

We thank the reviewer for his/her review of our paper which helped to improve the manuscript. We thoroughly worked on the comment, and the responses are given below.

### **General comments**

*The paper by YU et al. presents analysis of water quality conditions and nutrient chemistry in polders found in the Amsterdam area. I found the analysis to be well done and I have no issues with it.*

*My main criticism of the paper is the lack of context for any readers outside of the Amsterdam area. The authors immediately jump into the specifics of the Amsterdam/Netherlands region and describe the area in great detail. Many times, the paper reads like a history of the region and monitoring activities conducted in the area. Those reading the paper from anywhere other than the Netherlands are left wondering why they should care about it. The authors need to spend some time introducing and discussing the larger issues relevant to the rest of the world. How are the issues and study methods and results used in the paper relevant to other locations and issues? This is a matter of doing some homework to see what has been done related to these systems or similar environments.*

*This is my only comment but it is not trivial. In my opinion, the authors need to provide some global relevance for this analysis before it can be accepted. The authors need to make a case for why anyone outside of the Netherlands area should care about this topic and their results.*

Agreed. We thank the reviewer for the compliments and we agree with the comment that we should elaborate more on the relevance of our study for other areas outside Amsterdam and The Netherlands. Although we mentioned in the abstract that “we expect that taking account of groundwater-surface water interaction is also important in other subsiding and urbanising deltas around the world, where water is managed intensively in order to enable agricultural productivity and achieve water sustainable cities.”, we agree that we did not make this very specific in the rest of the manuscript. We intend to add text on this issue in the revised paper. We will elaborate on the international relevance of the paper in the introduction, the discussion and the conclusions part of the paper.

In the introduction, we will add the following text after the first sentence:

Lowland deltas account for 2 % of the world’s land, but accommodated around 600 million people in 2000, and about 1400 million by 2060 as was estimated by Neumann et al. (2015)<sup>1</sup>. The reclamation of swamps and lakes and the drainage of peat areas to enable urbanisation and agriculture severely change the hydrological, chemical and ecological environment of these areas (Ellis et al., 2005; Yan et al., 2017)<sup>2,3</sup>. Lowland delta areas are vulnerable for water

---

<sup>1</sup> B. Neumann, A.T. Vafeidis, J. Zimmermann, R. J. Nicholls: Future Coastal Population Growth and Exposure to Sea-Level Rise and Coastal Flooding - A Global Assessment, Plos One, 10, 3, 2015. e0118571. doi:10.1371/journal.pone.0118571.

<sup>2</sup> J. B. Ellis, J. Marsalek, B. Chocat: Encyclopedia of Hydrological Sciences, Urban Water Quality, 1<sup>st</sup> edition, M G Anderson, John Wiley & Sons, Ltd, United States, 8, 97, 2005.

quality deterioration by processes like salinization and eutrophication, which can be amplified by climate change (Wu et al., 2015)<sup>4</sup> and land subsidence (Minderhoud et al., 2017)<sup>5</sup>.

In the discussion section, our study indicates that groundwater seepage can be a significant and even dominating source of nutrients in lowland areas where water is pumped out of polder systems that without pumping would turn into fresh water lakes. Our study shows that the groundwater seepage leads eutrophication and that redistributing water out of some deep elevation polders with upconing brackish water had further spread the nutrients to the whole water system. We will add the following paragraphs:

*Section 4.2 Similar patterns are expected to be present in other lowland areas, which are highly manipulated by human. 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)<sup>6</sup>, and the Sacramento-San Joaquin delta (Drexler et al., 2009)<sup>7</sup>. 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)<sup>8</sup>.*

*Section 4.3 line 20-21: However, the results indicates that reducing the amounts of manure and fertilizer and the associated N and P inputs in agriculture might not contribute enough in reducing N and P concentrations and fluxes for environmental purposes, as the N and P concentrations in the surface water are dominantly caused by seepage of groundwater. This certainly holds for urban areas where these inputs are absent (see new Figure Supplementary Info). 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*

---

<sup>3</sup> R. Yan, J. Huang, L. Li, J. Gao: Hydrology and phosphorus transport simulation in a lowland polder by a coupled modeling system, *Environ Pollut*, 227, 613-625, 2017.

<sup>4</sup> J. Wu, M. E. Malmstrom: Nutrient loadings from urban catchments under climate change scenarios: Case studies in Stockholm, Sweden, *Sci Total Environ*, 518-519, 393-406, 2015.

<sup>5</sup> P. S. J. Minderhoud, G. Erkens, V. H. Pham, V. T. Bui, L. Erban, H. Kooi, E. Stouthamer: Impacts of 25 years of groundwater extraction on subsidence in the Mekong delta, Vietnam, *Environ Res Lett.*, 12, 2017.

<sup>6</sup> T. E. Törnqvist, D. J. Wallace, J. E. A. Storms, J. Wallinga, R. L. Van Dam, M. Blaauw, M. S. Derksen, C. J. W. Klerks, C. Meijneken, E. M. A. Snijders: Mississippi Delta subsidence primarily caused by compaction of Holocene strata. *Nat Geosci*, 1, 3, 173-176, 2008.

<sup>7</sup> J. Z. Drexler, C. S. De Fontaine, S. J. Deverel: The legacy of wetland drainage on the remaining peat in the Sacramento San Joaquin Delta, California, USA, *Wetlands*, 29,1, 372-386, 2009.

<sup>8</sup> B. Kronvang, J. Køgestrand, J. Windolf, N. Ovesen, L. Troldborg: Background phosphorus concentrations in Danish groundwater and surface water bodies, EGU General Assembly 2013, 7-12 April, 2013, Vienna, Austria, id. EGU2013-2249.

*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.*

In the conclusion, we will add the following sentences:

*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. The discharge and redistribution of nutrient rich water from reclaimed lakes and swamps enhances eutrophication in downstream water resources and is hard to mitigate.*

We thank the reviewer for his/her review of our paper which helped to improve the manuscript. We thoroughly worked on the comments, and the responses are given below.

### **General comments**

*In the present work, the authors attempt to characterize the impacts of groundwater seepage on the polder network around Amsterdam by exploiting data from the dense network of groundwater and surface water monitoring in this area. The authors combine water quality monitoring data with other biophysical characteristics of 144 polders and take a statistical approach to bettering our understanding of sources, transport mechanisms, and pathways in this area. They conclude that groundwater is a major source of nutrients in this mixed urban/agricultural catchment. In particular, they note that elevated nutrient and bicarbonate concentrations in the groundwater seepage originate from decomposition of organic matter in subsurface sediments coupled to sulfate reduction and possibly methanogenesis. Their results suggest that groundwater-surface water interactions are important to nutrient dynamics in urbanizing delta regions.*

*The current work is important, as it attempts to tease out the relative importance of natural and anthropogenic sources of nutrients within the region and to elucidate why implementation of nutrient management practices may not effectively reduce surface water concentrations to target levels, particularly in urban areas. The approach used in the paper, which combines correlation analysis between surface water and groundwater quality, as well as statistical analysis of relationships between landscape characteristics provides an interesting perspective on the drivers of various solute concentrations in surface water.*

We acknowledge the reviewer for his thorough review and the positive words about our manuscript.

*The study does, however, leave some questions unanswered. First, in the abstract it is claimed that “land use” is used as a variable in the multiple linear regression, which attempts to identify the strongest drivers of surface water nutrient concentrations. In the analysis, however, the only land-use variable that I see is “paved area.” As the authors mention more than once that agriculture in the polder catchments could be driving surface water nutrient concentrations (and I would agree), I find it puzzling that this is not used as a potential variable for the regression analysis.*

Agreed. The reviewer is correct that we did not explicitly use agricultural land use and inputs in our analysis. Implicitly, there is land use in the analysis already, because both the soil types and elevation variables distinguish between dairy farming (shallow water level peat polders with somewhat higher elevation) and arable farming (deeper clay polders with deeper ditches). The higher N and P loads in low elevation polders may be partly caused by more intensive arable land use. Evaluating this major comment of the reviewer, we acknowledge that paved area percentage, elevation and soil types are very poor measures of agricultural practices, and we therefore now included the application rates of manure and fertilizer in the analysis which are relatively well known in The Netherlands because of

the advanced bookkeeping system of farmers and the central registration. In the revised paper, we will describe the newly introduced data (N and P inputs in kg/ha/y), compare the N and P inputs with surface water annual loads, show the spatial distribution of N and P inputs in maps in the Supplementary Info, which allows the reader to visually compare the nutrient inputs spatial pattern with the pattern of surface water loads.

The newly introduced data include the annual animal manure and fertilizer inputs of N and P. These new data have been retrieved from the central farmer bookkeeping data for nutrient fate and transport model calculations using INITIATOR (Wolf et al. 2003)<sup>1</sup>. The N and P input data are valid for the year 2011, which corresponds with most of our surface water data.

The determination coefficients ( $R^2$ ) of the new statistical analysis including the 2 new land use variables are shown in the table below (Table 1). All determination coefficients for the newly included variables are remain below the threshold of 0.40 (Table 1), but a slight negative correlation was found between the N inputs in kg/ha/y and the normalized concentrations of HCO<sub>3</sub> in surface water and the total N concentrations of groundwater (range -0.30 ~ -0.33).

This analysis confirms our initial assumption that the inputs of N and P from agriculture are not the major factors determining the N and P concentrations in surface water and groundwater in this area. The additional analysis strongly confirms our earlier findings and will help us to even better describe the large influence of groundwater seepage, the related subsurface geochemical processes that define them and the subsequent redistribution of water through these polder systems on surface water chemistry and nutrient concentrations. This is interesting to other readers, as the lowlands in the western Netherlands around Amsterdam are still part of one of the most intensive agricultural regions worldwide, and unraveling nutrient problems in this region can help to understand other lowland regions better. Naturally, we will include this analysis in the final revised paper and thank the reviewer for his/her comment that we think really helped to emphasize our conclusions and certainly will improve the manuscript.

Using the newly introduced variables, we updated Table 1 of the original paper. We intend to add 2 extra maps to the Supplementary Info of the paper (see below), showing the distribution of the N and P inputs over the greater Amsterdam regions, which enable the visual comparison of the N and P patterns in groundwater and surface water, with the inputs from agriculture. The visual comparison confirms the statistical conclusions that N and P input patterns don't match the N and P concentrations and load maps. Especially in the urban areas of the city of Amsterdam, high concentrations of N and P appear in groundwater and surface water whereas the agricultural inputs in those areas are minimal. These results will be discussed in the discussion part of the paper.

---

<sup>1</sup> J. Wolf, A.H.W. Beusen, P. Groenendijk, T. Kroon, R. Rotter, H. van Zeijts: The integrated modeling system STONE for calculating nutrient emissions from agriculture in the Netherlands, *Environ Modell & Softw*, 18: 597–617, 2003.

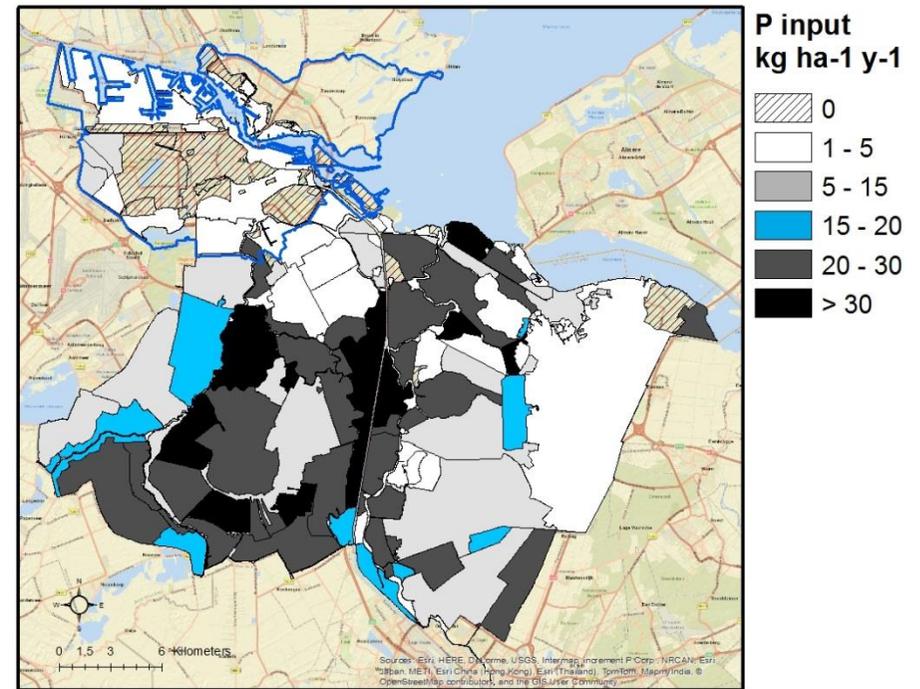
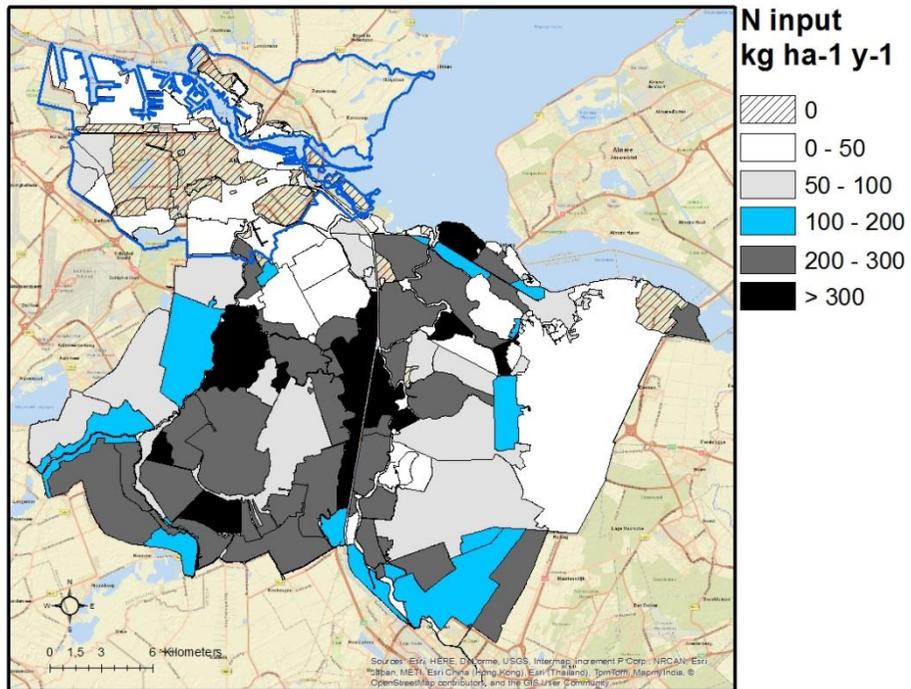
Revised Table 1 Coefficients of determination between groundwater quality and surface water quality

	TP GW	TN GW	NH <sub>4</sub> GW	NO <sub>3</sub> GW	HCO <sub>3</sub> GW	SO <sub>4</sub> GW	Ca GW	Cl GW	TP SW	TN SW	NH <sub>4</sub> SW	NO <sub>3</sub> SW	HCO <sub>3</sub> SW	SO <sub>4</sub> SW	Ca SW	Cl SW
TP <sub>GW</sub>	1															
TN <sub>GW</sub>	0,65	1														
NH <sub>4</sub> <sub>GW</sub>	0,77	0,84	1													
NO <sub>3</sub> <sub>GW</sub>				1												
HCO <sub>3</sub> <sub>GW</sub>	0,68	0,63	0,82		1											
SO <sub>4</sub> <sub>GW</sub>	-0,46			0,41		1										
Ca <sub>GW</sub>					0,50		1									
Cl <sub>GW</sub>					0,48	0,40	0,77	1								
TP <sub>SW</sub>	0,49	0,51	0,60		0,64				1							
TN <sub>SW</sub>	0,45		0,44		0,52				0,58	1						
NH <sub>4</sub> <sub>SW</sub>			0,44		0,51				0,49	0,77	1					
NO <sub>3</sub> <sub>SW</sub>										0,57		1				
HCO <sub>3</sub> <sub>SW</sub>	0,57	0,55	0,64		0,68			0,41	0,62	0,47	0,67		1			
SO <sub>4</sub> <sub>SW</sub>										0,57		0,50		1		
Ca <sub>SW</sub>	0,59	0,54	0,63		0,71			0,41	0,55	0,57	0,64		0,88		1	
Cl <sub>SW</sub>					0,47		0,47	0,69	0,47	0,51			0,52	0,49	0,55	1
N input kg ha <sup>-1</sup> y <sup>-1</sup>																
P input kg ha <sup>-1</sup> y <sup>-1</sup>																
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 coefficients higher than or equal to 0.40 were shown in the table

TP sw: surface water TP concentration in mg L<sup>-1</sup>

TP gw: groundwater TP concentration in mg L<sup>-1</sup>



Maps to be included in the Supplementary Info showing the spatial distribution of N and P inputs from agricultural land use.

