55	0.64		0.68			0.41	0.62	0.47	0.67					
SO ₄ _{SW}										0.57		0.50				
Ca _{SW}	0.59	0.54	0.63		0.71			0.41	0.55	0.57	0.64		0.88			
Cl _{SW}					0.47		0.47	0.69	0.47	0.51			0.52	0.49	0.55	

* Only 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	n_4	R^2	R^2 with only seeping polders	
TP _{SW}	+ HCO ₃ GW	+ TP _{GW}	- Elevation	-SO ₄ GW/Cl _{GW}	0.42	0.51	(9)
TN _{SW}	+ HCO ₃ GW	- Elevation	+ P _{Humus}	-SO ₄ GW/Cl _{GW}	0.54	0.50	(10)
NH ₄ SW	+ HCO ₃ GW	+ NH ₄ GW	- Elevation	-SO ₄ GW/Cl _{GW}	0.41	0.58	(11)
NO ₃ SW	- Elevation	- Cl _{GW}	-SO ₄ GW		0.18	0.23	(12)
HCO ₃ SW	+ HCO ₃ GW	+ Seepage			0.53	0.62	(13)
SO ₄ SW	- Elevation				0.21	0.20	(14)
Ca _{SW}	+ HCO ₃ GW	- Elevation			0.59	0.59	(15)
Cl _{SW}	+ HCO ₃ GW	+ Cl _{GW}	- Elevation		0.54	0.54	(16)

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

n_1 : first variable, the most significant variable

TP_{SW}: surface water TP concentration in mg L⁻¹

TP_{GW}: groundwater TP 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

Table 3 Main hydrogeochemical reactions in the study area

Process	Reactions	No
Organic matter decomposition	$\text{CH}_2\text{O N}_x\text{P}_y \rightarrow x\text{N} + y\text{P} + \text{HCO}_3^- + \text{other components}$	[2]
	$\text{CH}_2\text{O N}_x\text{P}_y + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + x\text{N} + y\text{P}$	[3]
	$5\text{CH}_2\text{O N}_x\text{P}_y + 4\text{NO}_3^- \rightarrow 2\text{N}_2 + \text{CO}_2 + 4\text{HCO}_3^- + 3\text{H}_2\text{O} + 5x\text{N} + 5y\text{P}$	[4]
	$2\text{CH}_2\text{O N}_x\text{P}_y + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- + 2x\text{N} + 2y\text{P}$	[5]
Pyrite oxidation	$2\text{CH}_2\text{O N}_x\text{P}_y \rightarrow \text{CH}_4 + \text{CO}_2 + 2x\text{N} + 2y\text{P}$	[6]
	$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$	[7]
	$5\text{FeS}_2 + 14\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{Fe}^{2+} + 10\text{SO}_4^{2-} + 7\text{N}_2 + 2\text{H}_2\text{O}$	[8]
Calcite dissolution	Closed system $\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$	[9]
	Open system $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$	[10]