



Effect of demand-driven fertilization on water chemistry

An assessment of Undersvik project

Charif Kanngo

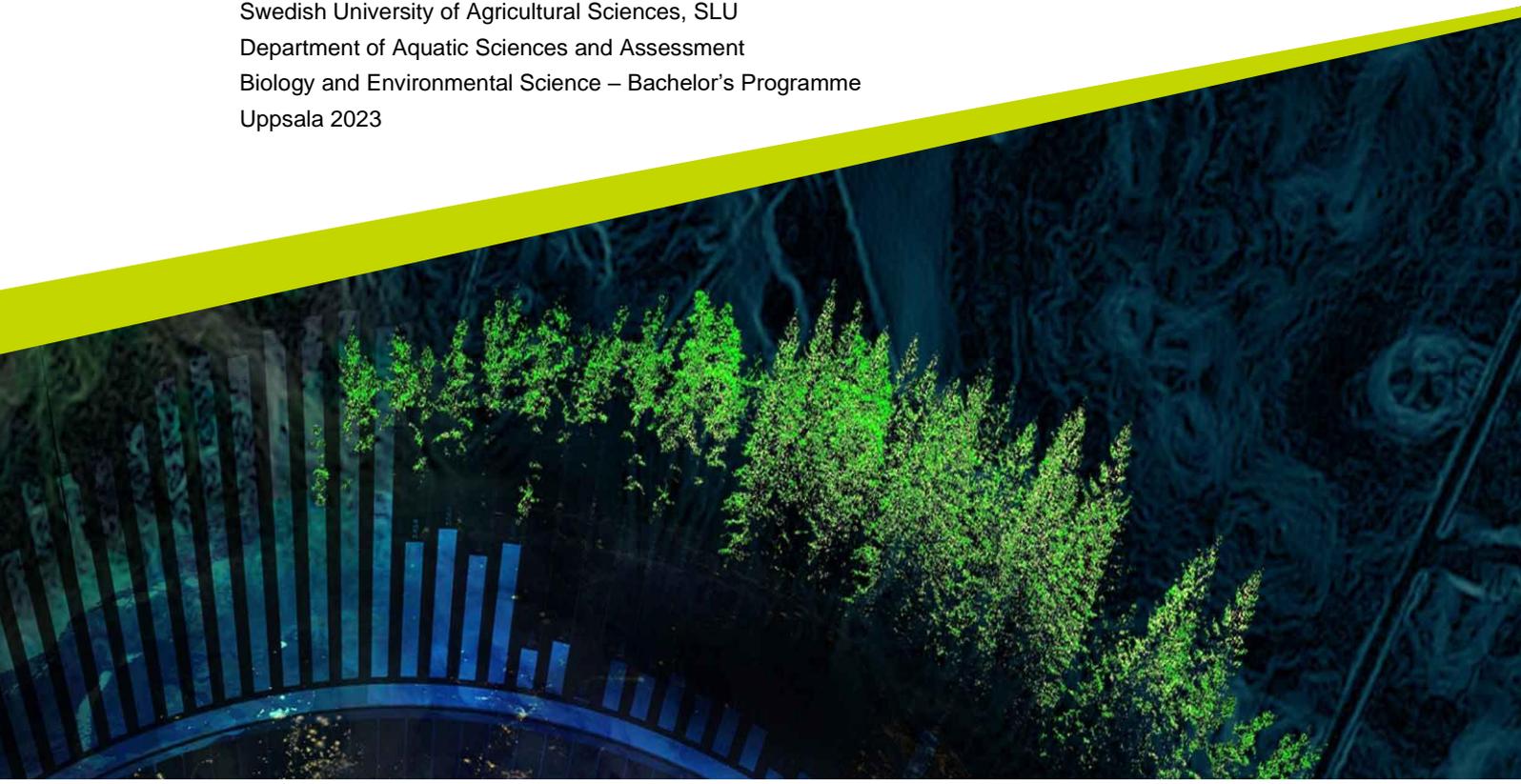
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Swedish University of Agricultural Sciences, SLU

Department of Aquatic Sciences and Assessment

Biology and Environmental Science – Bachelor's Programme

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Charif Kanngo

Supervisor: Kevin Bishop, Swedish University of Agricultural Sciences,
Department of Aquatic Sciences and Assessment

Examiner: Jens Fölster, Swedish University of Agricultural Sciences,
Department of Aquatic Sciences and Assessment

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Keywords: demand-driven fertilization, forestry, water chemistry, Undersvik, eutrophication, high-yield experimental forest

Swedish University of Agricultural Sciences
NJ Faculty
Department of Aquatic Sciences and Assessment

Abstract

Demand-driven fertilization is a silvicultural practice designed to enhance forest productivity while minimizing nutrient losses to aquatic systems. This study assesses the impact of demand-driven fertilization on water chemistry at the Undersvik High-Yield Experimental Forest in Sweden, analysing nutrient concentrations and exports from nine monitored sites. Using statistical models, including the Durbin-Watson test, Generalized Least Squares and Kruskal-Wallis's test, we examined temporal trends in dissolved organic carbon (DOC), nitrogen (NO_2+NO_3 , NH_4 , dissolved N), and phosphate (PO_4). The results indicate that DOC and PO_4 concentrations showed significant spatial variation, with treated sites displaying transient increases post-fertilization, particularly following the second application in June 2022. However, no clear long-term effects were detected, suggesting that hydrological variability may overshadow fertilization impacts. Continued monitoring is necessary to distinguish between fertilization-driven nutrient leaching and natural fluctuations. This study provides insights into the environmental trade-offs of intensive forestry and contributes to sustainable forest management discussions.

Keywords: demand-driven fertilization, forestry, water chemistry, Undersvik, eutrophication, high-yield experimental forest

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1. Introduction

Sweden is covered by 68% forest, of which 82% is productive forest land (Skogsdata 2023). This enables the forest products industry to be one of the leading ones in the country, and accounts for about 12% of the national total employment, exports, sales and added value (Royal Swedish Academy of Agriculture and Forestry 2015). Managed forestry in Sweden usually follows a cyclic program where you have four phases regeneration, thinning of young forest, thinning of older forest and final felling. This cycle can be everything between 50 years in the south with its nutrient enriched soil to 120 years in the north where the soil is poor in nutrients. Many managed forestry programs with bigger stand consider using fertilizer to enhance the forest growth rate, especially in the north.

Aquatic environments and soils in Sweden are affected by nutrient over enrichments e.g. eutrophication. Especially in southern Sweden where much of the land use is agricultural but is a problem all over the country. The run-off from areas where fertilizers are used is one of the sources to eutrophication (Naturvårdsverket 2008).

Eutrophication poses a major threat to biodiversity. In the Baltic Sea, the nutrient over enrichment promotes algae and plant growth whereupon excessive oxygen consumption that depletes the seafloor and may lead to changes in biodiversity (HELCOM). Much of the world's superior quality drinking water is found in forest areas in account for the composition and characteristics of the soil. The forest soils have the ability to filter the water that percolates through before it reaches the groundwater and then streams. That is why it is important to ensure the soil health because nutrient over enrichment may potentially affect drinking water adversely (Neary et al 2009, Futter et al 2010).