*Second, the authors average groundwater data taken over a period of more than 100 years, but do not discuss how groundwater levels may have change over time, and how these trajectories may have differed from place to place, thus affecting use of the GW data in the spatial analysis.*

We agree with the reviewer that we should have discussed the use of groundwater quality data of such a long period of time. We will elaborate on that in the revised version of the paper. The underlying assumption in our analysis was that groundwater composition changes very slowly over time, and we wanted to use as much of the available groundwater data as possible to cover the entire region and all the polders studied with sufficient data to enable the statistical analysis. The large majority of the groundwater quality data we used is from the last 30 years (for example, 85% for chloride and 93% of P is sampled after 1980) and we do not expect that using the older data 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 smoothing effect on the water composition in this area. Moreover, the overall flow patterns haven't 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 dramatically 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)<sup>2</sup>, but the process is known to be very slow and to continue over the next 200 years. We will further elaborate this issue in the revised version of the paper.

*Finally, it is unclear how issues of collinearity impact the results of the correlation analysis and development of the multiple linear regression model. A more complete treatment and subsequent discussion of possible collinearity between independent variables would strengthen the analysis.*

We agree with the reviewer that the method of the regression analysis is not well enough described in the paper. The variables to be integrated into multiple linear regression models for predicting surface water solute concentrations were selected based on the correlation matrix (Table 1). 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, landscape characteristics and the newly introduced N and P inputs from agriculture. We adopted the method described by Rozemeijer et al. (Rozemeijer et al., 2010)<sup>3</sup>, who describe a form of

---

<sup>2</sup> G. H. P. Oude Essink, E. S. Van Baaren, P. G. B. De Louw: Effects of climate change on coastal groundwater systems: A modeling study in the Netherlands, *Water Resour Res*, 46, 10, 2010.

<sup>3</sup> J. C. Rozemeijer, Y. Van der Velde, F. Van Geer, G.H. de Rooij, P. J. J. F. Torfs, H. P. Broers: Improving load estimates of N and P in surface waters by characterizing the concentration response to rainfall events, *Environ Sci & Technol*, 44, 6305-6312, 2010.

sequential multiple regression analysis, where subsequently variables were added to the regression evaluating the accumulating effect on the resulting coefficient of determination  $R^2$ . The regression analysis started with a singular regression with the highest coefficient of determination ( $R^2$ ) for explaining the surface water quality parameter under consideration. Subsequently, we searched for the best regression model with two and three explaining variables, where we accepted an additional variable only when the coefficient of determination  $R^2$  increased by at least 3%. 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 different explaining power of the individual variables. Based on the reviewer's comments, however, we carefully scrutinized the regression results and including the two new explaining variables and found some regressions that led to improved  $R^2$  in our analysis. The resulting regression table is reported below and will be described and discussed in the paper. For two surface water variables, we found the N inputs for agricultural led to a small but significant improvement of the explaining power of the regression.

**Revised 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 <sub>SW</sub>	+ HCO <sub>3</sub> GW	+ NH <sub>4</sub> GW		0.43	0.49	(9)
TN <sub>SW</sub>	- Elevation	+ HCO <sub>3</sub> GW	+ N <sub>input</sub>	0.57	0.48	(10)
NH <sub>4</sub> SW	- Elevation	+ HCO <sub>3</sub> GW	+ Seepage	0.50	0.61	(11)
NO <sub>3</sub> SW	- Elevation	+ N <sub>input</sub>		0.18	0.23	(12)
HCO <sub>3</sub> SW	+ HCO <sub>3</sub> GW	+ Seepage	+ NH <sub>4</sub> GW	0.57	0.70	(13)
SO <sub>4</sub> SW	- Elevation	+ SO <sub>4</sub> GW		0.25	0.22	(14)
Ca <sub>SW</sub>	+ HCO <sub>3</sub> GW	- Elevation	+ Seepage	0.65	0.63	(15)
Cl <sub>SW</sub>	+ Cl <sub>GW</sub>	+ HCO <sub>3</sub> GW	+ P <sub>Humus</sub>	0.57	0.51	(16)

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

$n_1$ : first variable, the most significant variable

HCO<sub>3</sub>SW: surface water HCO<sub>3</sub> concentration in mg L<sup>-1</sup>

HCO<sub>3</sub>GW: groundwater HCO<sub>3</sub> concentration in mg L<sup>-1</sup>

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

Seepage: seepage rate in mm y<sup>-1</sup>

P<sub>Humus</sub>: percentage of humus in the soil profile sample

N<sub>input</sub>: manure and fertilizer N input in kg ha<sup>-1</sup>y<sup>-1</sup>

**Specific comments:**

*p. 6, ll. 8-12 You describe here the variables used in your analysis, but do not include any landuse variable other than "paved area." Clearly, agricultural area is a major factor driving concentrations in your study area, so it seems a large omission to not include it in your analysis. Is it simply that the agricultural area was not included in the database that you utilized? If so, could you obtain that information through other sources of land-use data? It is possible that including agricultural area in your analysis would significantly change the findings of your analysis regarding significant drivers of surface water concentrations.*

Agreed and changed accordingly, see response 1 above.

*p. 6, ll. 14-18 In your methods, you mention that for each well, you average concentrations for each monitoring well (at individual monitoring screens) for all sampling dates. You also mention that the groundwater data is from the period 1910-2013 more than 100 years. I would assume that there could have been significant changes in groundwater quality over that period, and that the temporal patterns of change could have differed across the study period. Accordingly, is it correct to combine all sampling data across this 100-year period, or in doing so are you conflating spatial and temporal differences across the study area?*

Agreed and changed accordingly, see response 2 above.

*p. 8, ll. 20-30 You do not discuss here how you dealt with issues of collinearity among the explanatory variables. For example, there are clearly high correlations ( $r > 0.60$ ) among some of the groundwater solute concentrations (particularly with regard to  $\text{HCO}_3$ ). With this being the case, how do you (from a quantitative perspective) make decisions regarding inclusion in the multiple linear regression model? For example, in your MLR equation for TP, you include both  $\text{HCO}_3(\text{GW})$  and  $\text{TP}(\text{GW})$ , although your correlation table in Table 1 shows a reasonably high collinearity ( $r = 0.68$ ) between these two variables. How do you justify use of both of them in the MLR equation?*

Agreed and changed accordingly, see response 3 above.

*p. 12, ll. 22-23 You say here that ammoniums correlates more strongly with TN than nitrate and conclude that ammonium is therefore likely the main form of TN in the*

study area. When I look at Fig. 5, however, it appears that nitrate is likely the dominant form of N in the ice-pushed ridge area (5) and possibly the Vecht Lakes area (4). It might be more useful to discuss the actual variations among locations (and reasons why), rather than just to cite the simple regression results.

We agree that information should be added about the spatial differences in TN partitioning. We've changed the text of line 22-23 into:

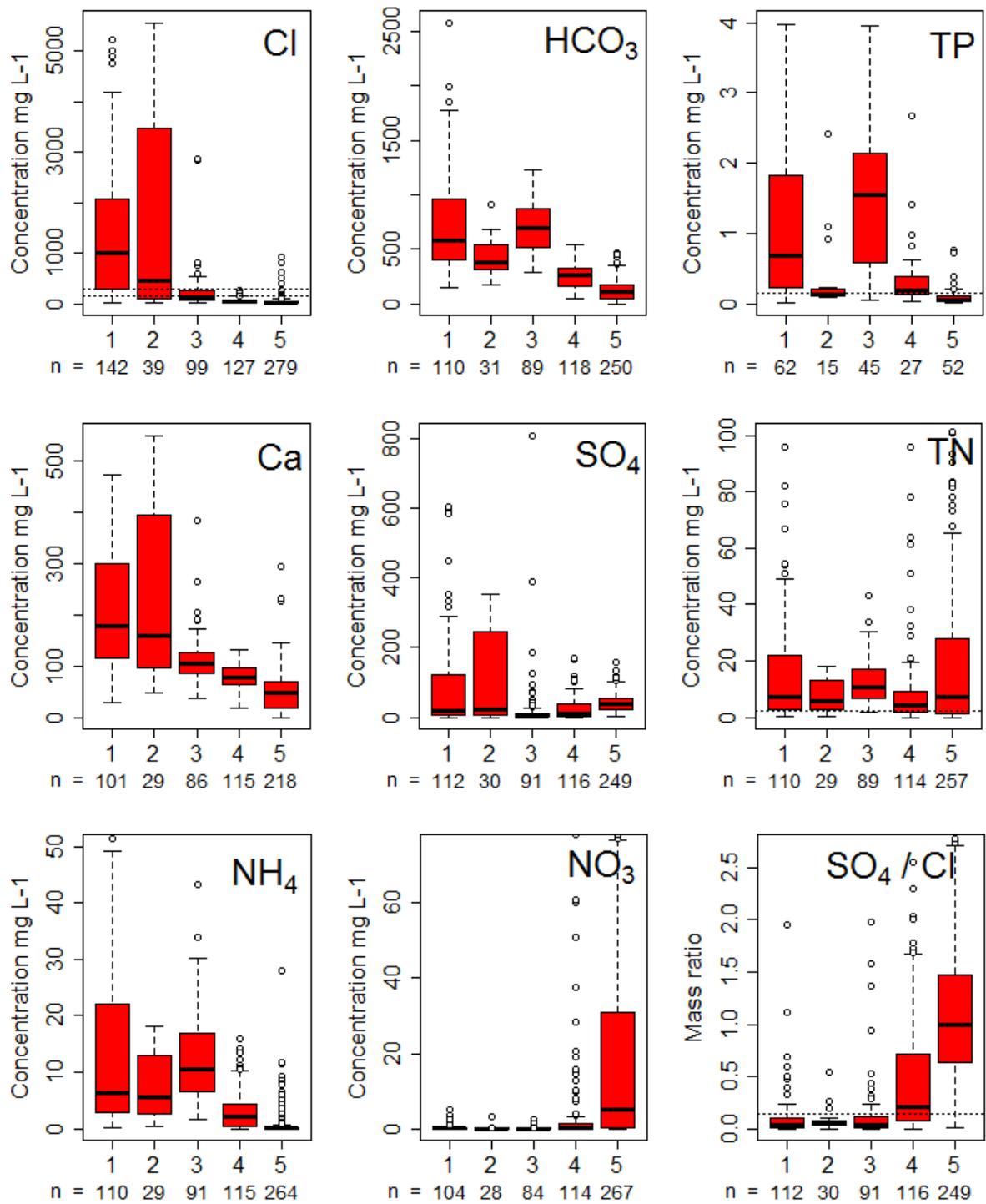
"Surface water TN correlated more closely to  $\text{NH}_4$  (0.77) than to  $\text{NO}_3$  (0.57). This reflects that  $\text{NH}_4$  is the dominant form of TN in the study area as a whole. This is especially true for the upconing area and the Central Holland area (see also Figure 9). The  $\text{NO}_3$  and  $\text{NH}_4$  contributions to TN are about equal in the Vecht lakes area. For the Ice pushed ridge area, we expect a dominance of  $\text{NO}_3$  in surface water (not shown in Figure 9 due to insufficient data) as was the case in the groundwater of that area, however there is only a limited amount of surface water that is draining the ice pushed ridge directly."

*p. 13, ll. 8-21 You discuss the results of the MLR analysis here, but do not reference the table that contains the results. Please include the table reference here.*

Agreed and changed accordingly.

*Fig. 5 It is very difficult to understand the variations in concentrations of solutes among locations in these figures due to the different concentration ranges from site to site. For example, for TN, all of the concentration ranges look very similar, simply because you scale the y-axis to include all of the outlier values for site #5. Is it important to include all of the outliers? I would recommend plotting these in such a way that you allow the reader to understand differences in median and interquartile range values, rather than prioritizing the representation of outliers.*

Agreed and changed accordingly as below.



*Table 1 For your correlation analysis, you should include the 1.0 values to show perfect correlation between two identical variables. This will help add structure to the table and make it easier to understand.*

Agreed and changed accordingly.

## Complete list of changes to the manuscript through pages

p. 1 line 5: change *Life and Earth Sciences* into "*Faculty of Science*"

p. 1 line 8: change to "*Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands*"

p. 1 line 14: add "*manure and*"

p. 1 line 16: delete "*combined*", change "*agriculture*" into "*agricultural*"

p. 1 line 18: *Twenty-three* ---- *Twenty-five*

p. 1 line 19: *N and P agricultural inputs*

p. 1 line 21: change "*these*" into "*the greater Amsterdam*", delete "*,*", given the higher nutrient levels in groundwater compared with surface water"

p. 2 line 5: *Lowland deltas account for 2 % of the world's land, but accommodated around 600 million people in 2000, and about 1400 million by 2060 as was estimated by Neumann et al. (2015). The reclamation of swamps and lakes and the drainage of peat areas to enable urbanisation and agriculture severely changed the hydrological, chemical, and ecological environment of these areas (Ellis et al., 2005; Yan et al., 2017). Lowland delta areas are vulnerable for water quality deterioration by processes like salinization and eutrophication, which can be amplified by climate change (Wu et al., 2015) and land subsidence (Minderhoud et al., 2017).*

*Make "The Netherlands is a densely populated..." into a new paragraph.*

p. 3 line 16: replace "*eight*" with "*ten*"

p. 3 line 17: add "*N and P agricultural inputs*"

p. 5 line 30-31: add "*and intensive arable farming*" and "*region*", replace "*system of*" with "*,* *where the*", delete "*boezems and*", delete "*which*"

p. 5 line 33: add "*with mostly dairy farming*"

p. 6 line 10: delete "*15*"

p. 6 line 10: add "*N and P agricultural inputs*"

p. 6 line 12: "*information*" changed to "*Information*"

p. 6 line 14: add "*(mostly after 1980)*"

p. 6 line 17: add "*in order to use as much of the available groundwater data as possible to cover the entire region and all the polders*"

*p. 6 line 18:* “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.”

*p. 7 line 10:* add “the N and P agricultural inputs”

*p. 8 line 25:* add “N and P agricultural inputs”

*p. 8 line 26-28:* replace “The number of selected explaining variables depends on the added value of an extra component. An extra explaining variable was only added to the regression when it improved the explained variance with at least 5%, and at most four variables were added.” with “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).”

*P 10 line 34:* add “No significant correlation was found with agricultural N and P inputs, except for a negative correlation between groundwater TN concentrations and N input (Table S2, absolute value lower than 0.4). This suggests that non-agriculture sources of N dominate in most areas.”

*p. 12 line 6:* delete “medians”

*p. 12 line 7:* EQS’s ---- EQSs

*p. 12 line 21:* add “, and agricultural N and P inputs”

*p. 12 line 22:* add “absolute values of” and “, but a slight negative correlation was found between the agricultural N input and the normalized concentrations of  $\text{HCO}_3$  in surface water (Table S2).”

p. 12 line 22-23: add “This is especially true for the Zuiderzee margin, the Upconing area and the Central Holland area (Fig.9). The  $\text{NO}_3$  and  $\text{NH}_4$  contributions to TN are about equal in the Vecht lakes area. For the Ice pushed ridge (not shown in Fig.9 due to insufficient data), a dominance of  $\text{NO}_3$  in surface water was expected as was the case in groundwater of this area. However, there is only limited amount of surface water that is draining the Ice pushed ridge directly”

p. 12 line 30-31: EQS's ---- EQSs

p. 13 line 3-7: Table 1 shows that TP,  $\text{NH}_4$ ,  $\text{HCO}_3$ , and Cl concentrations in groundwater correlate with the same components in surface water ( $R^2$  0.49, 0.44, 0.68, and 0.69). In addition,  $\text{HCO}_3$  in groundwater showed moderate correlations with nutrient concentrations in surface water (TP ( $R^2$  0.64), TN ( $R^2$  0.52), and  $\text{NH}_4$  ( $R^2$  0.51)).  $\text{HCO}_3$  concentrations in surface water also correlated with nutrient concentrations in surface water (TP ( $R^2$  0.62), TN ( $R^2$  0.47), and  $\text{NH}_4$  ( $R^2$  0.67)).

p. 13 line 7: delete “Surface water  $\text{SO}_4$  weakly correlated to groundwater Cl ( $R^2$  0.47)”

p. 13 line 9: add “(Table 2)”

p. 13 line 11: add “N agricultural input,” and “and humus”

p. 13 line 12: 0.21 change to 0.25

p. 13 line 14: add “/Elevation”

p. 13 line 17: delete “9”

p. 13 line 17: add “For TN and  $\text{NO}_3$ , the  $R^2$  also improved after adding N agricultural input.”

p. 13 line 21: EQS-EQSs

p. 13 line 23: showed ----- shows

p. 14 line 23: add “The findings on the dominance of groundwater inputs is also supported by the poor correlation with agricultural nutrients inputs, which are usually assumed to be a large source of N and P in surface water.”

p. 15 line 5: add “the”

p. 16 line 14-15: add “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).”