The Eutrophication problem is represented in Sweden's environmental quality goals "*No eutrophication*" where the Swedish government defines the problem and measures that may have a positive effect. Management programs derived to ensure the water quality are also in place such as the Water Framework Directive which is EU-directive with programs for assessment of bodies of water. And the UN convention HELCOM, the convention on the protection of the marine environment of the Baltic Sea area, also known as the Helsinki convention. The majority input to the Baltic Sea of total nitrogen (tot-N) and total phosphorus (tot-P) has diffuse

sources nearly 50% and 58%, respectively. 1.8% of the diffuse sources for tot-N is derived from managed forestry and for tot-P it is 0.5% (HELCOM 2017).

In Sweden, a common forestry measure is fertilization; approximately 30 000 ha of forest is fertilized yearly. The typical process of fertilization is to apply it one or two times of about 150 kg nitrogen (N) per hectare in 10-year intervals in the end before clear-cutting. This may increase the production approximately 10-20 cubic meters per hectare and fertilization occasion (Skogforsk 2020). Many forests in Sweden are nitrogen limited; this implies that much of the nitrogen that falls on the forest is absorbed by the vegetation or microorganisms and the levels of export are under 0.1 mg/l. As fertilization is applied under management the risk of saturating the soil with nutrients is prevalent. The once nutrient poor soil now enriched can have its nitrogen processes disturbed. For example, lowering the plant uptake or increase in mineralization which can potentially lead to nitrogen being accumulated or leached out.

Studies show that if nutrient supply is suited to the plant demand the risk of losing nutrients to water and soil is limited (Eriksson 1981; Ingestad 1981). Which is the basis of demand-driven fertilization. This is a concept that explores the idea of supplying plants with nutrients in an adjusted manner relative to the estimated growth rate. It was first evaluated 40 years ago by Ingestad, and this idea was inspiration for many other studies to come (Ingestad & Lund 1986; Ingestad 1987). One development of this original idea was demand-driven fertilization. How it works is that fertilization is given in smaller supplies repeatedly relative to the demand for the plant's growth during the first years. This is increased exponentially with time as the demand for the plant's growth and their biomass increases. In later years projects for managing forest growth with a demand-driven fertilization program have started up in Sweden, so-called *Behovsanpassad gödsling* (BAG). High-yield forests have been established, such as *Asa High-yield Experimental Forest*, where research can be conducted on relatively smaller areas before they are applied all through the country. With these types of experimental forests possibilities are introduced to research the environmental effects from intensive forestry. With a goal of increasing the forest growth by 50% and the financial benefits that may follow.

The purpose for this study is to evaluate the risk of nutrient losses (and thus eutrophication) in stream runoff when demand-driven fertilization is applied in operation forestry at a landscape scale (as opposed to a more limited experiment). To do this evaluation we will analyse data from nine sites at the Undersvik project. This to see if there is a difference in water chemistry between treated and untreated areas. And to find differences between the sites before and after the start of fertilization. The treatment being a demand driven fertilization program. The hypothesis of this study is that the treated sites will be different from the untreated sites and there is a difference before and after the first fertilization.

2. Material and methods

This study was conducted by processing field work data from Undersvik High - yield experimental forest and then analysing it in conjunction with a literary study.

2.1 Undersvik High-yield Experimental Forest

The project *Adaptivt Skogsbruk* (Adaptive Forestry) is a Swedish national project with the purpose to minimize uncertainties about atypical silvicultural measures through enhanced knowledge and dialogue. The project *Behovsanpassad gödsling* (demand-driven fertilization) is a part of this project. In this project *Sveaskog* and *Skogforsk* are establishing the high yield experimental forest Undersvik which is situated close to Simeå between Bollnäs and Ljusdal in middle of Sweden. Sveaskog being the company who owns the forest which in itself is owned by the Swedish government. And Skogforsk (the Forestry Research Institute of Sweden) is the central research body for the Swedish forestry sector and is financed jointly by the government and the members of the institute.

The project started in May 2019 with preparations. In 2020 coniferous analyses were made to identify possible nutrient limitations. Resulting in 155 hectares were chosen as suitable for treatment. A program was setup for the treatment year 1, 2, 4, 7 and 10 then every 10 years until clear cutting. Fertilizing with 100 kg N ha⁻¹ the first year and then 150 kg N ha⁻¹ every treatment.

For the analysis of whether the demand-driven fertilization has an effect on the water chemistry a monitoring program with sampling was started in July 2020 by SLU Umeå. For the best possible results nine sites were chosen (see figure 1). Three of the sites in an area where no fertilizer was applied, three sites with treatment and three extra sites who seemed suitable dependent on their locations. The frequency of the sampling was almost once every month.

The first fertilization was 27-28 of May 2021 and the second was 21-22 of June 2022. SLU Umeå lab has been analysing the data until April 2022 whereupon SLU Uppsala started the analysis from March 2022 overlapping two months.

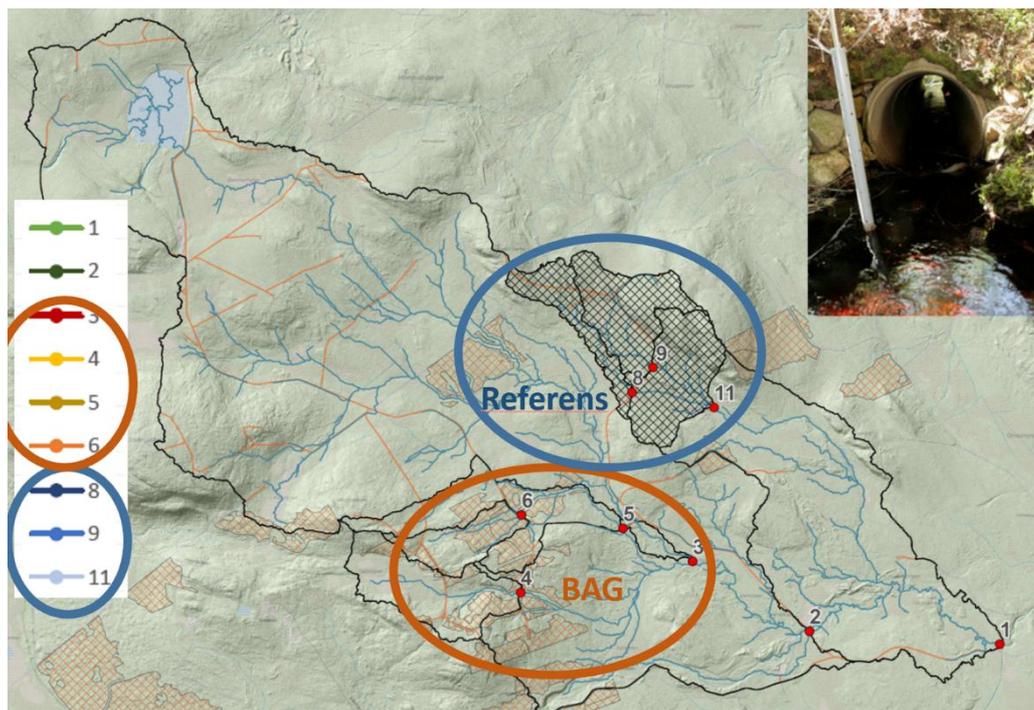


Figure 1. Map of catchment area with the nine sites where samples were made. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

2.2 Data analysis

For the data analysis the data processing programs RStudio and Excel was used. The raw data was made available and then put into excel or RStudio. The variables which were studied was dissolved organic carbon (DOC), dissolved organic nitrogen (dis-N), ammonium as mg nitrogen ($\text{NH}_4\text{-N}$), nitrite and nitrate as mg nitrogen ($\text{NO}_2+\text{NO}_3\text{-N}$) and phosphate as mg phosphor ($\text{PO}_4\text{-P}$). Total organic carbon (TOC) and total organic nitrogen (tot-N) was used instead of DOC and dis-N when the analysis switch to Uppsala lab.

In RStudio, the raw data was plotted against time so to visualise the changes of the parameters over time at each site. Since autocorrelation was suspected a Durbin-Watson test was conduct which is considered a satisfactory test for non-linear models (White 1992). From the results of the test two different models were considered to examine if there is a difference between the sites and before and after the first fertilization. For the cases where autocorrelation was encountered the model Generalized Least Squares (GLS) was used. GLS being a satisfactory model for accounting for autocorrelation (Beguiría & Pueyo 2009). For the remaining cases with no autocorrelation a Shapiro-Wilks test was conducted to assess if the variables are normally distributed. The Kruskal-Wallis test was used, since the data was not normally distributed, to assess the differences among the sites (McKight &

Najab 2010). And a post-hoc test was conducted to figure out what sites were statistically different from each other.

In Excel, the export was computed using flow data from the Swedish Metrological and Hydrological Institute (SMHI) and areal data for every site, the water flow for every site was calculated in litre per second. Values were interpolated for each variable, together with the water flow, this was used to determine the export per second which was then reconfigured into daily export and then further into total export, the later with pivot diagram. The monthly average was recomputed into kg ha^{-1} .

2.3 Literature study

To be able to analyse the data and background information a literary study has been conducted. The articles used were found using search engines like *Google Scholar* and *Web of Science*. The keywords used were eutrophication, Sweden, nitrogen leakage, forestry, demand-driven fertilization, organic carbon, phosphate, plant nutrition, plant growth etc. A fair part of grey literature has been used such as rapports from governmental agencies such as from Skogforsk, Naturvårdsverket (The Swedish Environmental Protection Agency), HELCOM, Havs- och vattenmyndigheten (Swedish Agency for Marine and Water Management). Other information was found through proper channels through the Undersvik project.

3. Results

In table 1 the average concentrations of each parameter for each site before the first fertilization are compiled. And in table 2 the average concentrations after the first fertilization are compiled. Before fertilization, DOC levels varied across sites, with Site 8 standing out due to its significantly higher concentration. After fertilization, DOC increased at all sites, with Site 8 increasing even more. Dis-N also saw a pronounced increase post-fertilization, most notably at Site 8, where it spiked from $480 \mu\text{g l}^{-1}$ to a striking $3058.1 \mu\text{g l}^{-1}$, and at Site 11, which rose from $328 \mu\text{g l}^{-1}$ to $1294.7 \mu\text{g l}^{-1}$. Similarly, Site 6 exhibited an extreme increase, with dis-N jumping from $405.4 \mu\text{g l}^{-1}$ to $2018.7 \mu\text{g l}^{-1}$. NH_4 concentration before fertilization were relatively low, except at Sites 5 and 8. However, after fertilization, NH_4 increased notably, with Site 6 experiencing the most dramatic jump, from just $7.6 \mu\text{g l}^{-1}$ to $378.3 \mu\text{g l}^{-1}$. NO_2+NO_3 levels were moderate before fertilization, generally between 6 and $31 \mu\text{g l}^{-1}$. However, after fertilization, there was an extreme spike at site 6, where levels surged from $6.1 \mu\text{g l}^{-1}$ to $2018.7 \mu\text{g l}^{-1}$, and at Site 5, which saw an increase from $14.7 \mu\text{g l}^{-1}$ to $387.6 \mu\text{g l}^{-1}$. PO_4 levels were relatively low before fertilization, with most sites under $5 \mu\text{g l}^{-1}$, except for Sites 4 and 8, which had slightly elevated concentrations. After fertilization, moderate increases were observed, particularly at Site 8 and site 4.

The differences between before and after are shown in figure 2. The difference in DOC and dis-N concentrations are statistically significant. In comparison the differences observed at NH_4 and NO_2+NO_3 are not statistically significant. The concentrations for PO_4 only sites 1 and 9 showed a statistical significance between before and after the first fertilization.

Table 1. Average concentrations before the first fertilization, of all parameters, at all sites. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Site	Site type	DOC ($\mu\text{g l}^{-1}$)	Dis-N ($\mu\text{g N l}^{-1}$)	NH ₄ -N ($\mu\text{g N l}^{-1}$)	NO ₂ +NO ₃ -N ($\mu\text{g N l}^{-1}$)	PO ₄ -P ($\mu\text{g P l}^{-1}$)
1	Outlet	16143	283,4	6,4	30,2	3,2
2	Flow station	15314	296,6	5,2	27,9	2,9
3	Untreated	14586	266,4	5,1	31,0	3,1
4	Untreated	20440	334,4	8,1	12,9	8,8
5	Untreated	21047	413,6	13,6	14,7	2,5
6	Untreated	19711	405,4	7,6	6,1	3,6
8	Treated	65850	480,0	17,8	14,2	7,7
9	Treated	25330	418,0	9,4	23,6	4,9
11	Treated	21125	328,0	8,1	22,2	3,8

Table 2. Average concentrations after the first fertilization, of all parameters, at all sites. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Site	Site type	DOC ($\mu\text{g l}^{-1}$)	Dis-N ($\mu\text{g N l}^{-1}$)	NH ₄ -N ($\mu\text{g N l}^{-1}$)	NO ₂ +NO ₃ -N ($\mu\text{g N l}^{-1}$)	PO ₄ -P ($\mu\text{g P l}^{-1}$)
1	Outlet	22981	717,4	12,1	46,9	4,5
2	Flow station	20505	634,5	8,1	48,2	3,4
3	Untreated	20043	724,5	7,4	47,3	4,1
4	Untreated	30687	643,4	14,4	35,3	12,1
5	Untreated	27513	805,5	28,2	387,6	2,8
6	Untreated	24640	596,4	378,3	2018,7	4,3
8	Treated	76886	3058,1	20,8	12,9	17,9
9	Treated	31807	636,0	13,3	29,3	8,2
11	Treated	29853	1294,7	13,2	19,3	6,3