*p. 16 line 27, 28 and 29: add “land use was incorporated in variables like”, delete “the”, add “and N and P inputs, (as well as agricultural land percentage, shown in Supplement Information), land use”, respectively.*

*p. 17 line 4: delete “the perspectives”*

*p. 17 line 17: add “data”*

*p. 17 line 18: add “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.”*

*p. 17 line 21-22: add “4.5 Perspectives”*

*p. 17 line 31: add “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.”*

*p. 18 line 7-8: add “in lowland deltas where water levels are lowered to enable urbanisation and agricultural land use”. Delete “in the subsurface of coastal peat land areas”*

*p. 18 line 10: EQS’s ----- EQSs*

*p. 18 line 11: add “The discharge and redistribution of nutrient rich water from reclaimed lakes and swamps enhances eutrophication in downstream water resources and is hard to mitigate.”*

*p. 18 line 11: delete “Redistribution of these high nutrient seepage waters in dry periods seems to lead to EQSs exceedances in adjacent boezem systems and in the receiving polders”*

*p. 19 line 3-4: Drexler J. Z., De Fontaine C. S., Deverel S. J.: The legacy of wetland drainage on the remaining peat in the Sacramento San Joaquin Delta, California, USA, Wetlands, 29,1, 372-386, 2009.*

p. 19 line 30-31: Kronvang B., Kjøgestrand J., Windolf J., Ovesen N., Troldborg L.: Background phosphorus concentrations in Danish groundwater and surface water bodies, EGU General Assembly 2013, 7-12 April, 2013, Vienna, Austria, id. EGU2013-2249.

p. 19 line 36-37: Minderhoud P. S. J., Erkens G., Pham V. H., Bui V. T., Erban L., Kooi H., Stouthamer E.: Impacts of 25 years of groundwater extraction on subsidence in the Mekong delta, Vietnam, *Environ Res Lett.*, 12, 2017.

Neumann B., Vafeidis A.T., Zimmermann J., Nicholls R. J.: Future Coastal Population Growth and Exposure to Sea-Level Rise and Coastal Flooding - A Global Assessment, *Plos One*, 10, 3, 2015. e0118571. doi:10.1371/journal.pone.0118571.

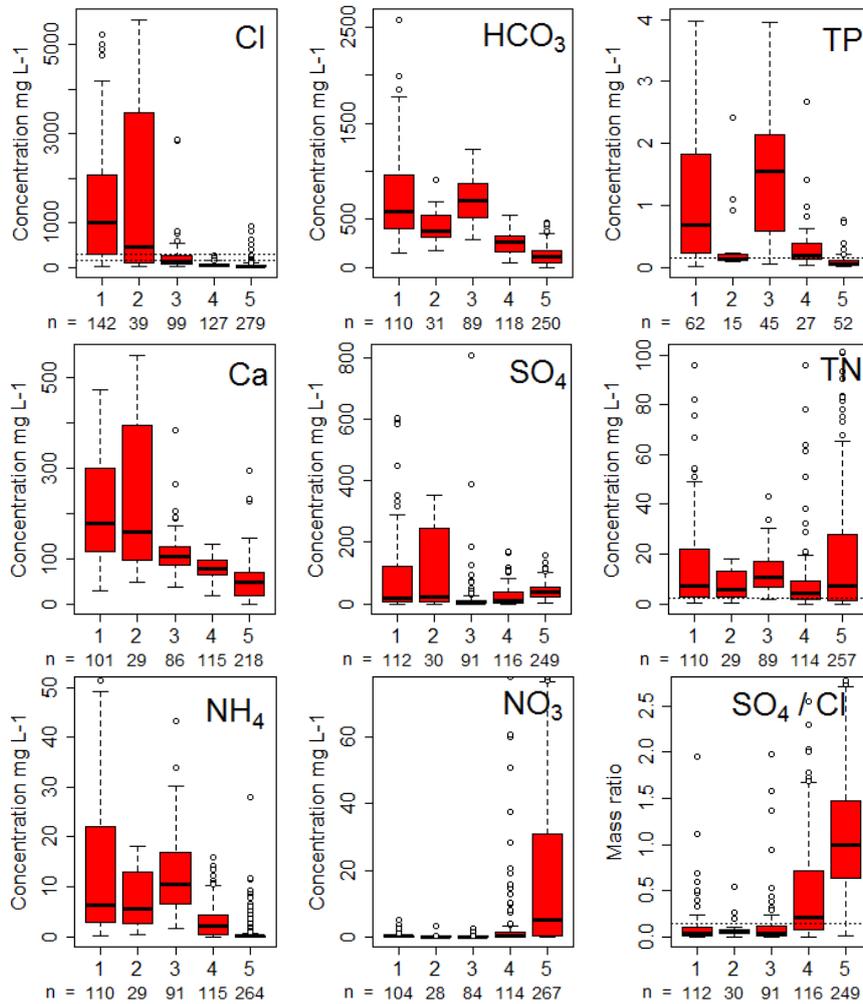
p. 20 line 7-8: Rozemeijer J. C., Van der Velde Y., Van Geer F., de Rooij G.H., Torfs P. J. J. F., Broers H. P.: Improving load estimates of N and P in surface waters by characterizing the concentration response to rainfall events, *Environ Sci & Technol*, 44, 6305-6312, 2010.

p. 20 line 16-17: Törnqvist T. E., Wallac D. J., Storms J. E. A., Wallinga J., Van Dam R. L., Blaauw M., Derksen M. S., Klerks C. J. W., Meijneken C., Snijders E. M. A.: Mississippi Delta subsidence primarily caused by compaction of Holocene strata. *Nat Geosci*, 1, 3, 173-176, 2008.

p. 20 line 34: Wu J. and Malmstrom M. E.: Nutrient loadings from urban catchments under climate change scenarios: Case studies in Stockholm, Sweden, *Sci Total Environ*, 518-519, 393-406, 2015.

Yan R., Huang J., Li L., Gao J.: Hydrology and phosphorus transport simulation in a lowland polder by a coupled modeling system, *Environ Pollut*, 227, 613-625, 2017.

p. 24 Figure 5 Changed into the following figure and add "Part of the outliers for TP, TN, NH<sub>4</sub>, NO<sub>3</sub> and SO<sub>4</sub>/Cl fall out of the range in the figure." to line 10



p. 32 Table 1 change into the following table. And change  $TP_{gw}$  with  $TN_{gw}$  into 0.66,  $TP_{sw}$  with  $TN_{sw}$  and  $HCO_{3\ sw}$  into 0.59 and 0.63, and  $TN_{sw}$  with  $Ca_{sw}$  into 0.56

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

	TP GW	TN GW	NH <sub>4</sub> GW	NO <sub>3</sub> GW	HCO <sub>3</sub> GW	SO <sub>4</sub> GW	Ca GW	Cl GW	TP SW	TN SW	NH <sub>4</sub> SW	NO <sub>3</sub> SW	HCO <sub>3</sub> SW	SO <sub>4</sub> SW	Ca SW	Cl SW
TP <sub>GW</sub>	1															
TN <sub>GW</sub>	0,66	1														
NH <sub>4</sub> <sub>GW</sub>	0,77	0,84	1													
NO <sub>3</sub> <sub>GW</sub>				1												
HCO <sub>3</sub> <sub>GW</sub>	0,68	0,63	0,82		1											
SO <sub>4</sub> <sub>GW</sub>	-0,46			0,41		1										
Ca <sub>GW</sub>					0,50		1									
Cl <sub>GW</sub>					0,48	0,40	0,77	1								
TP <sub>SW</sub>	0,49	0,51	0,60		0,64				1							
TN <sub>SW</sub>	0,45		0,44		0,52				0,59	1						
NH <sub>4</sub> <sub>SW</sub>			0,44		0,51				0,49	0,77	1					
NO <sub>3</sub> <sub>SW</sub>										0,57		1				
HCO <sub>3</sub> <sub>SW</sub>	0,57	0,55	0,64		0,68			0,41	0,63	0,47	0,67		1			
SO <sub>4</sub> <sub>SW</sub>										0,57		0,50		1		
Ca <sub>SW</sub>	0,59	0,54	0,63		0,71			0,41	0,55	0,56	0,64		0,88		1	
Cl <sub>SW</sub>					0,47		0,47	0,69	0,47	0,51			0,52	0,49	0,55	1
N input kg ha <sup>-1</sup> y <sup>-1</sup>																
P input kg ha <sup>-1</sup> y <sup>-1</sup>																
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<sup>-1</sup>

TP gw: groundwater TP concentration in mg L<sup>-1</sup>

p. 33 Table 2 change into the table below

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

	n <sub>1</sub>	n <sub>2</sub>	n <sub>3</sub>	R <sup>2</sup>	R <sup>2</sup> with only seeping polders	
TP <sub>SW</sub>	+ HCO <sub>3</sub> <sub>GW</sub>	+ NH <sub>4</sub> <sub>GW</sub>		0.43	0.49	(9)
TN <sub>SW</sub>	- Elevation	+ HCO <sub>3</sub> <sub>GW</sub>	+ N <sub>input</sub>	0.57	0.48	(10)
NH <sub>4</sub> <sub>SW</sub>	- Elevation	+ HCO <sub>3</sub> <sub>GW</sub>	+ Seepage	0.50	0.61	(11)
NO <sub>3</sub> <sub>SW</sub>	- Elevation	+ N <sub>input</sub>		0.18	0.23	(12)
HCO <sub>3</sub> <sub>SW</sub>	+ HCO <sub>3</sub> <sub>GW</sub>	+ Seepage	+ NH <sub>4</sub> <sub>GW</sub>	0.57	0.70	(13)
SO <sub>4</sub> <sub>SW</sub>	- Elevation	+ SO <sub>4</sub> <sub>GW</sub>		0.25	0.22	(14)
Ca <sub>SW</sub>	+ HCO <sub>3</sub> <sub>GW</sub>	- Elevation	+ Seepage	0.65	0.63	(15)
Cl <sub>SW</sub>	+ Cl <sub>GW</sub>	+ HCO <sub>3</sub> <sub>GW</sub>	+ P <sub>Humus</sub>	0.57	0.51	(16)

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

n<sub>1</sub>: first variable, the most significant variable

HCO<sub>3</sub><sub>SW</sub>: surface water HCO<sub>3</sub> concentration in mg L<sup>-1</sup>

HCO<sub>3</sub><sub>GW</sub>: groundwater HCO<sub>3</sub> concentration in mg L<sup>-1</sup>

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

Seepage: seepage rate in mm y<sup>-1</sup>

P<sub>Humus</sub>: percentage of humus in the soil profile sample

N<sub>input</sub>: manure and fertilizer N input in kg ha<sup>-1</sup>y<sup>-1</sup>

## Supplementary Information

p. 1: upconing area ----- Upconing area, Centre Holland ----- Central Holland, ice ---- Ice

p. 5 delete \* 0 – Boezem 1 – Zuiderzee margin 2 – Upconing area 3 – Centre Holland 4 – Vecht Lakes 5 – Ice pushed ridge

p. 7 add Figure S3, Table S2 and Table S3

Add description of Agricultural N and P inputs data in Table S4

## Database

Add Agricultural N and P inputs and Agricultural land percentage data in sheet "Database1"

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

Liang Yu<sup>1,2</sup>, Joachim Rozemeijer<sup>3</sup>, Boris M. van Breukelen<sup>4</sup>, Maarten Ouboter<sup>2</sup>, Corné van der Vlugt<sup>2</sup>, Hans Peter Broers<sup>5</sup>

<sup>1</sup>~~Faculty of Science Life and Earth Sciences~~, Vrije University Amsterdam, Amsterdam, 1181HV, The Netherlands

<sup>2</sup>Waternet Water Authority, Amsterdam, 1096 AC, The Netherlands

<sup>3</sup>Deltares, Utrecht, 3508 TC, The Netherlands

<sup>4</sup>~~Delft University of Technology, Delft, 2628 CN, The Netherlands~~ Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands

<sup>5</sup>TNO Geological Survey of The Netherlands, Utrecht, 3584 CB, The Netherlands

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

**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 ~~combined~~ with both urban and agricultural real 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~~three variables (concentrations of Total-N, Total-P, NH<sub>4</sub>, NO<sub>3</sub>, HCO<sub>3</sub>, SO<sub>4</sub>, 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 Amsterdamse mixed urban/agricultural catchments, ~~given the higher nutrient levels in groundwater compared with surface water~~. 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<sup>2</sup> 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<sub>3</sub> 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 in 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 teneight  
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<sup>2</sup>, 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

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

## 8 **2.1.1 Landscape history and hydrology**

### 9 **Landscape history**

10 Our study area is located in the western part of The Netherlands where large rivers and the sea have intensively interacted for  
11 millions of years. The main topographic feature is a Pleistocene sandy ice pushed ridge with elevations ranging from 0 to 30  
12 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  
13 periglacial Pleistocene river plains of the Rhine delta. During the Holocene, these sandy river plains were covered with peat  
14 and clay, which are currently found at the surface throughout the western part of the Netherlands, on top of Pleistocene  
15 sands. The average thickness of the Holocene peat and clay cover is 20 m, although it increases to over 50 m in former tidal  
16 inlet channels (Hijma, 2009).

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

25 The long history of marine influence stopped after closing off the estuaries and the inland sea in the 20<sup>th</sup> century ( Huisman,  
26 1998). In 1932, the construction of the Closure Dike (Afsluitdijk) created the fresh water Lake IJssel out of the former salt  
27 water Zuiderzee (‘Southern Sea’) to protect the surroundings from floods and to enable land reclamation. The former marine  
28 impact is still reflected by the presence of brackish groundwater in the shallow subsurface (Schot, 1992 b).

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

1 Mainly during the 20<sup>th</sup> 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 ( $\sim 1000 \text{ mg Cl L}^{-1}$  on average) and Horstermeer ( $\sim 500 \text{ mg Cl L}^{-1}$ ) is pumped into the Boezem system and is  
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

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

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

## 11 **2.2 Data processing**

12 The database that was compiled and used for this study covers 144 individual polders and includes monthly surface water  
13 quality data, spatiotemporally averaged groundwater quality data (TN, NO<sub>3</sub>, NH<sub>4</sub>, SO<sub>4</sub>, TP, Ca, HCO<sub>3</sub>, and Cl), daily  
14 pumping station discharge time series, and ~~15~~ polder averages of the following statistic variables: N and P agricultural  
15 inputs, polder seepage rates, elevations, surface water and paved area percentages, and calcite, clay, and humus percentages  
16 of the upper soil layer. More information about the data processing and the database can be found in the Supplementary  
17 information.

### 18 **2.2.1 Groundwater data**

19 A total of 802 observation wells of groundwater quality are available from the period 1910-2013 (mostly after 1980), largely  
20 drawn from the National Groundwater Database DINO (TNO, DINOLoket). We selected analyses from the upper 50 m of  
21 the subsurface, which corresponds with the thickness of the first main Pleistocene aquifer in the area and the Holocene cover  
22 layer. For our analyses, in order to use as much of the available groundwater data as possible to cover the entire region and  
23 all the polders, we averaged concentrations at individual monitoring screens of each monitoring well for all sampling dates  
24 available. The large majority of the groundwater quality data we used is from the last 30 years (for example, 85% of the  
25 chloride and 93% of the P measurements are from after 1980). In this study area, we do not expect that using some data from  
26 before 1980 creates a significant bias to the results of the study, because hydrogeochemical processes in the reactive  
27 subsurface such as sulfate reduction and methanogenesis have a stabilizing effect on the water composition in this area.  
28 Moreover, the overall flow patterns have not changed much in the past 30 to 100 years, because the flow systems are  
29 completely determined by the water levels maintained in the polder systems which have not changed much over the past 100  
30 years. However, the interface between fresh and salt water is known to slowly move into the direction of a new equilibrium  
31 (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:

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

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

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):

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

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:

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

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  $kg \text{ ha}^{-1} \text{ d}^{-1}$ . This was calculated using the  
9 daily average loads of each solute divided by the polder areas using Eq. (5):

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

10 Where L is daily load  $kg \text{ d}^{-1}$ , A is polder area (ha), C is daily solute concentration in  $mg \text{ L}^{-1}$  and Q is daily discharge in  $m^3 \text{ d}^{-1}$ .  
11 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):

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

21 In this equation, C is the normalized concentration ( $mg \text{ L}^{-1}$ ), Load per area is from Eq. (1), Q is the pumping discharge ( $m^3 \text{ y}^{-1}$ )  
22 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  $2.4 \text{ mg}$   
26  $\text{L}^{-1}$  and  $0.15 \text{ mg L}^{-1}$ , 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

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

### 3 **2.2.3 Surface water compared with groundwater solute concentrations**

4 We statistically analysed the groundwater and surface water quality data and landscape characteristic variables by (1)  
5 calculating the correlation coefficients between averaged groundwater solutes concentrations and normalized concentrations  
6 of surface water using the Spearman method, and (2) by selecting variables (based on the correlation matrix above) to be  
7 integrated into multiple linear regression models for predicting surface water solute concentrations. Again, the Spearman  
8 method was applied and linear regression was based on ranks in order to avoid outliers to determine the outcomes. The  
9 explaining variables for surface water concentrations include groundwater solute concentrations, N and P agricultural inputs,  
10 landscape characteristics, and the SO<sub>4</sub>/Cl ratio in groundwater. ~~The number of selected explaining variables depends on the~~  
11 ~~added value of an extra component. An extra explaining variable was only added to the regression when it improved the~~  
12 ~~explained variance with at least 5%, and at most four variables were added.~~ We adopted the method described by Rozemeijer  
13 et al. (2010), who described a form of sequential multiple regression analysis, where variables were added to the regression  
14 depending on their effects on the coefficient of determination R<sup>2</sup>. The regression analysis started with a singular regression  
15 using the explaining variable with the highest coefficient of determination (R<sup>2</sup>) for explaining the surface water quality  
16 parameter under consideration. Subsequently, the best regression models were searched with two and three explaining  
17 variables, where we accepted an additional variable only when the coefficient of determination R<sup>2</sup> increased with at least  
18 0.03. In this method, dependent variables can still add to the resulting R<sup>2</sup> as the coefficient of determination R<sup>2</sup> of the  
19 individual dependent variable pair is seldom larger than 0.7, pointing to some explaining power may still be present in the  
20 uncorrelated part (0.3). For comparison purposes, we also used the surface water EQSs as reference concentration values in  
21 the groundwater quality maps and boxplots, although the EQS's have no administrative meaning for groundwater itself.