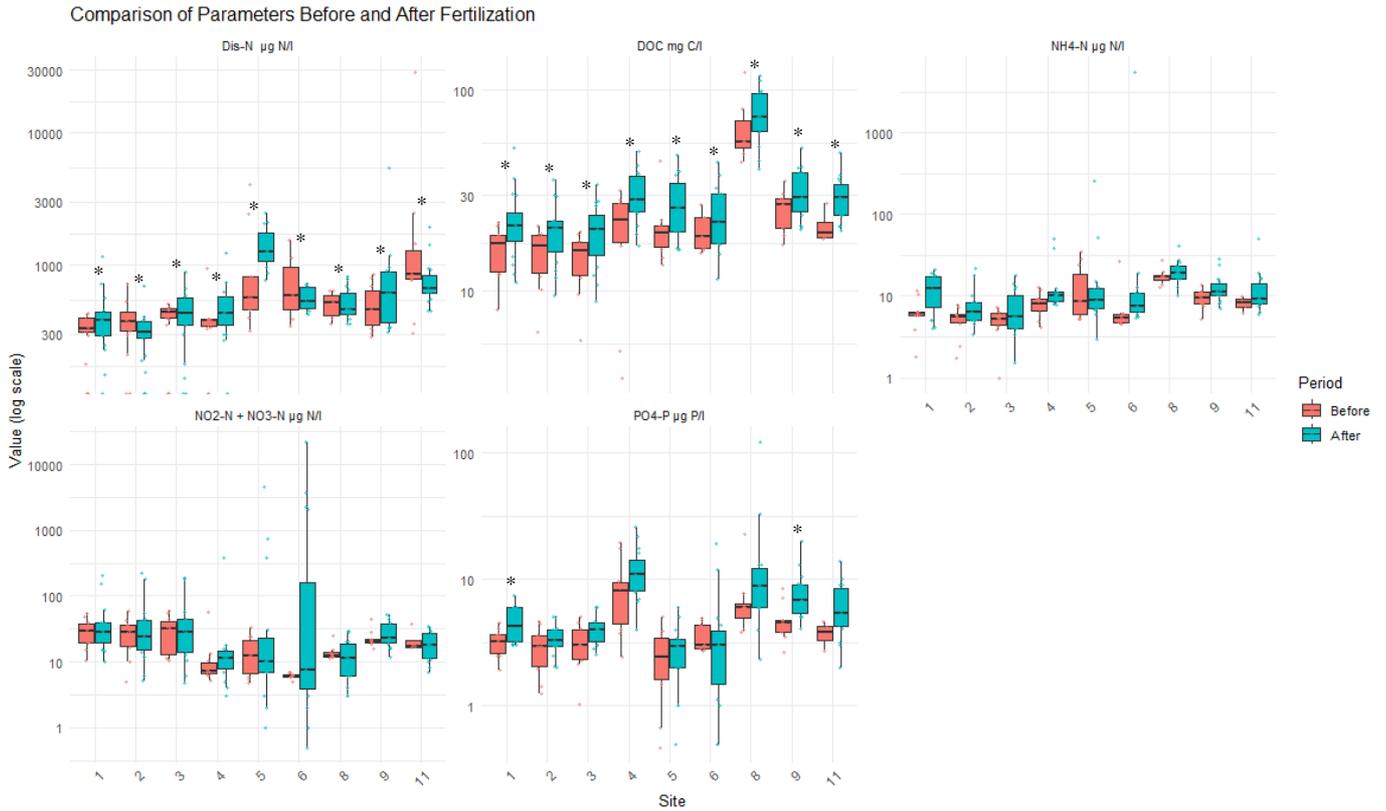


Figure 2 Boxplot of average concentrations at each site before and after first fertilization. Star indicating if the difference before and after the first fertilization is statistically significant. The y-axis is on a logarithmic scale to enhance visibility of values after fertilization.

Table 3 compiles the total transport of each parameter for each site before the first fertilization, and table 4 compiles them after the first fertilization. Before fertilization, exports of DOC were notably higher in treated sites (e.g., 199 kg/ha at Site 8) compared to untreated and control sites, which ranged between 27 and 69 kg/ha. Exports of Dis-N followed a similar trend, with treated sites exhibiting higher concentrations (3.53 kg/ha at Site 8) than untreated sites, which remained around 1.1–1.24 kg/ha. NH₄-N and NO₂+NO₃-N values were generally low across all sites, with minor variations. The exports of PO₄-P were relatively uniform, with slight increases at certain untreated sites (e.g., 0.023 kg/ha at Site 4).

After fertilization, the export of DOC declined across all sites, with the most substantial drop in treated sites (e.g., from 199 to 153 kg/ha at Site 8). Dis-N also decreased at most locations, except for Site 6, where it rose sharply from 1.24 to 1.99 kg/ha. The exports of NH₄-N remained mostly stable, except for a spike at Site 6 (from 0.02 to 0.14 kg/ha). The most striking change occurred in NO₂+NO₃-N at Site 6, increasing from 0.08 to 0.93 kg/ha. Meanwhile, PO₄-P showed minor fluctuations but remained within a similar range.

Overall, fertilization appears to have led to a general reduction of the exports of DOC and Dis-N, except for localized increases in nitrogen forms at Site 6.

Table 3. Total export of each parameter based on flow data, interpolated values and area of catchment for each site, before the first fertilization. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Site	Site type	DOC (kg/ha)	Dis-N (kg/ha)	NH4-N (kg/ha)	NO2+NO3-N (kg/ha)	PO4-P (kg/ha)
1	Outlet	59	1.24	0.02	0.1	0.011
2	Flow station	57	1.16	0.02	0.09	0.01
3	Untreated	54	1.11	0.02	0.11	0.01
4	Untreated	69	1.1	0.03	0.03	0.023
5	Untreated	61	1.21	0.04	0.05	0.009
6	Untreated	63	1.24	0.02	0.08	0.011
8	Treated	199	3.53	0.05	0.04	0.019
9	Treated	85	1.59	0.03	0.08	0.013
11	Treated	27	0.6	0.01	0.03	0.004

Table 4. Total export of each parameter based on flow data, interpolated values and area of catchment for each site, after the first fertilization. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Site	Site type	DOC (kg/ha)	Dis-N (kg/ha)	NH4-N (kg/ha)	NO2+NO3-N (kg/ha)	PO4-P (kg/ha)
1	Outlet	50	1.09	0.03	0.08	0.010
2	Flow station	43	0.92	0.02	0.08	0.008
3	Untreated	42	0.87	0.02	0.08	0.009
4	Untreated	62	1.04	0.04	0.03	0.023
5	Untreated	50	1.16	0.04	0.20	0.006
6	Untreated	50	1.99	0.14	0.93	0.006
8	Treated	153	2.57	0.04	0.03	0.021
9	Treated	67	1.28	0.03	0.06	0.015
11	Treated	62	1.21	0.03	0.04	0.012

After conducting the Durbin-Watson test the conclusion that all parameters except PO₄ showed autocorrelation (see appendix). All the parameters' data was put through the GLS model except the data for PO₄. This data was tested using the Kruskal-Wallis's test. Since the Kruskal-Wallis's test showed significant differences between the groups ($p\text{-value} = 2.2 \times 10^{-16}$) a post-hoc test was conducted, Dunn's test. The GLS results (see appendix) comparison for each of the parameter and the results from Dunn's test for PO₄ (see appendix, table A14) are presented in

table 3. The results showed that when it comes to DOC concentrations Site 8 is the most distinct and site 9 shows moderate differences from 2 and 3. The concentrations of PO₄ at site 4 and site 5 are the most distinct, although the treated sites 8 and 9 also displayed some differences. However, the remaining parameters showed no significant differences between sites.

4. Discussion

The results of this study gave an insight to the understanding of the effects of demand-driven fertilization. The first fertilization which took place 27-28 of May 2021 may have influenced the water chemistry. When the treated sites are compared to the control sites a similar trend for all variables materializes. From the end of May 2021, the average concentrations in the water and total export increases for all sites (see tables 1, 2, 3, 4) e.g. no apparent difference between the treated and the untreated site. The profound increase is most evident with the nitrogen concentrations, as can be seen in the figures A2, A3 and A4 in the appendix. The PO_4 concentrations did only increase moderately (see appendix, figure A5) in relations to the nitrogen concentrations which could indicate a more limited mobility of phosphorus or retention in the system. This increase may be a short-term cause by the fertilization which saturates the soil with nutrients and may cause leaching to surface water (Eriksson et al. 2019).

It may also be caused by seasonal variation in water flow where the leaching flux is increased because of snowmelts whereupon spring flood occurs (see appendix, figure A6). The latter is more probable because it follows trends of other studies of seasonal patterns such as Landon et.al. (2004).

After the second fertilization, which took place 21-22 of June 2022, there is still no major differences between the treated and untreated sites. DOC levels (see appendix, figure A1), across the sites, experience similar patterns with all sites having an increase. The dis-N concentrations are a little different having similar patterns at all sites except the treated sites 8 and 11, which clear spikes in levels of dis-N can be observed (see appendix, figure A2) Similar spikes can be observed at several sites for the rest of the nutrients not only at sites 8 and 11. E.g. the NH_4 concentrations at sites 4, 5 and 6 (see appendix, figure A3), or the concentrations of NO_2+NO_3 at all of the untreated sites (see appendix, figure A4) These spikes could be a sign that the fertilization in fact did have an effect on the water chemistry. The elevated values may also be caused by other factors such as flow and turbidity which with higher flow and suspended particles may reveal itself as these heightened values. The latter is more probable since the spikes were not only at the treated sites but at the untreated sites as well. Additionally, Field observations of high flow and turbidity were made and in figure A6 (in the appendix) the water flow was high in the period around the second fertilization.

The statistical tests showed that there are some differences between some of the treated sites and the control sites. The different sites concentrations of DOC and PO₄ had a significant difference between some of the treated sites and the control sites. However, there was no significant difference when it came to the other parameters that are included in this study. In contrast, earlier studies show that fertilization in the first year on forestland in Sweden should have an impact on nutrient load to surrounding surface water (Melin & Nõmmik 1988; Fröberg et al. 2013; Lundin & Nilsson 2014). When viewing the trends of the nitrogen nutrients especially for NO₂+NO₃ (see appendix, figure A4) there is a visible trend difference in the treated and untreated sites. This visual difference in combination with the studies conducted on similar matters show that some differences should have been detected by the statistical tests and models. This could be an uncertainty with the model, either in the handling of autocorrelation issues, sample size being too small or the variance being too large. The data has a large variance with a few outliers (see figure 2) this could be why the big changes in the average concentrations of the nutrients cannot be associated with statistically significant difference. The GLS is a proven powerful tool for solving similar problems but the need for large sample size to acquire better resolution could be why the differences were not registered by the model (Menke 2015).

To determine if the elevated values is a cause of short-term effects from fertilization or if it is caused by the much higher flow intensive sampling should be conducted following the days of the fertilization. With more replicates a statistical significance could be determined for this scenario.

Site 5 and site 6 have a couple of variables that may be telling what is more probable. The PO₄-P, NO₂+NO₃-N and dis-N follow what is typical for forest streams they have generally low nutrients, but here an extreme value for the months shortly after the fertilizations appear. This may prelude to that a short-term effect is in fact prevalent. More replicates in the coming period after the fertilization is still needed to be sure if it is the cause for the extreme values or an effect of hydrological variability.

For the long-term effects of the demand-driven fertilization it is hard to determine anything probable at this point in time. The time series data that is present is about three years which is just too short. The number of outliers decrease with the increase of length of time that is studied. A shorter time series shows more erratic results than longer which show more consistency in the results. Climatic variability influences the time series when it has a small window. Therefore, time series of this length is signifying this type of variability rather than fundamental system behaviour. To enable a true assessment of the long-term effects of the demand driven fertilization on water chemistry a period of at least 12 years with constant monitoring must be in place. This is the time which is required to

reasonably conclude that the variation in hydrology between the years is negligible (Howden et al. 2011).

4.1 Conclusion

For continuing work with assessing and analysing the effects of demand-driven fertilization on water chemistry at Undersvik high-yield experimental forest two main conclusions has been derived. Firstly, it is hard to derive if the variation in the nutrient's concentrations is caused by the fertilization or if it is caused by climatic variability without more replicants after each fertilization and a longer time period. So, moving forward a suggestion is to add more replicates and continue monitoring during the project. When sufficient data has been acquired, apply once more a statistical model to determine if the differences between the sites and before and after the fertilization has a true statistical significance.

Appendix

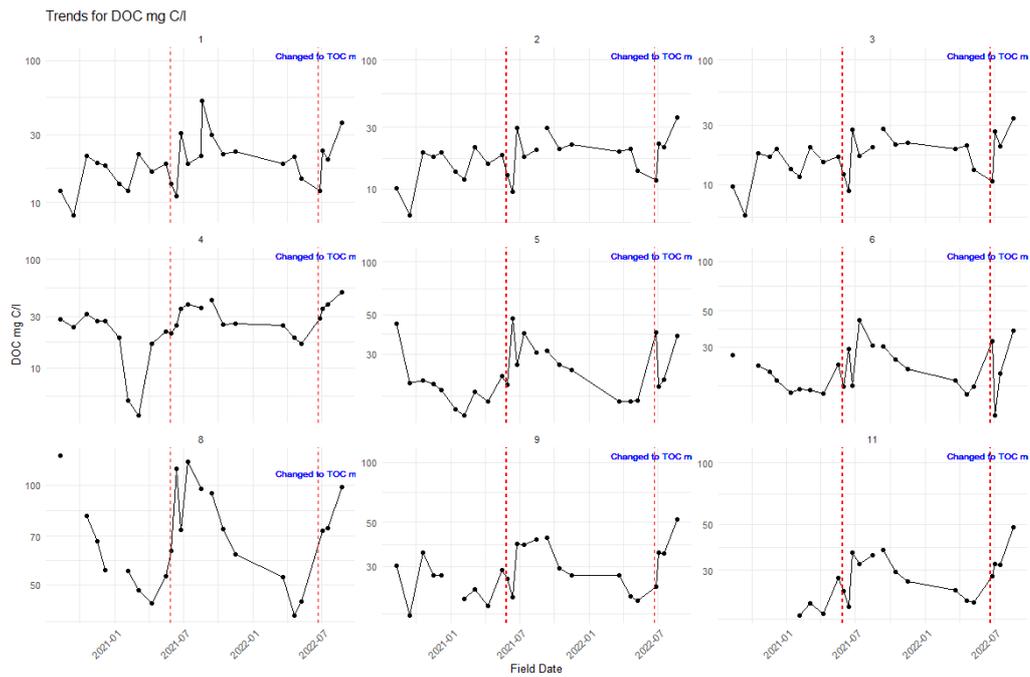


Figure A1. DOC mg C/l plotted against time for each site. A logarithmic scale so to visualise the shifts of the data. The read dotted line indicates the first and the second fertilization event. An annotation at the end of the time series 2022-04-20 to indicate the shift from DOC mg C/l to TOC mg C/l. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Table A1. Results of Durbin-Watson test of DOC mg C/l. Each site with correlating DW and p-value as well as interpretation of results into the presence of autocorrelation. $\alpha=0.05$

Site	DW	p-value	Autocorrelation
1	1.52	0.07	No
2	1.73	0.18	No
3	1.81	0.24	No
4	0.59	3.42×10^{-6}	Strong positive
5	1.51	0.07	No
6	1.70	0.16	No
8	0.86	0.0005	Strong positive
9	1.08	0.004	Strong positive
11	0.89	0.001	Strong positive

Table A2. Results from generalized least squares model. To evaluate if there is a different in DOC mg C/l between sites, while considering the strong positive autocorrelation. $\alpha=0.05$