### 22 **2.2.4 Solutes redistribution in surface water**

23 Loads were used to assess the impact of different polders as sources of solutes for the boezems and the receiving water  
24 bodies further downstream. In general, the spatial patterns can be distinguished through maps of the surface water solute  
25 loads per area if there are no other influences. However, there are exceptions such as the seepage water which is pumped out  
26 of the two upcoming polders Groot Mijdrecht and Horstermeer, which is discharged into the Boezem system and used as inlet  
27 water for the surrounding polders during summer. To show the impact of this inlet water on the receiving polders' water  
28 quality, we analysed the inlet solute loads and the resulting surface water concentrations for polder Botshol. Polder Botshol  
29 (part of polder # 104 Noorderpolder of Botshol (zuid and west)) with an area of 1.3 km<sup>2</sup> receives inlet water from the Amstel  
30 boezem system that has a significant contribution of seepage water that is pumped out of the polder Groot Mijdrecht.  
31 Two models were applied for simple solute concentration calculations based on inlet water quality. Model 1 calculates the  
32 accumulation of solutes in the water body, with evaporation as the only output for water (leaving the solutes behind). Model

1 2 models the complete mixing and outlet of both water and solutes via other routes like the outlet weir, infiltration, and  
2 leakage. In reality, water leaves Polder Botshol partly via evaporation (Model 1) and partly via other routes (Model 2):

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

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

5 where,  $C_{i+1}$  is the predicted solute concentration after getting inlet water at time  $i$ ;  $C_i$  is the predicted solute concentration in  
6 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  
7 polder ( $800.000 \text{ m}^3$ ), which is assumed to be constant as water levels are tightly controlled;  $C_{inlet}$  is the estimated Cl  
8 concentration in the inlet water ( $1000 \text{ mg L}^{-1}$ );  $Q_{inlet}$  is estimated constant inlet water volume,  $6000 \text{ m}^3 \text{ d}^{-1}$ . All parameters  
9 are shown in supplementary information Excel spread sheets. The models were applied in the year 2006, 2008, 2009, 2010,  
10 2011 and 2012.

## 11 **3 Results**

### 12 **3.1 Spatial pattern and statistical analysis of groundwater quality**

13 Fig. 5 and Fig. 6 show the groundwater quality for the upper main aquifer under the 144 polders for Cl, Ca,  $\text{HCO}_3$ ,  $\text{SO}_4$ , TN,  
14  $\text{NH}_4$ ,  $\text{NO}_3$ , and TP. The relations between groundwater solutes, landscape variables, and potential hydrochemical reactions in  
15 the subsurface were explored by correlation analysis of which the results are shown in Table 1 (yellow part) and Fig. 7 and  
16 Fig. 8.

#### 17 **Cl, Ca, and $\text{HCO}_3$**

18 In Fig. 5, the Zuiderzee margin, where brackish groundwater is dominant, P25 and P75 of concentrations are between 290  
19 and  $2100 \text{ mg L}^{-1}$  Cl,  $100\text{-}300 \text{ mg L}^{-1}$  Ca, and  $400\text{-}1000 \text{ mg L}^{-1}$   $\text{HCO}_3$ . Relatively high concentrations of Cl, Ca and  $\text{HCO}_3$   
20 were also for the two deep polders Groot Mijdrecht (# 80) and Horstermeer (Upconing area) with known upconing of salt  
21 groundwater. The Central Holland area was dominated by fresh groundwater with low Cl and Ca concentrations, but with  
22 considerable amounts of  $\text{HCO}_3$ . Polders with relatively high chloride ( $>1000 \text{ mg L}^{-1}$ ) are distributed along the former  
23 Zuiderzee margin, plus the Upconing area which is two deep polders with known upconing of brackish water. Relative to the  
24 regions above, the Vecht lakes area and the Ice pushed ridge showed significantly less mineralized waters with lower  $\text{HCO}_3$   
25 and Cl concentrations. For example, the P75s of Cl in these two regions are below  $150 \text{ mg L}^{-1}$  and the P75s of  $\text{HCO}_3$  below  
26  $350 \text{ mg L}^{-1}$ . The groundwater  $\text{HCO}_3$  concentrations (Fig. 6) show an east-west increasing trend with highest concentrations  
27 in both the fresh and brackish areas west of the Amsterdam Rhine Canal.

#### 28 **$\text{SO}_4$ and $\text{SO}_4/\text{Cl}$**

29 The Zuiderzee margin and the Upconing area showed large ranges of  $\text{SO}_4$  concentrations (P25 and P75:  $7\text{-}125 \text{ mg L}^{-1}$  and  $7\text{-}$   
30  $250 \text{ mg L}^{-1}$ , respectively) with the  $\text{SO}_4/\text{Cl}$  mass ratios generally lower than the 0.14 ratio for diluted seawater. The polders in

1 the eastern Zuiderzee margin showed the highest average  $\text{SO}_4$  levels (Fig. 6). The Central Holland area exhibited the lowest  
2  $\text{SO}_4$  concentrations with the smallest variability, with  $\text{SO}_4/\text{Cl}$  P75 typically lower than 0.14. However, some outliers in this  
3 region reached quite high sulfate concentration levels ( $>200 \text{ mg L}^{-1}$ ). The Vecht lakes and the Ice pushed ridge showed  
4 intermediate sulfate concentrations and typically have a  $\text{SO}_4/\text{Cl}$  ratio clearly above 0.14.

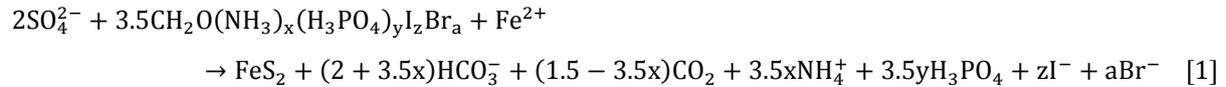
#### 5 **$\text{NH}_4$ , TN, $\text{NO}_3$ , and TP**

6 The higher groundwater  $\text{NH}_4$  and TP concentrations generally locate in the western part of the study area (Zuiderzee margin,  
7 Upconing area, and Central Holland regions). Median  $\text{NH}_4$  concentrations in the Zuiderzee margin ( $6.4 \text{ mg L}^{-1}$ ) and Central  
8 Holland ( $10.6 \text{ mg L}^{-1}$ ) were far higher than in the Vecht lakes ( $2.1 \text{ mg L}^{-1}$ ) and Ice pushed ridge regions ( $0.07 \text{ mg L}^{-1}$ ). The  
9 same was observed for TP ( $0.7, 1.6, 0.2$  and  $0.06 \text{ mg P L}^{-1}$ , respectively). Nutrient concentrations in the Upconing area  
10 (medians  $5.7 \text{ mg NH}_4 \text{ L}^{-1}$  and  $0.14 \text{ mg P L}^{-1}$ ) were relatively low compared with the groundwater in the Zuiderzee margin  
11 and Central Holland areas, although we consider the  $\text{NH}_4$  concentration levels to be substantial given the surface water EQS  
12 of  $2.4 \text{ mg N L}^{-1}$ . TN showed the highest median concentration levels in the Zuiderzee margin and Central Holland regions, as  
13 well as in the Ice pushed ridge ( $7.3 \text{ mg N L}^{-1}$ ). The Ice pushed ridge region also showed the highest level of  $\text{NO}_3$ . In the latter  
14 region, nitrate is the main component of TN, while  $\text{NH}_4$  is the main component in the other regions.

15 Groundwater quality varied from fresh, low mineralized in the eastern parts (Vecht lakes and Ice pushed ridge, Figure 4)  
16 towards brackish, highly mineralized and nutrient rich groundwater in the northwest (Zuiderzee margin and Central Holland,  
17 Fig. 4). This relationship was further indicated by the strong correlations between Ca and Cl (Spearman  $R^2$  0.77) and  
18 between  $\text{HCO}_3$ , TP and  $\text{NH}_4$  ( $R^2$  0.68-0.82) (Table 1, yellow part). The spatial Ca pattern corresponds largely with the Cl  
19 pattern (Fig. 6), showing higher Ca concentrations in the brackish waters, which is related to the high Ca concentrations in  
20 (diluted) seawater (Section 4.1). The strong correlation between TN and  $\text{NH}_4$  ( $R^2$  0.81) showed the dominance of  $\text{NH}_4$  in TN,  
21 except in the suboxic groundwaters under the Ice pushed ridge where nitrate dominates TN.  $\text{HCO}_3$ , TP and  $\text{NH}_4$  were all  
22 weakly negatively correlated with elevation, indicating that higher concentrations exist in the deeper polders which are more  
23 affected by brackish groundwater seepage. No significant correlation was found with agricultural N and P inputs, except for  
24 a negative correlation between groundwater TN concentrations and N input (Table S2, absolute value lower than 0.4). This  
25 suggests that non-agriculture sources of N dominate in most areas.

26 In the more mineralized groundwater systems, sulfate reduction is a potential cause of the significant relationship between  
27  $\text{HCO}_3$ , TP, and  $\text{NH}_4$ . From using the  $\text{SO}_4/\text{Cl}$  ratio of the samples and comparing them with the  $\text{SO}_4/\text{Cl}$  ratio in seawater (Eq.  
28 3), it appears that most of the brackish groundwater showed signs of sulfate reduction. Figure 7 shows that the amount of  
29  $\text{SO}_4$  consumed in the sulfate reduction process increased with the chloride concentration of the groundwater, and that sulfate  
30 reduction was complete only in part of the groundwaters. Note that groundwater below polders with excess  $\text{SO}_4$  are all in  
31 water with  $\text{Cl} < 1000 \text{ mg L}^{-1}$ . It follows from Figure 8 that high  $\text{HCO}_3$ , TP, and  $\text{NH}_4$  concentrations mostly occurred in  
32 groundwater with a  $\text{SO}_4/\text{Cl}$  ratio lower than 0.14, indicating sulfate reduction which induces the release of N and P from the  
33 mineralized organic matter in the subsurface and the production of alkalinity during that process. Therefore, these waters  
34 typically have increased  $\text{HCO}_3$  concentrations above  $480 \text{ mg L}^{-1}$  (Fig. 8A and 8B) and are often associated with brackish

1 groundwater that once contained sulfate (Fig. 8C:  $\text{Cl} > 300 \text{ mg L}^{-1}$ ). The hypothetical chemical relation between sulfate  
2 reduction ( $\text{SO}_4$  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  
3 reaction equation below (Stuyfzand, 2006):



### 4 **3.2 Spatial patterns and statistical analysis of surface water quality**

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

#### 9 **Cl, Ca, and $\text{HCO}_3$**

10 Highest chloride levels ( $>300 \text{ mg L}^{-1}$ ) were found in the Upconing polders with brackish seepage and in a minority of the  
11 polders in the Zuiderzee margin and Central Holland regions (Fig. 9 and 10). The high Ca and  $\text{HCO}_3$  concentrations in these  
12 polders are also related to the occurrence of brackish water. However, most of the surface water in the Zuiderzee margin and  
13 the Central Holland area is fresh with relatively low Cl concentrations (Fig. 10). The Vecht lakes area exhibits the most fresh  
14 and least mineralized surface water.

#### 15 **$\text{SO}_4$ and $\text{SO}_4/\text{Cl}$**

16 The highest  $\text{SO}_4$  concentration levels and  $\text{SO}_4/\text{Cl}$  mass ratios mostly occurred in the Central Holland area, especially the  
17 western part. The elevated  $\text{SO}_4$  and  $\text{SO}_4/\text{Cl}$  ratios indicate the presence of sulfate sources other than (relict) seawater in this  
18 area, probably atmospheric deposition, agriculture and/or oxidation of pyrite exposed in the upper soils which developed in  
19 marine clay deposits and are denoted as “cat clays” (Wallenberg, 1975). In the Zuiderzee margin and the two upconing  
20 polders, the median  $\text{SO}_4$  levels are 64 and 62  $\text{mg L}^{-1}$ , respectively, and  $\text{SO}_4/\text{Cl}$  mass ratios of the two upconing polders are  
21 below 0.14. A generally lower  $\text{SO}_4$  with  $\text{SO}_4/\text{Cl}$  ratios far exceeding the 0.14 were found in the Vecht lakes region.

#### 22 **TN, $\text{NH}_4$ , $\text{NO}_3$ , and TP**

23 According to Fig. 9 and Fig. 10, surface water EQSs of TN ( $2.4 \text{ mg N L}^{-1}$ ) and TP ( $0.15 \text{ mg P L}^{-1}$ ) were exceeded in most  
24 polders of the study area. The outliers with even higher nutrient concentrations are mainly located in the west of the Central  
25 Holland region. P25 and P75 of TP and TN in the Zuiderzee margin and in Central Holland regions all significantly  
26 exceeded EQSs for surface water. In the two upconing polders, polder Groot Mijdrecht showed higher concentrations of TP  
27 and TN than polder Horstermeer (~~medians of~~  $0.28$  vs.  $0.11 \text{ mg P L}^{-1}$  and  $5.4$  vs.  $1.8 \text{ mg N L}^{-1}$ ). Polders with concentrations  
28 below the EQS<sup>2</sup>s were mainly situated in the Vecht lakes area where large open water areas exist. In this region, TP slightly  
29 exceeded the EQS with a median concentration of  $0.22 \text{ mg L}^{-1}$ , while the median TN concentration of  $2.26 \text{ mg L}^{-1}$  was just  
30 below the EQS. The concentrations of  $\text{NO}_3$  and  $\text{NH}_4$  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<sub>3</sub> are both correlated with NH<sub>4</sub> (Spearman R<sup>2</sup> are 0.64  
3 and 0.67), TP (R<sup>2</sup> 0.55, 0.62), and TN (R<sup>2</sup> 0.57, 0.47). In surface water, Ca and HCO<sub>3</sub> had a significant correlation (R<sup>2</sup> 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<sup>2</sup> 0.55), HCO<sub>3</sub> (R<sup>2</sup> 0.52), SO<sub>4</sub> (R<sup>2</sup> 0.49) and NH<sub>4</sub> (R<sup>2</sup> 0.51), as well as SO<sub>4</sub> with TN (R<sup>2</sup> 0.57) and NO<sub>3</sub> (R<sup>2</sup> 0.50). A  
7 more direct indication for the groundwater impact is that NH<sub>4</sub>, HCO<sub>3</sub> 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<sup>2</sup> -0.67, NH<sub>4</sub>: R<sup>2</sup> -0.59, NO<sub>3</sub>: R<sup>2</sup> -0.40, HCO<sub>3</sub>: R<sup>2</sup> -  
10 0.48, SO<sub>4</sub>: R<sup>2</sup> -0.47 and Ca: R<sup>2</sup> -0.57).