Contrast	p-value
Site1-Site2	1.000
Site1-Site3	1.000
Site1-Site4	1.000
Site1-Site5	1.000
Site1-Site6	1.000
Site1-Site8	< 0.0001
Site1-Site9	0.1878
Site1-Site11	0.9216
Site2-Site3	1.000
Site2-Site4	0.4093
Site2-Site5	1.000
Site2-Site6	1.000
Site2-Site8	< 0.0001
Site2-Site9	0.0299
Site2-Site11	0.2082
Site3-Site4	0.2462
Site3-Site5	1.000
Site3-Site6	1.000
Site3-Site8	< 0.0001
Site3-Site9	0.0161
Site3-Site11	0.1259
Site4-Site5	1.000
Site4-Site6	1.000
Site4-Site8	< 0.0001
Site4-Site9	1.000
Site4-Site11	1.000
Site5-Site6	1.000
Site5-Site8	< 0.0001
Site5-Site9	1.000
Site5-Site11	1.000
Site6-Site8	< 0.0001
Site6-Site9	1.000
Site6-Site11	1.000
Site8-Site9	< 0.0001
Site8-Site11	< 0.0001
Site9-Site11	1.000

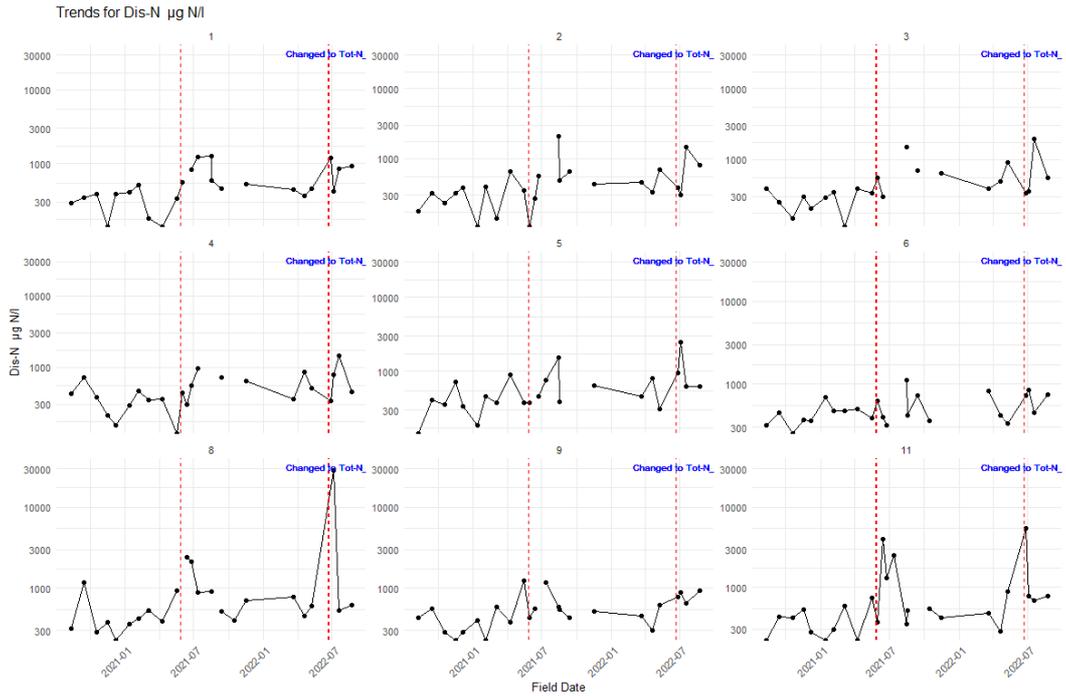


Figure A2. Dis-N $\mu\text{g N/l}$ plotted against time for each site. the scale is logarithmic so to visualise the shifts of the data. The read dotted line indicates the first and the second fertilization event. An annotation at the end of the time series 2022-04-20 to indicate the shift from dis-N $\mu\text{g N/l}$ to tot-N $\mu\text{g N/l}$. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Table A3. Results of Durbin-Watson test of dis-N $\mu\text{g N/l}$. Each site with correlating DW and p-value as well as interpretation of results into the presence of autocorrelation. $\alpha=0.05$

Site	DW	p-value	Autocorrelation
1	1.22	0.01	Strong positive
2	1.98	0.39	No
3	2.39	0.75	No
4	1.87	0.29	No
5	2.14	0.55	No
6	2.66	0.93	Slight negative
8	2.34	0.72	No
9	1.90	0.31	No
11	2.01	0.42	No

Table A4. Results from generalized least squares model. To evaluate if there is a different in dis-N μ g N/l between sites, while considering the strong positive autocorrelation. $\alpha=0.05$

Contrast	p-value
Site1-Site2	1.000
Site1-Site3	1.000
Site1-Site4	1.000
Site1-Site5	1.000
Site1-Site6	1.000
Site1-Site8	0.6496
Site1-Site9	1.000
Site1-Site11	1.000
Site2-Site3	1.000
Site2-Site4	1.000
Site2-Site5	1.000
Site2-Site6	1.000
Site2-Site8	0.5346
Site2-Site9	1.000
Site2-Site11	1.000
Site3-Site4	1.000
Site3-Site5	1.000
Site3-Site6	1.000
Site3-Site8	0.6804
Site3-Site9	1.000
Site3-Site11	1.000
Site4-Site5	1.000
Site4-Site6	1.000
Site4-Site8	0.6139
Site4-Site9	1.000
Site4-Site11	1.000
Site5-Site6	1.000
Site5-Site8	1.000
Site5-Site9	1.000
Site5-Site11	1.000
Site6-Site8	0.5941
Site6-Site9	1.000
Site6-Site11	1.000
Site8-Site9	0.6751
Site8-Site11	1.000
Site9-Site11	1.000

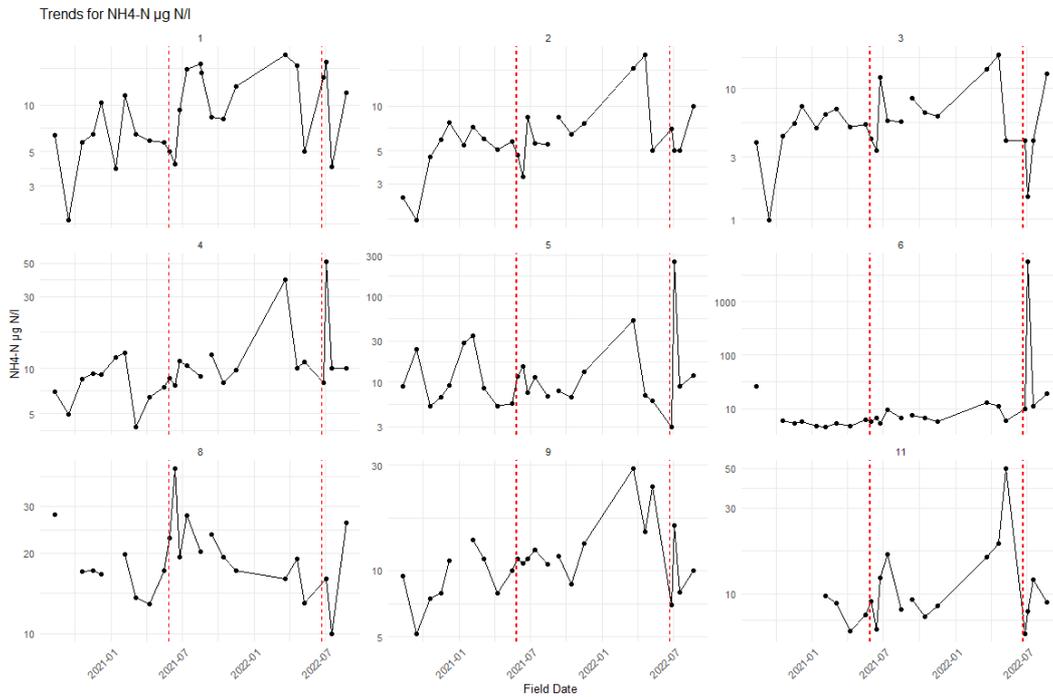


Figure A3. $\text{NH}_4 \mu\text{g N/l}$ plotted against time for each site. the scale is logarithmic so to visualise the shifts of the data. The read dotted line indicates the first and the second fertilization event. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Table A6. Results of Durbin-Watson test of $\text{NH}_4 \mu\text{g N/l}$. Each site with correlating DW and p-value as well as interpretation of results into the presence of autocorrelation. $\alpha=0.05$

Site	DW	p-value	Autocorrelation
1	1.64	0.12	No
2	1.36	0.03	Strong positive
3	1.56	0.09	No
4	2.53	0.88	Slight negative
5	2.38	0.77	No
6	2.31	0.71	No
8	1.69	0.16	No
9	2.00	0.41	No
11	2.00	0.39	No

Table A7. Results from generalized least squares model. To evaluate if there is a different in NH₄ μg N/l between sites, while considering the strong positive autocorrelation. $\alpha=0.05$

Contrast	p-value
Site1-Site2	1.000
Site1-Site3	1.000
Site1-Site4	1.000
Site1-Site5	1.000
Site1-Site6	1.000
Site1-Site8	1.000
Site1-Site9	1.000
Site1-Site11	1.000
Site2-Site3	1.000
Site2-Site4	1.000
Site2-Site5	1.000
Site2-Site6	1.000
Site2-Site8	1.000
Site2-Site9	1.000
Site2-Site11	1.000
Site3-Site4	1.000
Site3-Site5	1.000
Site3-Site6	1.000
Site3-Site8	1.000
Site3-Site9	1.000
Site3-Site11	1.000
Site4-Site5	1.000
Site4-Site6	1.000
Site4-Site8	1.000
Site4-Site9	1.000
Site4-Site11	1.000
Site5-Site6	1.000
Site5-Site8	1.000
Site5-Site9	1.000
Site5-Site11	1.000
Site6-Site8	1.000
Site6-Site9	1.000
Site6-Site11	1.000
Site8-Site9	1.000
Site8-Site11	1.000
Site9-Site11	1.000

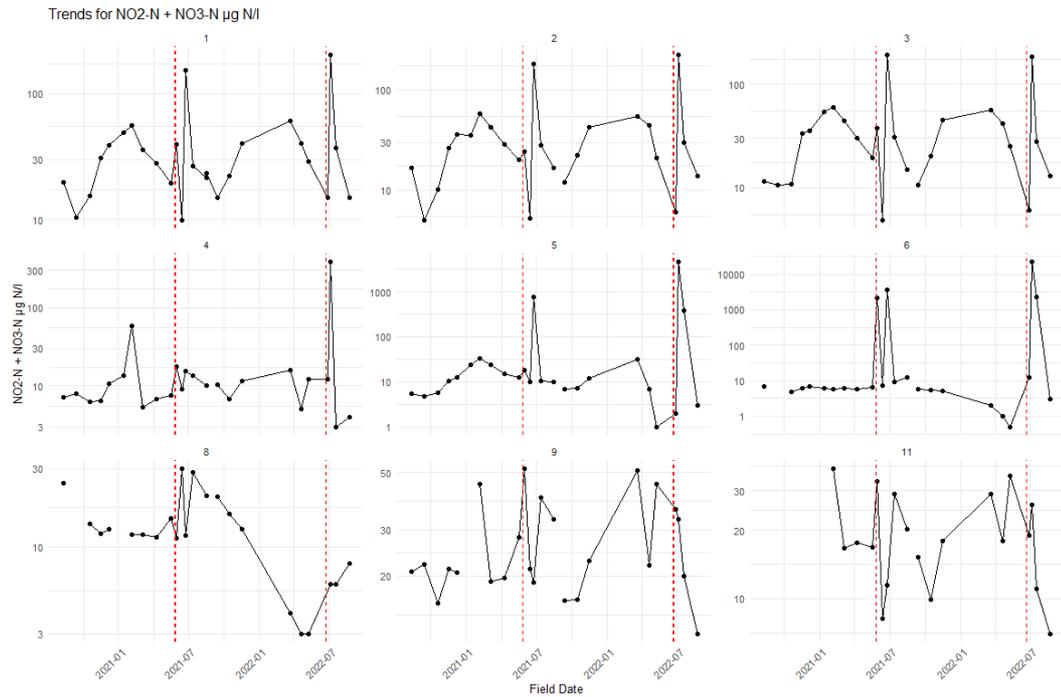


Figure A4. $NO_2+NO_3 \mu\text{g N/l}$ plotted against time for each site. the scale is logarithmic so to visualise the shifts of the data. The read dotted line indicates the first and the second fertilization event. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Table A8. Results of Durbin-Watson test of $NO_2+NO_3 \mu\text{g N/l}$. Each site with correlating DW and p-value as well as interpretation of results into the presence of autocorrelation. $\alpha=0.05$

Site	DW	p-value	Autocorrelation
1	2.36	0.77	No
2	2.39	0.78	No
3	2.36	0.76	No
4	2.31	0.72	No
5	2.20	0.61	No
6	2.18	0.59	No
8	1.43	0.05	Positive
9	2.00	0.41	No
11	1.93	0.34	No

Table A9. Results from generalized least squares model. To evaluate if there is a different in of NO_2+NO_3 $\mu g N/l$ between sites, while considering the strong positive autocorrelation. $\alpha=0.05$

Contrast	p-value
Site1-Site2	1.000
Site1-Site3	1.000
Site1-Site4	1.000
Site1-Site5	1.000
Site1-Site6	0.2139
Site1-Site8	1.000
Site1-Site9	1.000
Site1-Site11	1.000
Site2-Site3	1.000
Site2-Site4	1.000
Site2-Site5	1.000
Site2-Site6	0.2306
Site2-Site8	1.000
Site2-Site9	1.000
Site2-Site11	1.000
Site3-Site4	1.000
Site3-Site5	1.000
Site3-Site6	0.2316
Site3-Site8	1.000
Site3-Site9	1.000
Site3-Site11	1.000
Site4-Site5	1.000
Site4-Site6	0.2104
Site4-Site8	1.000
Site4-Site9	1.000
Site4-Site11	1.000
Site5-Site6	0.7915
Site5-Site8	1.000
Site5-Site9	1.000
Site5-Site11	1.000
Site6-Site8	0.2513
Site6-Site9	0.2298
Site6-Site11	0.3542
Site8-Site9	1.000
Site8-Site11	1.000
Site9-Site11	1.000