11 For the soil variables (lutum, humus and calcite), only humus showed correlations with TN, NH<sub>4</sub>, 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<sub>3</sub> in surface water (Table S2).  
15 Surface water TN correlated more closely to NH<sub>4</sub> (0.77) than to NO<sub>3</sub> (0.57), which reflects that NH<sub>4</sub> 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<sub>3</sub> and NH<sub>4</sub> 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<sub>3</sub> 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<sub>4</sub> 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 EQS<sup>2</sup>s in 93 % of the polders for TP, and in 91 % for TN. Polders with  
27 groundwater nutrient levels below the EQS<sup>2</sup>s 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<sub>3</sub> 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<sub>4</sub>, HCO<sub>3</sub>, and Cl concentrations in groundwater correlate with the same components in surface  
32 water (R<sup>2</sup> 0.4953, 0.443, 0.686, and 0.6972). In addition, HCO<sub>3</sub> in groundwater showed moderate correlations with nutrient  
33 concentrations in surface water (TP (R<sup>2</sup> 0.64), TN (R<sup>2</sup> 0.520), and NH<sub>4</sub> (R<sup>2</sup> 0.5146)). HCO<sub>3</sub> concentrations in surface water

1 also correlated with nutrient concentrations in surface water (TP ( $R^2$  0.620), TN ( $R^2$  0.479), and  $\text{NH}_4$  ( $R^2$  0.6759)). ~~Surface~~  
2 ~~water  $\text{SO}_4$  weakly correlated to groundwater Cl ( $R^2$  0.47).~~

3 Based on these correlations, we selected groundwater parameters and landscape characteristics to be integrated in multiple  
4 linear regression models to predict concentrations of surface water components (Table 2). For most solutes (TP,  $\text{NH}_4$ , TN,  
5  $\text{HCO}_3$ , and Cl, the  $R^2$  of the regression models is around 0.5, which indicates that around 40 ~ 50% of the spatial variance in  
6 surface water can be explained by specific groundwater chemistry parameters, N agricultural input, seepage, and elevation  
7 and humus. For  $\text{NO}_3$  and  $\text{SO}_4$ , the  $R^2$  of the regression models (inverse with Elevation) are very low, 0.18 and 0.254,  
8 respectively. For all other parameters, the groundwater  $\text{HCO}_3$  concentration was the best explaining variable for the surface  
9 water concentrations. The spatial variation in  $\text{HCO}_3$ <sub>SW</sub> and  $\text{Ca}$ <sub>SW</sub> were relatively well explained by only  $\text{HCO}_3$ <sub>GW</sub> combined  
10 with Seepage/Elevation, respectively (Eq. 13 and Eq. 15).

11 The regression models were significantly improved by including groundwater concentrations of TP,  $\text{NH}_4$ , and Cl (Eq. 9, 11  
12 and 16). For TN and  $\text{NO}_3$ , the  $R^2$  also improved after adding N agricultural input. In regression models Eq. 9-10, 11, 12, 14,  
13 and 15, the elevation of the polders also explained part of the spatial variation in surface water concentrations. When only  
14 including polders with net groundwater seepage, the  $R^2$  improved significantly for TP,  $\text{NH}_4$  and  $\text{HCO}_3$ .

15 The results above strongly suggest that the groundwater composition puts limitations to the compliance of the receiving  
16 surface water towards the EQS<sub>s</sub> defined for N and P.

### 17 3.4 Surface water solute redistribution

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

21 A clear similarity between the spatial patterns of the solute loads and the average seepage rate patterns was observed in Fig.  
22 3 and Fig. 11. In general, polders with high seepage rates also discharge relatively high loads to the Boezem system. Some  
23 examples of polders with relatively high seepage rates are polder #119 (Bethunepolder, 13 mm d<sup>-1</sup>), #79 (Horstermeer, 8.7  
24 mm d<sup>-1</sup>), #50 (Polder De Toekomst, 2.4 mm d<sup>-1</sup>), #131 (Hilversumse Meent, 2.4 mm d<sup>-1</sup>), #98 (Polder Wilnis-Veldzijde, 3.7  
25 mm d<sup>-1</sup>), #80 (Polder Groot Mijdrecht en Polder de Eerste Bedijking (oost), 5.0 mm d<sup>-1</sup>), #74 (Polder de Nieuwe Bullewijk  
26 en Holendrecht- en Bullewijker Polder noord, 1.8 mm d<sup>-1</sup>) and #75 (Bijlmer, 2.0 mm d<sup>-1</sup>). The highest loads are discharged  
27 from the two upconing polders: Groot Mijdrecht (#80) and Horstermeer (#79).

28 The influence of the redistribution of the large water volumes and loads from deep polders was also observed in Fig. 3 and  
29 Fig. 11. Polders that receive inlet water from Groot Mijdrecht and Horstermeer (see section 2.1.1, Fig. 3) showed relatively  
30 high solute loads, independent of their own seepage or infiltration fluxes. This especially holds for polders downstream of  
31 Groot Mijdrecht and Horstermeer, like polder #73 (Holendrecht- en Bullewijker Polder (zuid en west), -0.05), #74 (Polder  
32 de Nieuwe Bullewijk en Holendrecht- en Bullewijker Polder noord, 1.8 mm d<sup>-1</sup>), #104 (Noorderpolder of Botshol (zuid en

1 west),  $-1.4 \text{ mm d}^{-1}$ ), #105 (Noorderpolder of Botshol (Nellestein),  $-0.7 \text{ mm d}^{-1}$ ), #106 (Polder de Rondehoep,  $-1.1 \text{ mm d}^{-1}$ ),  
2 and polder #107 (Polder Waardassacker en Holendrecht,  $-0.15 \text{ mm d}^{-1}$ ).

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

## 11 **4 Discussion**

12 This study aimed at identifying the impact of groundwater on surface water quality in the polder catchments of the greater  
13 Amsterdam city area. According to the statistical analysis of data over five regions in the study area, a clear influence was  
14 identified. Solute concentrations in groundwater and surface water correlated well, although groundwater solute  
15 concentrations were generally much higher than normalized concentrations in surface water. The latter seems logical given  
16 the dilution of surface water by the precipitation surplus on an annual basis, with the annually discharged surface water being  
17 a mixture of seeping groundwater and precipitation. Moreover, similar spatial patterns in solute concentrations were found in  
18 groundwater and surface water. [The findings on the dominance of groundwater inputs is also supported by the poor](#)  
19 [correlation with agricultural nutrients inputs, which are usually assumed to be a large source of N and P in surface water.](#)  
20 Polders that are influenced by groundwater seepage or by redistributed seepage water from nearby deep polders are at risk of  
21 non-compliance, as groundwater concentrations exceeded the TN and TP EQSs for surface water in more than 90% of the  
22 polders. Consequently, the groundwater nutrients input hinders achieving water quality targets in the surface water in those  
23 lowland landscapes.

### 24 **4.1 Key hydro chemical processes**

25 In general, the groundwater chemistry corresponds with the geological history of the study area. In the peat land polder  
26 catchments within the Dutch delta system of marine, peri-marine and fluvial unconsolidated deposits, abundant organic  
27 matter is present in the subsurface (e.g. Hijma, 2009). The presence of reactive organic matter in the shallow subsurface  
28 depletes the infiltrating groundwater from oxygen and nitrate, leading to an overall low redox potential in groundwater,  
29 which enables the further decomposition of organic matter downstream.

30 Our data strongly suggests that sulfate reduction, sometimes in combination with methanogenesis, is the main process  
31 releasing nutrients (N, P) and  $\text{HCO}_3$  from the organic rich subsurface in the study area, especially in both the fresh and

1 | brackish groundwater of the Zuiderzee margin, the Upconing polders, and [the](#) Central Holland that are characterized by low  
2 |  $\text{SO}_4/\text{Cl}$  ratios (Table 1, Fig. 8). The Holocene marine transgression undoubtedly influenced the chemistry of groundwater by  
3 | salinizing processes that also increased sulfate availability derived from diluted sea water. Refreshing of the aquifers by  
4 | infiltration of fresh water from rivers and rain in more elevated polders and lakes further influenced part of the groundwater.  
5 | We examined the amount of freshening and salinization using the exchange Na ( $\text{Na}_{\text{ex}}$ ) and investigated how this process may  
6 | have influenced the release of P as was suggested by Griffioen et al. (2004). Figure S2 shows that high P (and  $\text{HCO}_3$ , not  
7 | 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  $\text{SO}_4/\text{Cl}$  ratio is  
8 | below 0.14. Therefore, we infer that sulfate reduction/organic matter decomposition is the prime process in releasing P, and  
9 | is more discriminating high P than cation exchange processes. There is a high probability for sulfate reduction dominated  
10 | polder catchments to have very high  $\text{HCO}_3$  concentration in groundwater according to Eq. [1]. In our study area, high  $\text{HCO}_3$   
11 | concentration levels in both groundwater and surface water were mainly present in areas with marine sediments that contain  
12 | shell fragments and organic matter. The base level groundwater alkalinity from the dissolution of shell fragments and  
13 | carbonate minerals is further increased by the organic matter decomposition in the subsurface. This observation confirms the  
14 | earlier findings of Griffioen et al. (2013) who highlighted the relation between the nutrient concentrations and  $\text{pCO}_2$  in these  
15 | marine sediments. The main chemical reactions involved are listed in Table 3.

16 | The seepage of the alkalized groundwater increases alkalinity of the surface water, which is indicated by the high correlation  
17 | between groundwater and surface water  $\text{HCO}_3$ , and with Ca in surface water (Table 1). Subsurface organic matter  
18 | mineralization by processes like sulfate reduction and methanogenesis (Chapelle et al., 1987; Griffioen et al., 2013) (Table 3  
19 | [2], [6]), is a probable major reason for enhanced surface water  $\text{HCO}_3$  in polders with brackish groundwater, like the  
20 | polders in the Zuiderzee margin and the Upconing polders (Fig. 8).

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

25 | Sulfate concentrations are higher in the receiving surface water than in the groundwater. We ascribe the sulfate surpluses  
26 | (Fig. 7) to additional sources affecting the surface water, including atmospheric deposition, agricultural inputs, sewer  
27 | leakage (Ellis, et al., 2005), storm runoff, and/or the oxidation of pyrite ( $\text{FeS}_2$ ). Pyrite is ubiquitously present in this area  
28 | (Griffioen et al., 2013) and oxidizes in the topsoil, where either  $\text{O}_2$  or  $\text{NO}_3$  can act as electron acceptor (Wallenburg, 1975).  
29 | We suggest that sulfate concentrations are especially high in polders where shallow groundwater flow is enhanced by the  
30 | presence of tile drains in clay rich polders that needed this drainage system to prevent water tables rising into the root zone in  
31 | wet periods. Tile drain flow can bring the released  $\text{SO}_4$  to the surface water. For urban polders with high  $\text{SO}_4$  concentrations,  
32 | like the Zuiderzee margin region polders, sewer system leakage may be an additional source of  $\text{SO}_4$ . Aging and faulty  
33 | connections of pipes may result in a leakage of water with high  $\text{SO}_4$  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  $\text{NO}_3$  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  $\leq 0$ ), 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  $\text{HCO}_3$  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,

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

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

#### 13 | **4.4 Uncertainties and perspectives**

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

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

#### 30 | **4.5 Perspectives**

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

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

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

## 17 **5 Conclusion**

18 In this paper, a clear groundwater impact on surface water quality was identified for the greater Amsterdam area. It was  
19 concluded that this groundwater seepage significantly impacts surface water quality in the polder catchments by introducing  
20 brackish, alkaline, and nutrient rich water. In general, nutrient concentrations in groundwater were much higher than in  
21 surface water and often exceeded surface water Environmental Quality Standards (EQSs) (in 93 % of the polders with  
22 available data for TP and in 91 % for TN) which indicates that groundwater is a large potential source of nutrients in surface  
23 water. Our results strongly suggest that organic matter mineralization is a major source of nutrients in lowland deltas where  
24 water levels are lowered to enable urbanisation and agricultural land use in the subsurface of coastal peat land areas. High  
25 correlations ( $R^2$  up to 0.88) between solutes in groundwater and surface water confirmed the effects of surface water-  
26 groundwater interaction on surface water quality. Especially in seepage polders, groundwater is a major source of Cl,  $\text{HCO}_3$ ,  
27 Ca and the nutrients N and P, leading to general exceedances of EQS~~s~~ for N and P in surface waters. The discharge and  
28 redistribution of nutrient rich water from reclaimed lakes and swamps enhances eutrophication in downstream water  
29 resources and is hard to mitigate. Redistribution of these high nutrient seepage waters in dry periods seems to leads to EQS  
30 exceedances in adjacent boezem systems and in the receiving polders. Surface water quality in the Amsterdam urban area is  
31 also influenced by groundwater seepage, but other anthropogenic sources, such as leaking and overflowing sewers might  
32 amplify the eutrophication problems.

## 1 **Acknowledgements**

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

## 5 **References**

- 6 Appelo, C. A. J., Postma, D.: Geochemistry, groundwater and pollution, Second Edition, A.A. Balkema Publishers, Leiden, The  
7 Netherlands, 2005.
- 8 Brabec, E., Schulte, S., Richards, P. L.: Impervious Surfaces and Water Quality: A Review of Current Literature and Its Implications for  
9 Watershed Planning, *Journal of Planning Literature*, 16, 499-513, 2002.
- 10 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<sub>2</sub>  
11 to groundwater. *Water Resour Res*, 23, 1625-1632, 1987.
- 12 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  
13 dominant mechanism of salinization in deep polders, The Netherlands. *J Hydrol*, 394, 494-506, 2010.
- 14 Delsman, J. R.: Saline Groundwater - Surface Water Interaction in Coastal Lowlands. Ph. D. thesis, VU University Amsterdam,  
15 Amsterdam, The Netherlands, 2015.
- 16 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-  
17 modeling of coastal saltwater intrusion during the Holocene: an application to the Netherlands, *Hydrol Earth Syst Sc*, 18, 10, 3891-  
18 3905, 2014.
- 19 [Drexler J. Z., De Fontaine C. S., Deverel S. J.: The legacy of wetland drainage on the remaining peat in the Sacramento San Joaquin](#)  
20 [Delta, California, USA, \*Wetlands\*, 29,1, 372-386, 2009.](#)
- 21 Dinoloket: <https://www.dinoloket.nl/>, last access: date October, 14, 2016.
- 22 Ellis, J. B., Marsalek, J., Chocat, B.: *Encyclopedia of Hydrological Sciences, Urban Water Quality*, 1<sup>st</sup> edition, M G Anderson, John Wiley  
23 & Sons, Ltd, United States, 8, 97, 2005.
- 24 EU (2017) Commission Staff Working Document; the EU Environmental Implementation Review. Country Report – The Netherlands.  
25 The EU Environmental Implementation Review: Common Challenges and how to combine efforts to deliver better results.  
26 COM(2017) 63 final, [http://ec.europa.eu/environment/eir/pdf/report\\_nl\\_en.pdf](http://ec.europa.eu/environment/eir/pdf/report_nl_en.pdf)
- 27 Garrett, C. G., Vulava, V. M., Callahan, T. J., Jones, M. L.: Groundwater-surface water interactions in a lowland watershed: source  
28 contribution to stream flow. *Hydrol Process*, 26, 3195-3206, 2012.
- 29 Göbel, P., Dierkes, C., Coldewey, W. G.: Storm water runoff concentration matrix for urban areas, *J Contam Hydrol*. 91, 26-42, 2007.
- 30 Grift, B. van der, Broers, H. P., Berendrecht, W., Rozemeijer, J. R., Osté, L., and Griffioen, J.: High-frequency monitoring reveals nutrient  
31 sources and transport processes in an agriculture-dominated lowland water system, *Hydrol. Earth Syst. Sci.*, 20, 1851-1868,  
32 doi:10.5194/hess-20-1851-2016, 2016.
- 33 Griffioen, J.: Uptake of phosphate by iron hydroxides during seepage in relation to development of groundwater composition in coastal  
34 areas. *Environmental science & technology*, 28, 675-681, 1994.

- 1 Griffioen, J., Vermooten, S., Janssen, G.: Geochemical and palaeohydrological controls on the composition of shallow groundwater in the  
2 Netherlands. *Appl geochem*, 39, 129 -149, 2013.
- 3 Heinis, F. and C. H. M. Evers: Toelichting op ecologische doelen voor nutriënten in oppervlaktewateren. STOWA-report (in Dutch),  
4 Utrecht, The Netherlands, 2007.
- 5 Helsel, D. R. and Hirsch, R. M.: *Statistical Methods in Water Resources, Techniques of Water Resources Investigations*, 2<sup>nd</sup> edition, U. S.  
6 Geological Survey, U. S. A, Book 4, chapter A3, 2002.
- 7 Hellmann, F. and Vermaat, J. E.: Impact of climate change on water management in Dutch peat polders. *Ecol Model*, 240, 74-83, 2012.
- 8 Holman, I. P., Whelan, M. J., Howden, N. J. K., Bellamy, P. H., Willby, N. J., Rivas-Casado, M., McConvey, P.: Phosphorus in  
9 groundwater - an overlooked contributor to eutrophication, *HYDROL PROCESS*, 22, 5121-5127, 2008.
- 10 Huisman, P., Cramer, W., van Ee, G., Hooghart, J. C., Salz, H. Zuidema, F. C.: *Water in the Netherlands*. Netherlands Hydrological  
11 Society, Rotterdam, the Netherlands, 1998.
- 12 Hijma, M. P.: From river valley to estuary: the early-mid Holocene transgression of the Rhine-Meuse valley, Ph. D. thesis, Utrecht  
13 University, Utrecht, The Netherlands, 2009.
- 14 [Kronvang B., Køgestrand J., Windolf J., Ovesen N., Trolborg L.: Background phosphorus concentrations in Danish groundwater and](#)  
15 [surface water bodies, EGU General Assembly 2013, 7-12 April, 2013, Vienna, Austria, id. EGU2013-2249.](#)
- 16 Meinikmann, K., Hupfer, M., Lewandowski, J.: Phosphorus in groundwater discharge - A potential source for lake eutrophication, *J*  
17 *Hydrol*, 524, 214 - 226, 2015.
- 18 Morris, A. W. and Riley, J. P.: The bromide/chlorinity and sulphate/chlorinity ratio in sea water, *Deep Sea Research and Oceanographic*  
19 *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.
- 20 Mourad, D. S. J. and van der Perk, M.: Spatio-temporal patterns of nutrient concentrations and export in a north-eastern European lowland  
21 catchment. *Hydrol. Process*, 23: 1821- 1833, 2009.
- 22 [Minderhoud P. S. J., Erkens G., Pham V. H., Bui V. T., Erban L., Kooi H., Stouthamer E.: Impacts of 25 years of groundwater extraction](#)  
23 [on subsidence in the Mekong delta, Vietnam, \*Environ Res Lett.\*, 12, 2017.](#)
- 24 [Neumann B., Vafeidis A.T., Zimmermann J., Nicholls R. J.: Future Coastal Population Growth and Exposure to Sea-Level Rise and](#)  
25 [Coastal Flooding - A Global Assessment, \*Plos One\*, 10, 3, 2015. e0118571. doi:10.1371/journal.pone.0118571.](#)
- 26 Oude Essink, G. H. P., Houtman, H., Goes, B. J. M.: Chloride concentration at the bottom of the Holocene aquitard in the Netherlands (in  
27 Dutch), Rep. NITG 05-056-A, 17 pp., TNO, Utrecht, Netherlands, 2005.
- 28 Oude Essink, G. H. P., Van Baaren, E. S., De Louw, P. G. B.: Effects of climate change on coastal groundwater systems: a modeling  
29 study in the Netherlands, *Water Resour Res*, 46, 10, 2010.
- 30 Rozemeijer, J. C. and Broers, H. P.: The groundwater contribution to surface water contamination in a region with intensive agricultural  
31 land use (Noord-Brabant, The Netherlands). *Environ Pollut*, 148, 695-706, 2007.
- 32 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  
33 groundwater flow route contributions to surface water contamination: From field-scale concentration patterns in groundwater to  
34 catchment-scale surface water quality, *Environ Pollut*, 158, 3571-3579, 2010.
- 35 [Rozemeijer J. C., Van der Velde Y., Van Geer F., de Rooij G.H., Torfs P. J. J. F., Broers H. P.: Improving load estimates of N and P in](#)  
36 [surface waters by characterizing the concentration response to rainfall events, \*Environ Sci & Technol\*, 44, 6305-6312, 2010.](#)

- 1 Rozemeijer, J. C., Klein, J., Broers, H. P., van Tol-Leenders, T. P., van der Grift, B.: Water quality status and trends in agriculture-  
2 dominated headwaters; a national monitoring network for assessing the effectiveness of national and European manure legislation  
3 in The Netherlands, *Environ Monit Assess*, 186, 8981-8995, 2014.
- 4 Schot, P. P. and Molenaar, A.: Regional changes in groundwater flow patterns and effects on groundwater composition, *J Hydrol*, 130,  
5 151-170, 1992 a.
- 6 Schot, P. P. and van der Wal, J.: Human impact on regional groundwater composition through intervention in natural flow patterns and  
7 changes in landuse. *J Hydrol*, 134, 297-313, 1992 b.
- 8 Stuyfzand, P. J. and Stuurman, R. J.: Origin, distribution and chemical mass balances of non-anthropogenic, brackish and (hyper) saline  
9 groundwaters in the Netherlands, 1<sup>st</sup> SWIM-SWICA Joint Saltwater Intrusion Conference, Cagliari-Chia Laguna, Italy, 2006.
- 10 [Törnqvist T. E., Wallac D. J., Storms J. E. A., Wallinga J., Van Dam R. L., Blaauw M., Derksen M. S., Klerks C. J. W., Meijneken C.,](#)  
11 [Snijders E. M. A.: Mississippi Delta subsidence primarily caused by compaction of Holocene strata. \*Nat Geosci\*, 1, 3, 173-176,  
12 \[2008.\]\(#\)](#)
- 13 Van Loon, A. H.: Unravelling hydrological mechanisms behind fen deterioration in order to design restoration strategies, Ph. D. thesis,  
14 Utrecht University, Utrecht, The Netherlands, 2010.
- 15 Van Beek, C. L., Droogers, P., van Hardeveld, H. A., van den Eertwegh, G. A. P. H., Velthof, G. L., Oenema, O.: Leaching of solutes  
16 from an intensively managed peat soil to surface water, *Water Air Soil Poll*, 182, 291-301, 2007.
- 17 Van Wallenburg, C.: Kattekleigronden en potentiële kатteklei in droogmakerijen in het Westen van Nederland. Boor en Spade: verspreide  
18 bijdragen tot de kennis van de bodem van Nederland, 19, 116-133, 1975.
- 19 Vermaat, J. E., Hellmann, F.: Covariance in water- and nutrient budgets of Dutch peat polders: what governs nutrient retention?  
20 *Biogeochemistry*, 99, 109-126, 2010.
- 21 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.,  
22 Hendriks, A. J.: Does upward seepage of River water and storm water runoff determine water quality of urban drainage system in  
23 lowland areas? A case study for the Rhine-Meuse delta, *Hydrol. Process*, 23, 3110-3120, 2009.
- 24 Vos, P.: Origin of the dutch coastal landscape: long-term landscape evolution of the Netherlands during the Holocene, described and  
25 visualized in national, regional and local palaeogeographical map series, Ph. D. thesis, Utrecht University, Utrecht, The  
26 Netherlands, 2015.
- 27 Wade, A. J., Palmer-Felgate, E. J., Halliday, S. J., Skeffington, R. A., Loewenthal, M., Jarvie, H. P., Bowes, M. J., Greenway, G. M.,  
28 Haswell, S. J., Bell, I. M., Joly, E., Fallatah, A., Neal, C., Williams, R. J., Gozzard, E., Newman, J. R.: Hydrochemical processes in  
29 lowland rivers: insights from in situ, high-resolution monitoring, *Hydrol Earth Syst Sc*, 16, 4323-4342, 2012.
- 30 [Wu J. and Malmstrom M. E.: Nutrient loadings from urban catchments under climate change scenarios: Case studies in Stockholm,](#)  
31 [Sweden, \*Sci Total Environ\*, 518-519, 393-406, 2015.](#)
- 32 [Yan R., Huang J., Li L., Gao J.: Hydrology and phosphorus transport simulation in a lowland polder by a coupled modeling system,](#)  
33 [\*Environ Pollut\*, 227, 613-625, 2017.](#)
- 34  
35  
36  
37

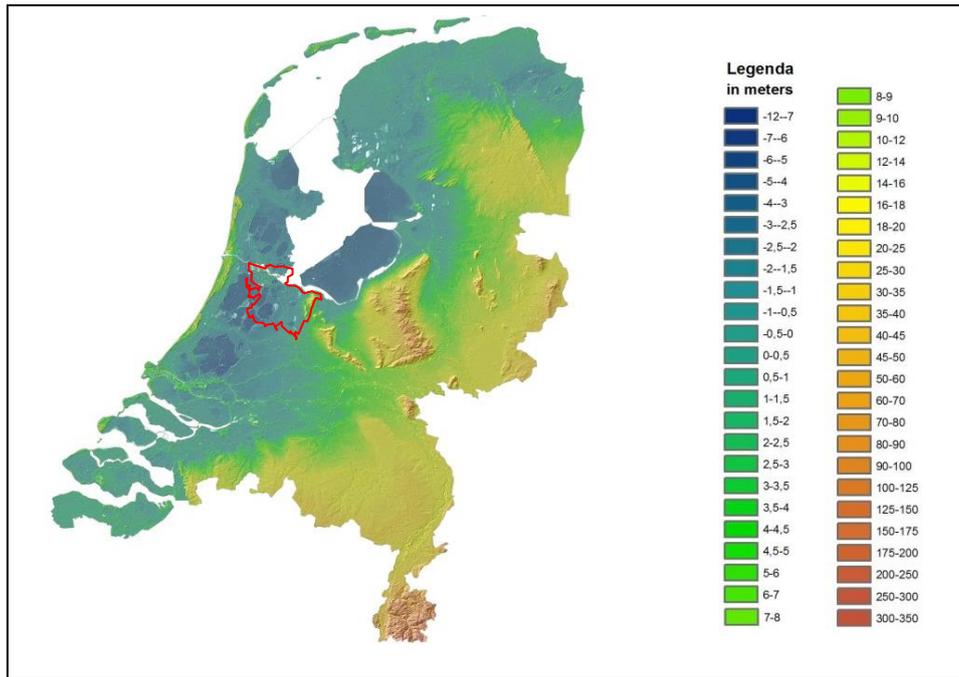


Figure 1: Location of the research area (red) projected on the elevation map of The Netherlands (elevations in meters above mean sea level (MSL))

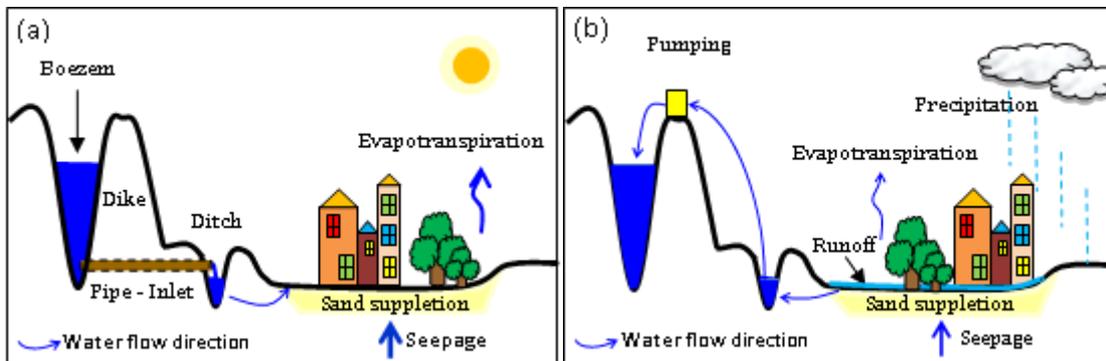
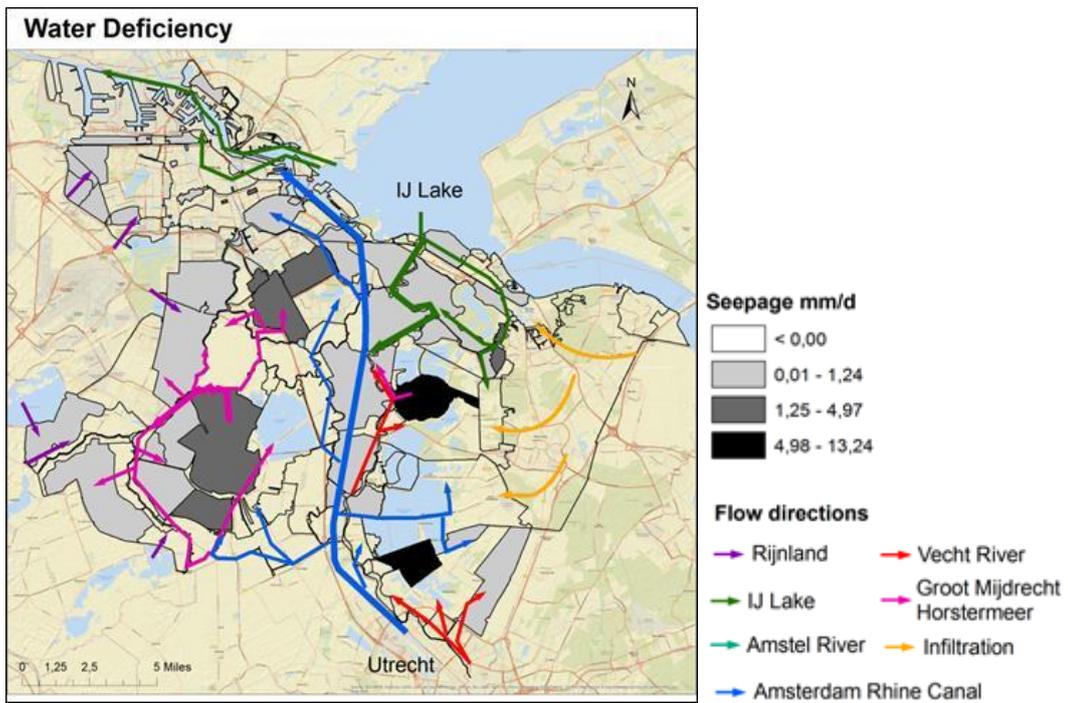
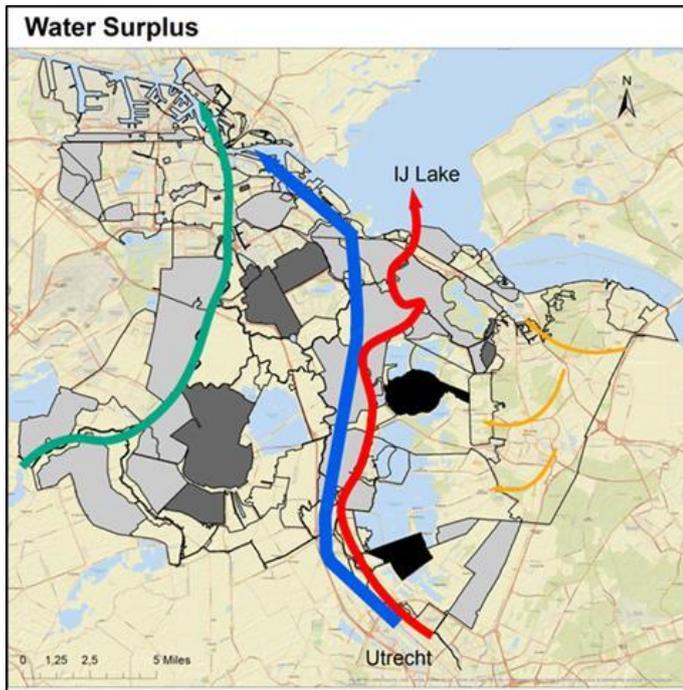


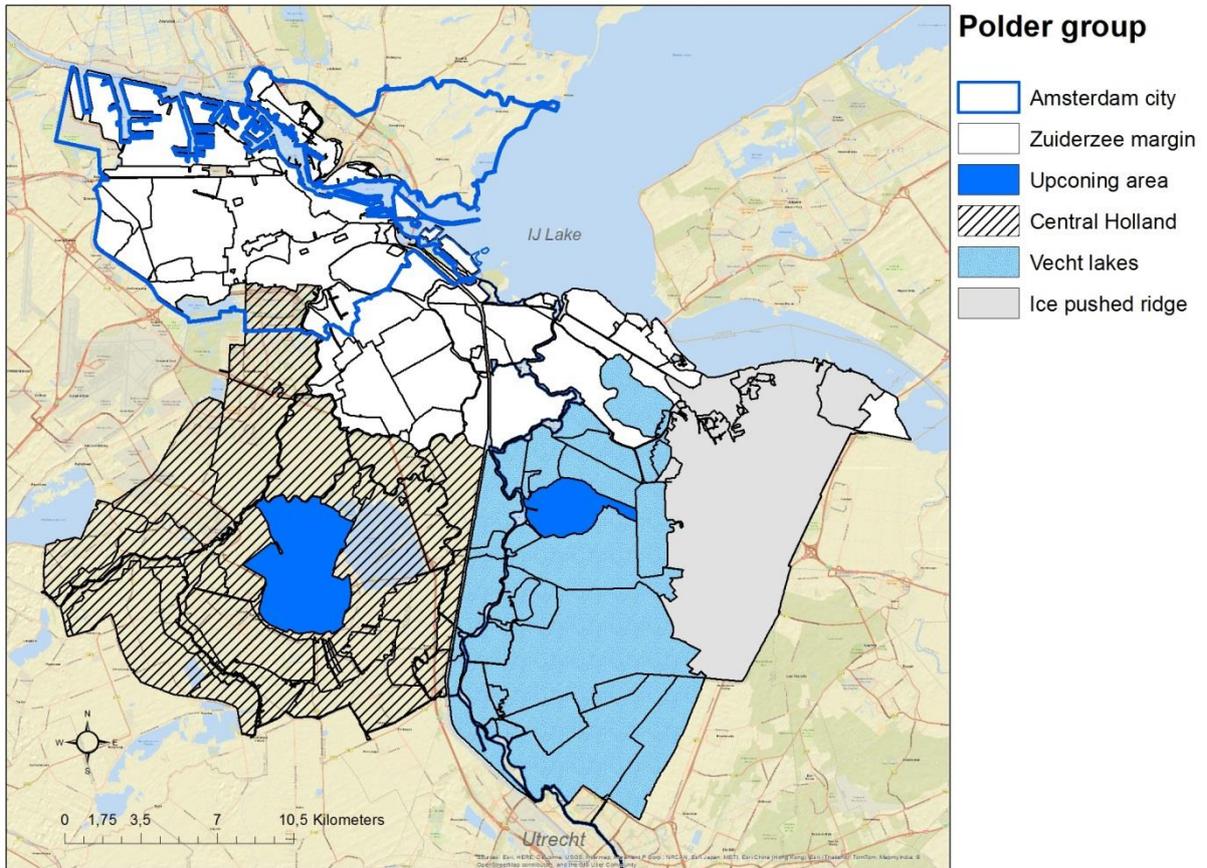
Figure 2: Conceptual model of water fluxes in a polder system in times of water deficiency (a) and surplus (b).