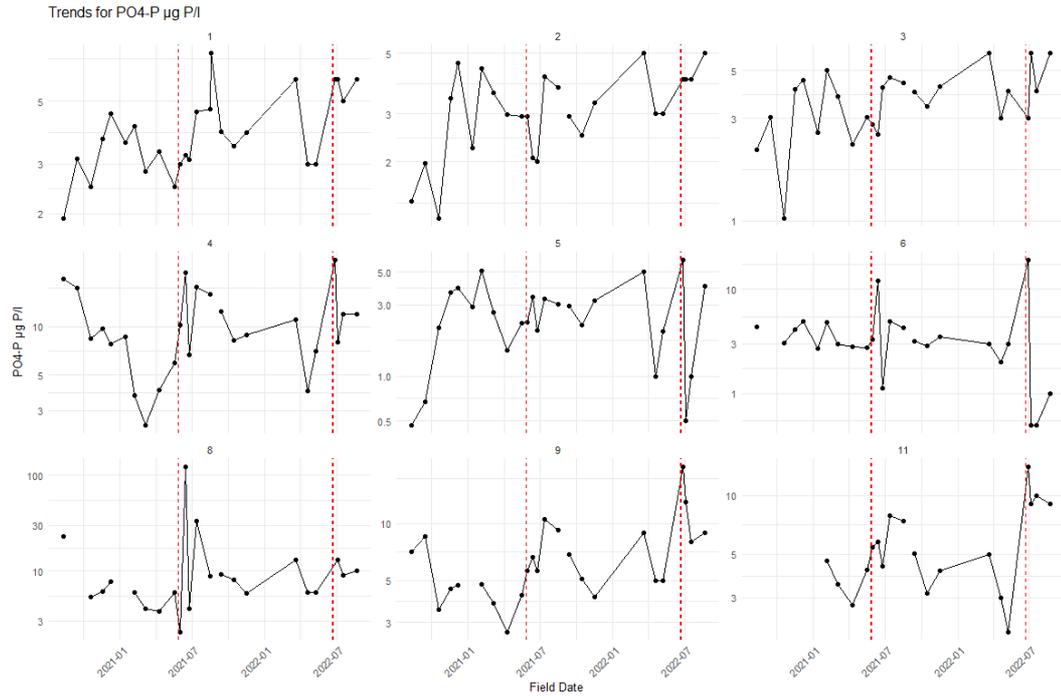


Figure A5. $PO_4 \mu g P/l$ plotted against time for each site. the scale is logarithmic so to visualise the shifts of the data. The read dotted line indicates the first and the second fertilization event. Sites 3, 4, 5 and 6 are treated. Sites 8, 9 and 11 are the control. Site 2 is situated so water from both the treated and untreated areas flow through this point. Site 1 has the outflow for the whole catchment area.

Table A10. Results of Durbin-Watson test of $PO_4 \mu g P/l$. Each site with correlating DW and p-value as well as interpretation of results into the presence of autocorrelation. $\alpha=0.05$

Site	DW	p-value	Autocorrelation
1	1.69	0.16	No
2	1.75	0.19	No
3	2.30	0.70	No
4	1.65	0.13	No
5	2.00	0.42	No
6	2.37	0.76	No
8	2.30	0.68	No
9	1.63	0.12	No
11	1.62	0.13	No

Table A11. Result of Shapiro-Wilk test of PO₄ µg P/l showing whether the residuals are normally distributed. If p-value ≤ 0.05 not normally distributed and if p-value > 0.05 the residuals are normally distributed. α=0.05

Site	p-value
1	0.0487
2	0.692
3	0.515
4	0.0657
5	0.564
6	0.00000139
8	0.0000000223
9	0.000469
11	0.0403

Table A13. Result of Kruskal-Wallis's test of differences between site when it comes PO₄ concentrations. α=0.05

df	8
p-value	2.2×10 ⁻¹⁶

Table A14. Results from post-Hoc tests comparing all the sites to each other to determine where there is a difference in PO_4 $\mu\text{g P/l}$. $\alpha=0.05$

Contrast	p-value
Site1-Site11	1
Site1-Site2	1
Site11-Site2	0.06
Site1-Site3	1
Site11-Site3	1
Site2-Site3	1
Site1-Site4	0.0002
Site11-Site4	0.6
Site2-Site4	10^{-8}
Site3-Site4	0.00005
Site1-Site5	0.7
Site11-Site5	0.003
Site2-Site5	1
Site3-Site5	1
Site4-Site5	10^{-10}
Site1-Site6	1
Site11-Site6	0.003
Site2-Site6	1
Site3-Site6	1
Site4-Site6	2×10^{-6}
Site5-Site6	1
Site1-Site8	0.005
Site11-Site8	1
Site2-Site8	8×10^{-6}
Site3-Site8	0.001
Site4-Site8	1
Site5-Site8	6×10^{-8}
Site6-Site8	8×10^{-5}
Site1-Site9	0.06
Site11-Site9	1
Site2-Site9	0.0002
Site3-Site9	0.02
Site4-Site9	1
Site5-Site9	2×10^{-6}
Site6-Site9	0.002
Site8-Site9	1

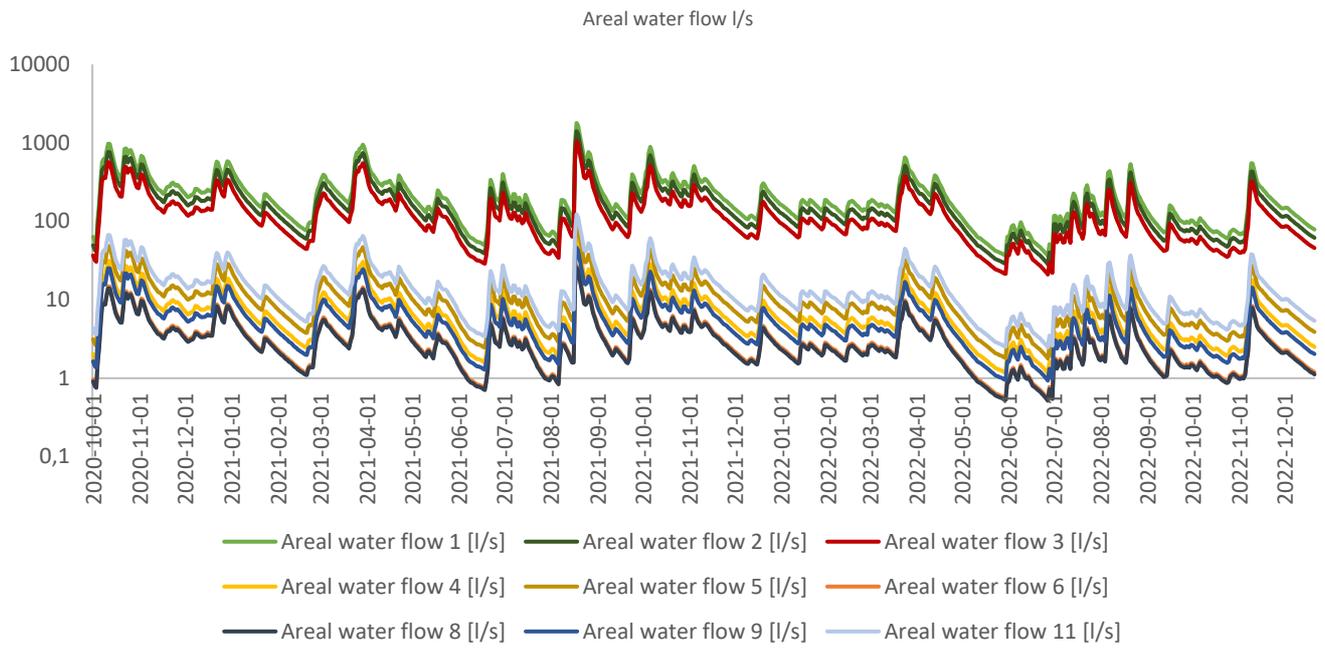


Figure A6. Areal water flow for each site. Total flow data and catchment area for each site from the Swedish Meteorological and Hydrological Institute was used to calculate.

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