1  
2 **Figure 3: Flow directions of surface water in water surplus and water deficiency period**

3

1  
2  
3



4  
5  
6

**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.**

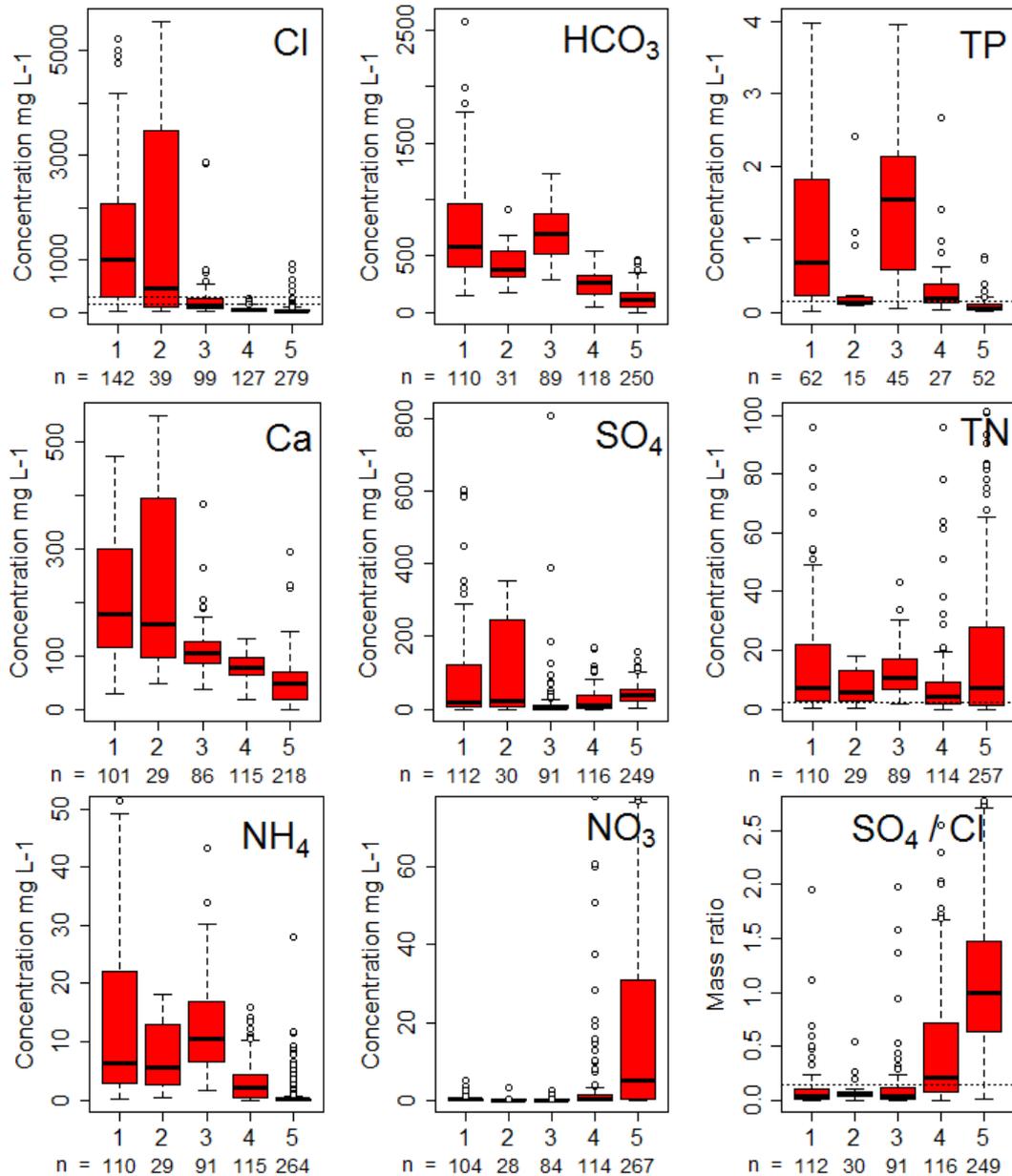
1

2

3

4

5



6 **Figure 5: Spatial variation of groundwater quality. 1-Zuiderzee margin, 2-Upcoming area (Groot Mijdrecht and Horstermeer), 3-**  
 7 **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**  
 8 **distribution of solutes in the five regions. The two horizontal dashed lines for Cl indicate fresh water (<150 mg L<sup>-1</sup>) and brackish**  
 9 **water (>300 mg L<sup>-1</sup>), respectively. Dashed lines represent EQSs for TN (2.4 mg L<sup>-1</sup>) and TP (0.15 mg L<sup>-1</sup>). The dashed line in the**  
 10 **SO<sub>4</sub>/Cl plot indicates the mass ratio of 0.14 in seawater (<0.14 indicates sulfate reduction; >0.14 indicates additional sources of**  
 11 **sulfate besides (diluted) seawater). Part of the outliers of TP, TN, NH<sub>4</sub>, NO<sub>3</sub> and SO<sub>4</sub>/Cl fell out of the ranges in the figures.**

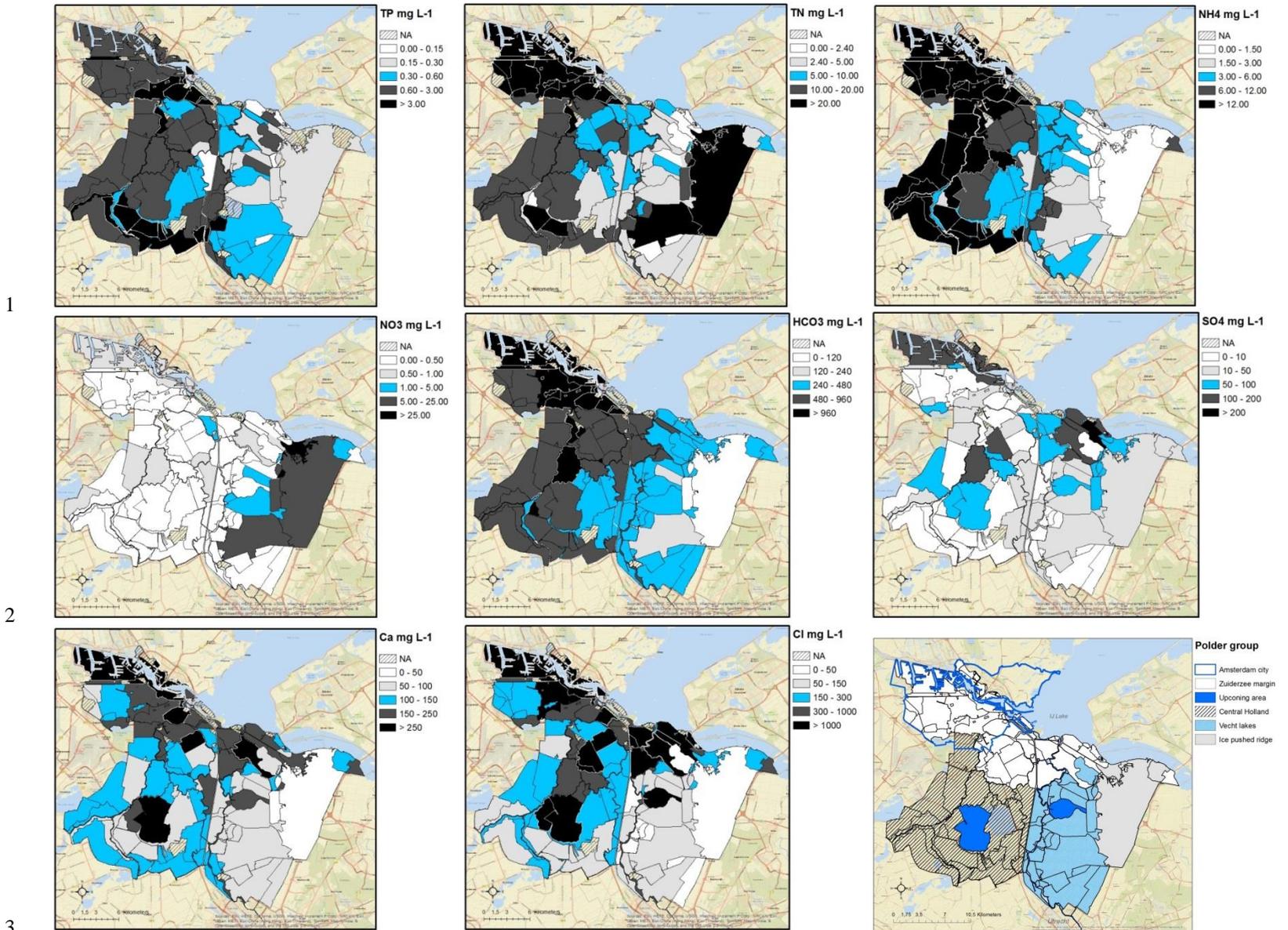
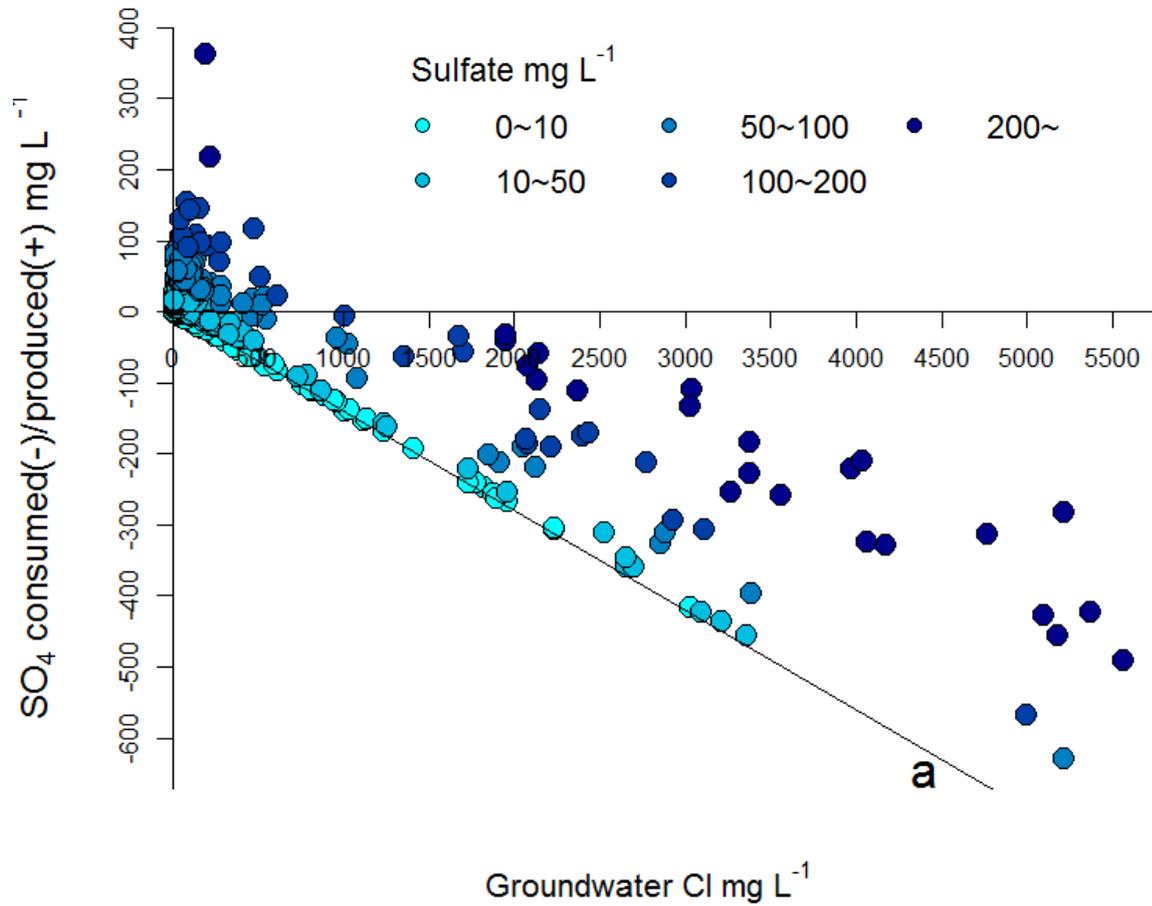


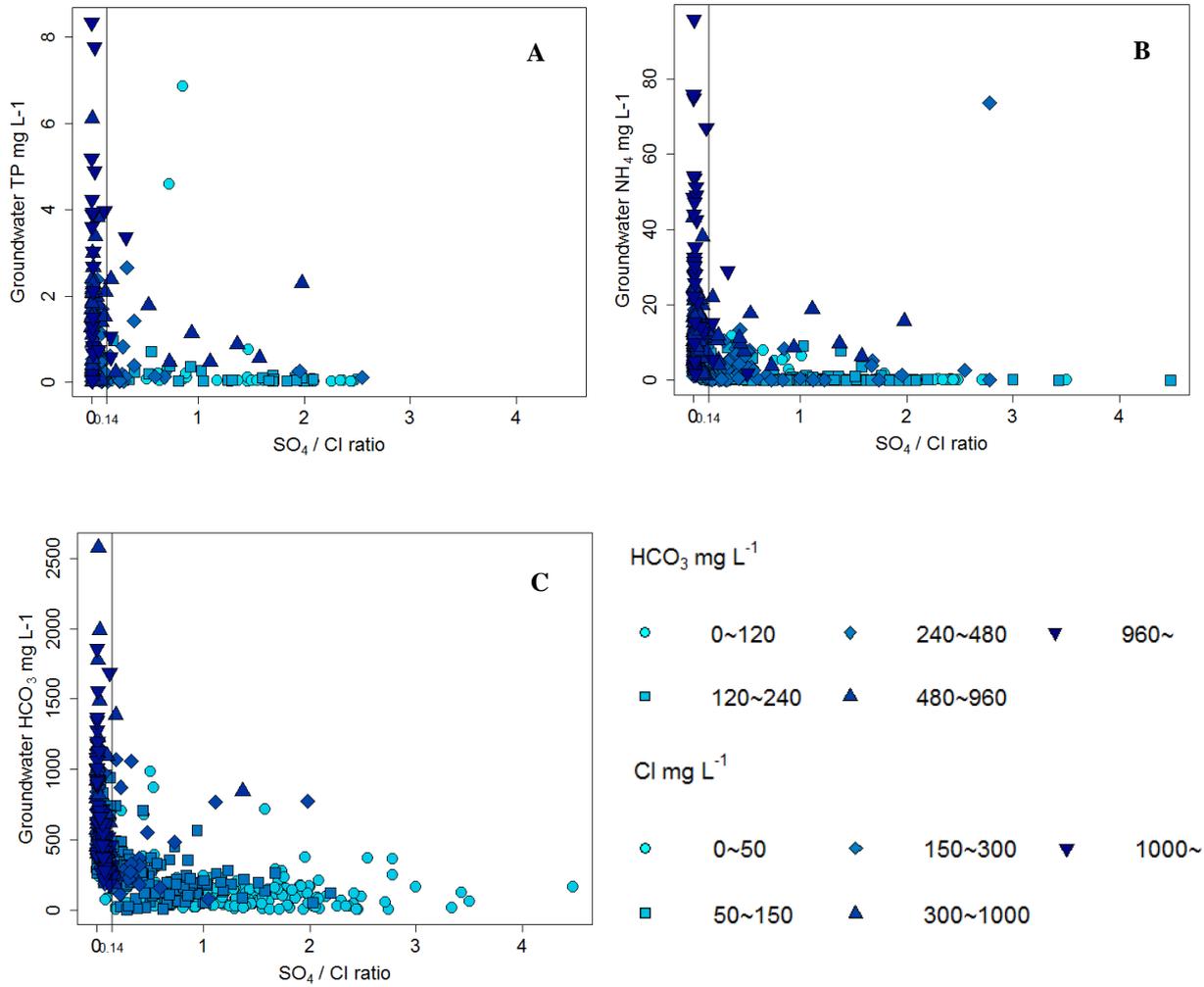
Figure 6: Average groundwater concentrations (mg L<sup>-1</sup>) per polder.

1  
2  
3  
4  
5



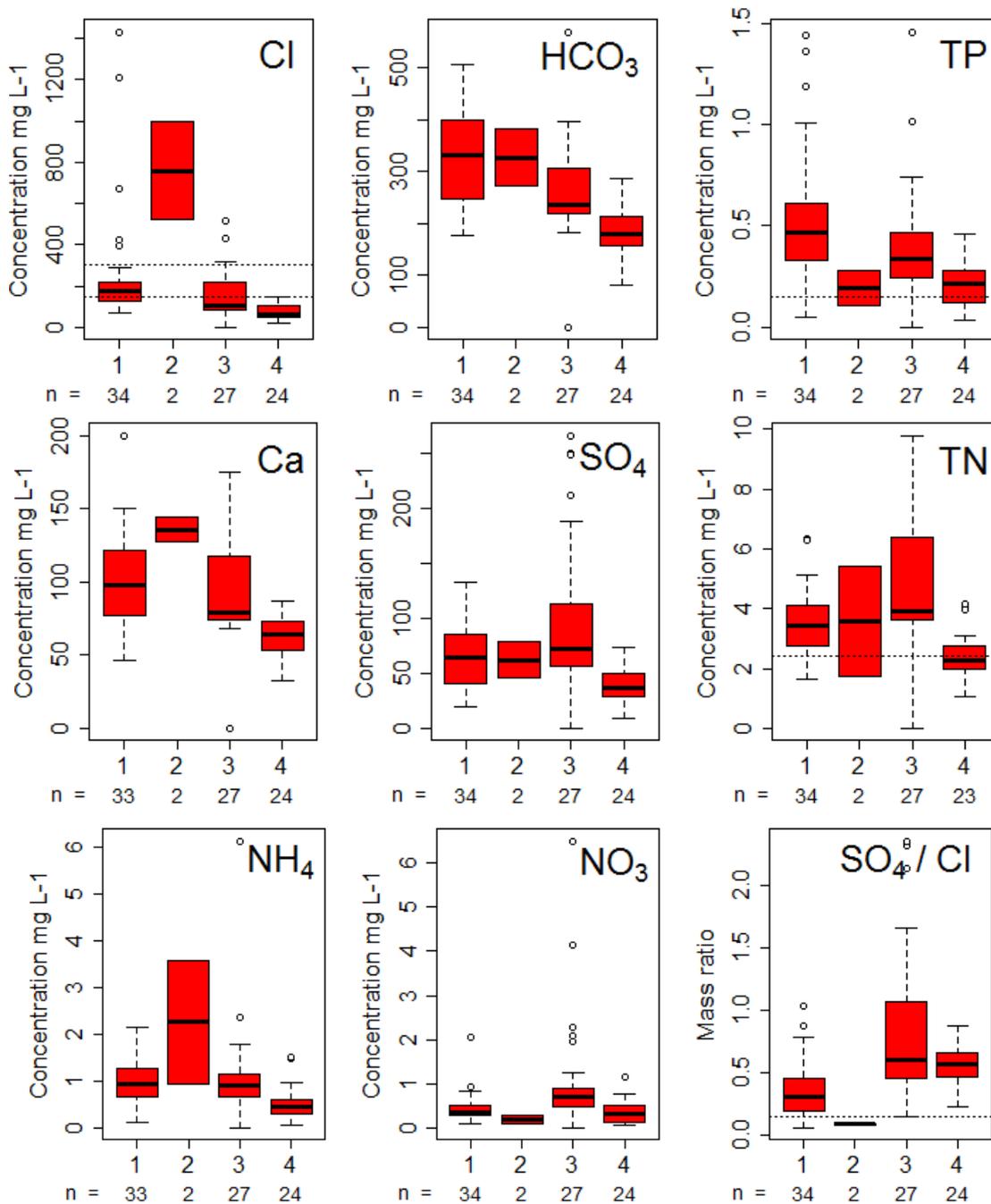
6  
7  
8

**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.**



1  
2  
3  
4  
5  
6  
7

**Figure 8: Groundwater nutrient (TP and NH<sub>4</sub>) concentrations with sulfate reduction (mass ratio SO<sub>4</sub>/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 HCO<sub>3</sub> concentration and in (C) by Cl concentration.**



1

2

3

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<sup>-1</sup>) and brackish water (>300 mg L<sup>-1</sup>), respectively. Dashed lines in TP and TN represent EQSs**  
 7 **for TN (2.4 mg L<sup>-1</sup>) and TP (0.15 mg L<sup>-1</sup>). The dashed line in the SO<sub>4</sub>/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).**

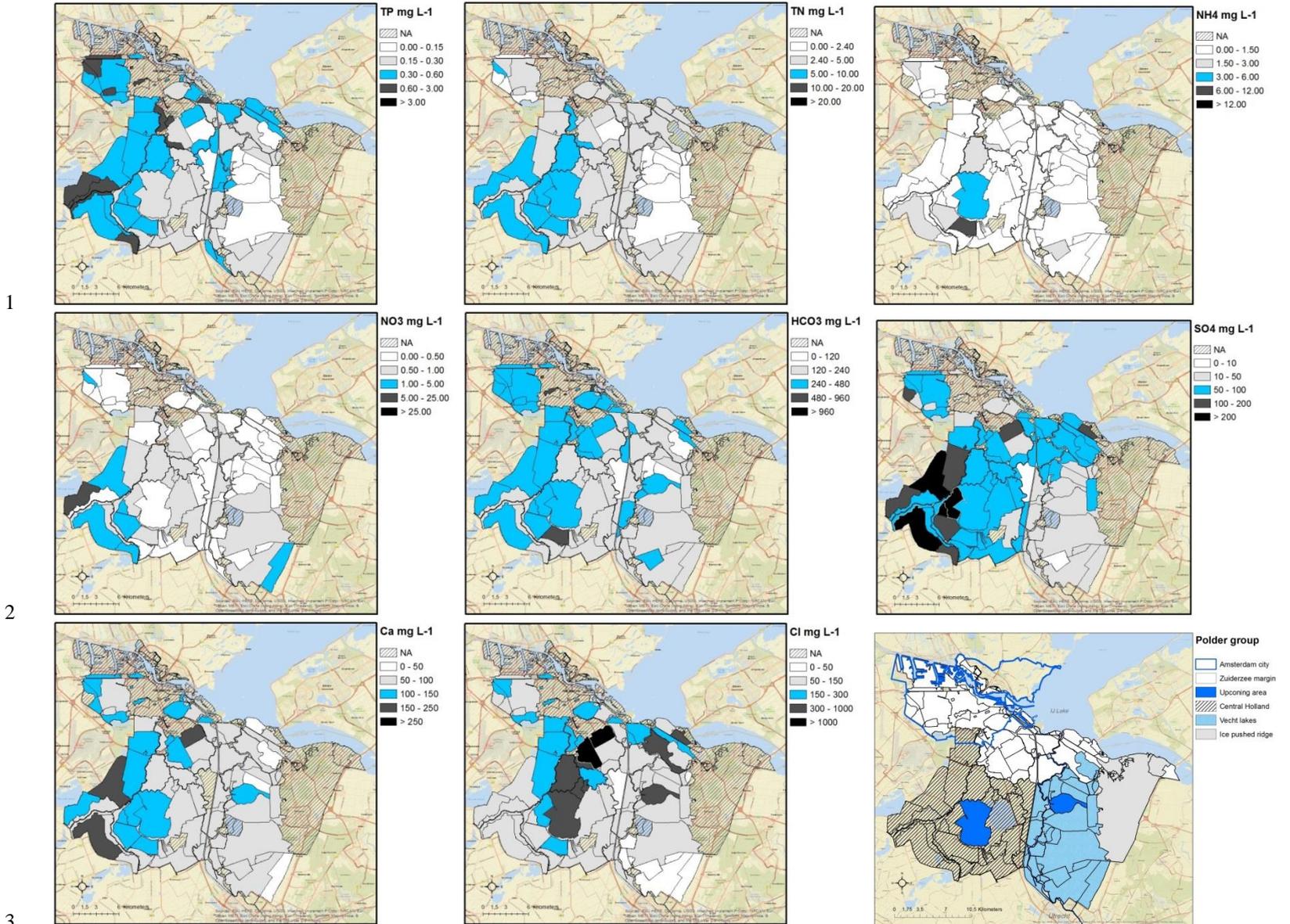


Figure 10: Discharge-normalized average concentrations (mg L<sup>-1</sup>) per polder

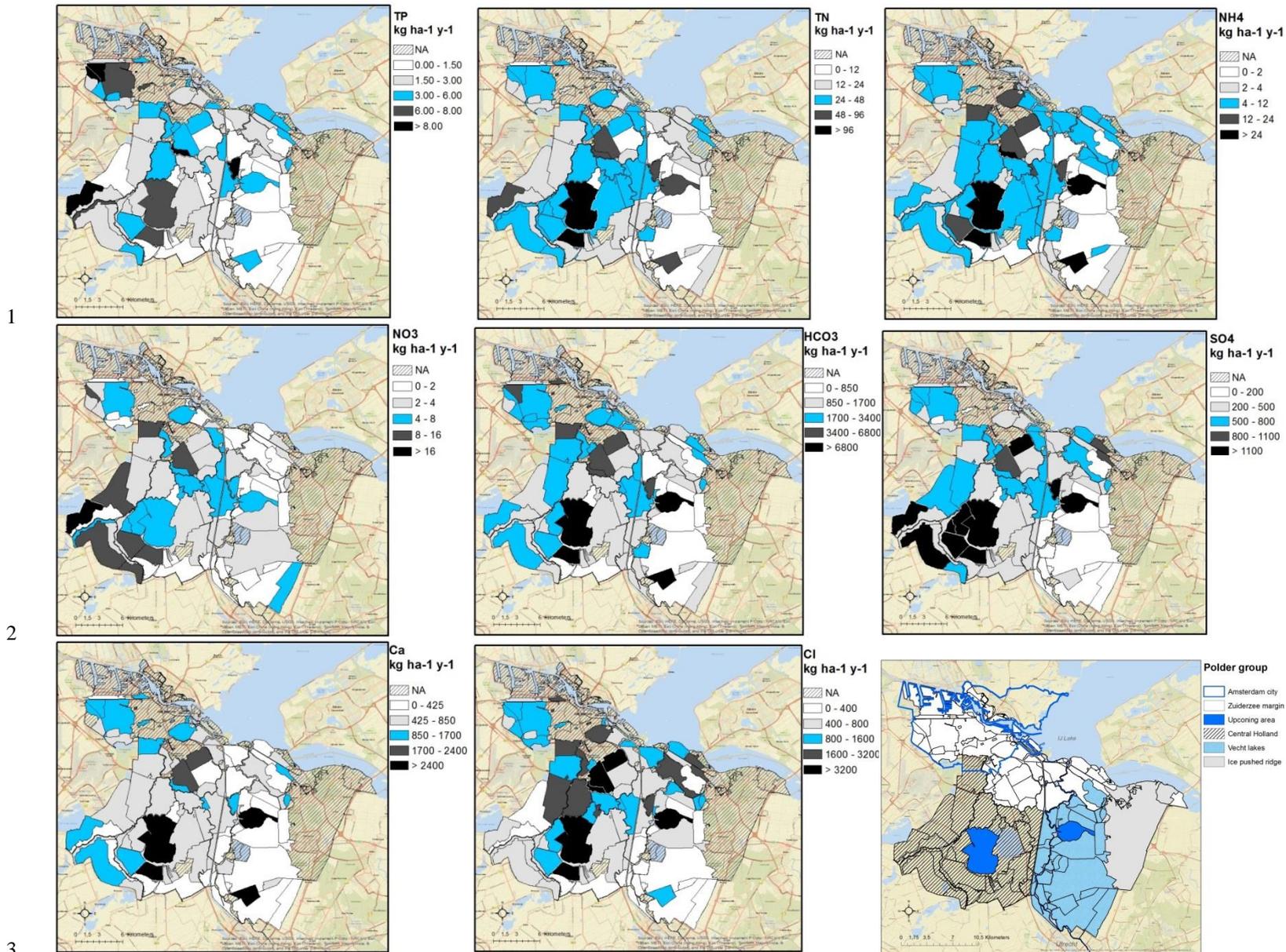
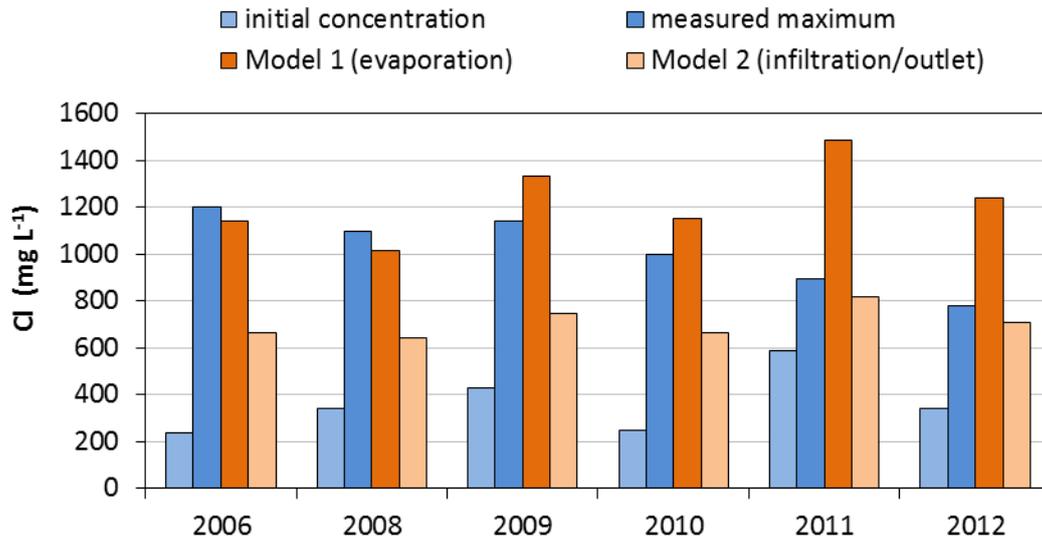


Figure 11: Surface water solute loads (average of 2010 to 2013) distribution maps in  $\text{kg ha}^{-1}\text{y}^{-1}$

1  
2  
3  
4  
5  
6  
7  
8



9

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 <sub>4</sub> GW	NO <sub>3</sub> GW	HCO <sub>3</sub> GW	SO <sub>4</sub> GW	Ca GW	Cl GW	TP SW	TN SW	NH <sub>4</sub> SW	NO <sub>3</sub> SW	HCO <sub>3</sub> SW	SO <sub>4</sub> SW	Ca SW	Cl SW
TP <sub>GW</sub>	1															
TN <sub>GW</sub>	0,665	1														
NH <sub>4</sub> <sub>GW</sub>	0,77	0,84	1													
NO <sub>3</sub> <sub>GW</sub>				1												
HCO <sub>3</sub> <sub>GW</sub>	0,68	0,63	0,82		1											
SO <sub>4</sub> <sub>GW</sub>	-0,46			0,41		1										
Ca <sub>GW</sub>					0,50		1									
Cl <sub>GW</sub>					0,48	0,40	0,77	1								
TP <sub>SW</sub>	0,49	0,51	0,60		0,64				1							
TN <sub>SW</sub>	0,45		0,44		0,52				0,59	1						
NH <sub>4</sub> <sub>SW</sub>			0,44		0,51				0,49	0,77	1					
NO <sub>3</sub> <sub>SW</sub>										0,57		1				
HCO <sub>3</sub> <sub>SW</sub>	0,57	0,55	0,64		0,68			0,41	0,63	0,47	0,67		1			
SO <sub>4</sub> <sub>SW</sub>										0,57		0,50		1		
Ca <sub>SW</sub>	0,59	0,54	0,63		0,71			0,41	0,55	0,56	0,64		0,88		1	
Cl <sub>SW</sub>					0,47		0,47	0,69	0,47	0,51			0,52	0,49	0,55	1
N input kg ha <sup>-1</sup> y <sup>-1</sup>																
P input kg ha <sup>-1</sup> y <sup>-1</sup>																
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<sup>-1</sup>

TP gw: groundwater TP concentration in mg L<sup>-1</sup>

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

	$n_1$	$n_2$	$n_3$	$R^2$	$R^2$ <i>with only seeping polders</i>	
$TP_{SW}$	+ $HCO_3_{GW}$	+ $NH_4_{GW}$		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	+ $NH_4_{GW}$	0.57	0.70	(13)
$SO_4_{SW}$	- Elevation	+ $SO_4_{GW}$		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	$CH_2O N_x P_y \rightarrow xN + yP + HCO_3^- + \text{other components}$	[2]
	$CH_2O N_x P_y + O_2 \rightarrow CO_2 + H_2O + xN + yP$	[3]
	$5CH_2O N_x P_y + 4NO_3^- \rightarrow 2N_2 + CO_2 + 4HCO_3^- + 3H_2O + 5xN + 5yP$	[4]
	$2CH_2O N_x P_y + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- + 2xN + 2yP$	[5]
Pyrite oxidation	$2CH_2O N_x P_y \rightarrow CH_4 + CO_2 + 2xN + 2yP$	[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]