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Land use, geology and soil properties control nutrient concentrations in headwater streams

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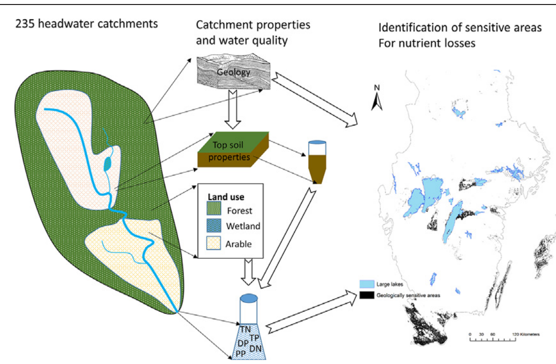
HIGHLIGHTS

- Land use, soil properties and catchment geology were drivers of nutrient loss.
- Proportion of arable land mainly drove nutrient losses in 235 headwater catchments.
- Forest and wetlands in catchments reduced nutrient losses.
- Arable soil properties influenced losses of different nutrient fractions.
- Catchment geology affected soil properties and thus nutrient losses.

GRAPHICAL ABSTRACT



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ABSTRACT

Nutrient losses from headwater catchments (<50 km^2) cause eutrophication problems downstream. Catchment properties are strongly reflected in the levels of nutrient concentrations in headwater streams. Based on measurements of total and dissolved nitrogen (TN, DN) and phosphorus (TP, DP) in 235 small headwater streams, we showed that proportion of arable land in a catchment had the strongest positive effect on nutrient concentrations, with coefficient of determination (R^2) of 0.54, 0.64, 0.45, and 0.51 for TN, DN, TP, and DP, respectively. In contrast, increased proportion of forest and wetland led to lower nutrient concentrations in streams. The geological composition of catchments had a major influence on the soil properties. In turn, certain soil properties, such as clay content and content of aluminum (Al), an important binding agent of P, influenced losses of particulate P (PP) and DP, respectively. Consequently, by using soil properties as a link between geology and water quality, areas potentially sensitive to nutrient losses were identified by classifying bedrock categories into three geological groups. Approximately 25% of Swedish arable land was identified as potentially sensitive. Sensitive catchments were found in regions with sedimentary bedrock and showed higher concentrations of dissolved nutrient fractions even when the proportion of agricultural land was small, indicating higher background concentrations.

1. Introduction

Nitrogen (N) and phosphorus (P) cycles have been identified as important Earth system processes and exceeding their boundaries could generate unacceptable environmental changes (Rockstrom et al., 2009). Eutrophication, accelerated by human activities resulting in an increase in N and P losses to water recipients, is the leading cause of impairment of many freshwater and coastal ecosystems world-wide (Chislock et al., 2013). These human activities include intensification of agriculture and continuous urbanization (Foley et al., 2005). There are many factors influencing the nutrient concentrations and fluxes in

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aquatic ecosystems. The upstream changes in land use and land cover distribution in general and the proportion of agricultural land in particular, are generally assumed to govern the changes in downstream nutrient concentrations (Mitchell et al., 2009; Wilson, 2015; Ide et al., 2019). However, the research studies so far related nutrient concentrations and loads mostly to the quantities (distribution of land use categories including agricultural land) and rarely to the quality of agricultural land (Beaulac and Reckhow, 1982; Tong and Chen, 2002; Tu and Xia, 2008; Soranno et al., 2015). For example, the soil texture of agricultural land influences nutrient losses. Kyllmar et al. (2014) found that N leaching was greater from small catchments dominated by sandy soils, whereas the opposite was true for P, for which higher losses were recorded in catchments dominated by clay soils. Sandström et al. (2020) showed that the clay content and proportion of agricultural land were significantly and positively correlated with transport of suspended sediment (SS), which in turn led to higher losses of particulate P (PP), but such relationship was not found for dissolved P (DP). Soil nutrient status may also influence nutrient losses, as shown in laboratory studies and at field plot level (Heckrath et al., 1995; Hooda et al., 2000; Djodjic and Mattsson, 2013). Another soil property that is important for P losses is P sorption capacity (PSC), often measured as the content of iron (Fe) and aluminum (Al) in the soil (Börling et al., 2004). Soil properties are closely connected with the parent geology at the site. For instance, Dillon and Kirchner (1975) found significant differences in export of total P from igneous catchments with forest and pasture compared with sedimentary catchments with similar land uses. Additionally, large agricultural N and P surpluses are often recorded in areas with high livestock density (Svanbäck et al., 2019), leading to increased riverine nutrient fluxes. In contrast, forest and wetlands are reported to have a positive effect on water quality, indicated by lower nutrient concentrations in streams draining catchments with higher proportion of forest and wetlands (Beaulac and Reckhow, 1982; Xiong and Hoyer, 2019). However, intensified harvesting in combination with other forest management practices could have large ecological consequences for both terrestrial and aquatic ecosystems (Laudon et al., 2011). Logging in combination with following soil preparation may lead to increased nutrient availability and leaching to receiving waters (Kreutzweiser et al., 2008; Pohjanmies et al., 2017). Further, the long-range transport and acid atmospheric deposition of nitrogen oxides and ammonia (and their reaction products) may act as fertilizers and cause eutrophication in many terrestrial, freshwater and marine ecosystems (Rodhe et al., 1995; Bergström and Jansson, 2006). However, recent evaluation of long-term changes (1990–2015) in the atmospheric deposition and runoff water chemistry shows predominantly decreasing trends in NO_3 concentrations in both deposition and runoff (Vuorenmaa et al., 2018).

According to Bol et al. (2018), research efforts should be focused on headwater catchments (<50 km^2), as they have a key influence on the initial chemistry of large river catchments, where many management interventions are most effectively implemented. Large variation in nutrient concentrations and fluxes between headwater catchments has been observed, illustrating higher resilience and lower vulnerability of some catchments (Bol et al., 2018). Although previous studies have revealed some of the relationships between land use, geology, and nutrient concentrations and fluxes, comprehensive studies involving large numbers of headwater catchments and different nutrient fractions are needed to disentangle the governing factors behind nutrient transport from terrestrial to aquatic systems.

In this study, we compiled a database on 235 headwater catchments smaller than 50 km^2 across the southern half of Sweden, to explore the effects of land use distribution, animal density, geology, and soil properties on long-term measured concentrations of total P (TP), DP, total N (TN), and the sum of oxidized N (DN). We also examined correlations between geological data and selected soil properties influencing water quality. The main objectives were to: (i) identify the most influential factors governing concentrations of dissolved fractions and total concentrations of N and P; and to (ii) identify areas in the Swedish landscape that might be less resilient and more sensitive to nutrient losses.

2. Material and methods

2.1. Selection of headwater catchments and their characteristics

In total, 235 small catchments were selected (Fig. 1). The main criteria for selection of sites were catchment size (less than 50 km^2) and a minimum number (12) of recorded water sample analyses with results for DP, TP, DN, and TN for the period 2000–2019. The composition of the streamwater reflects the discharge regimes and the water's pathways through the catchment in various ways (Grip and Rodhe, 2019). Although the minimum number of water samples for inclusion in this data set was set to 12, most of the included streams had higher number of water samples covering different flow regimes, please see the Results section and Fig. 2.

The study was also limited to the southern half of Sweden (below 62°10′N), for which data on soil properties of arable land are available (see Section 2.2). The three main sources of water quality data were the database at the Department of Aquatic Sciences and Assessment, SLU ($n = 196$), the water quality monitoring program on agricultural fields and catchments at the Department of Soil and Environment, SLU

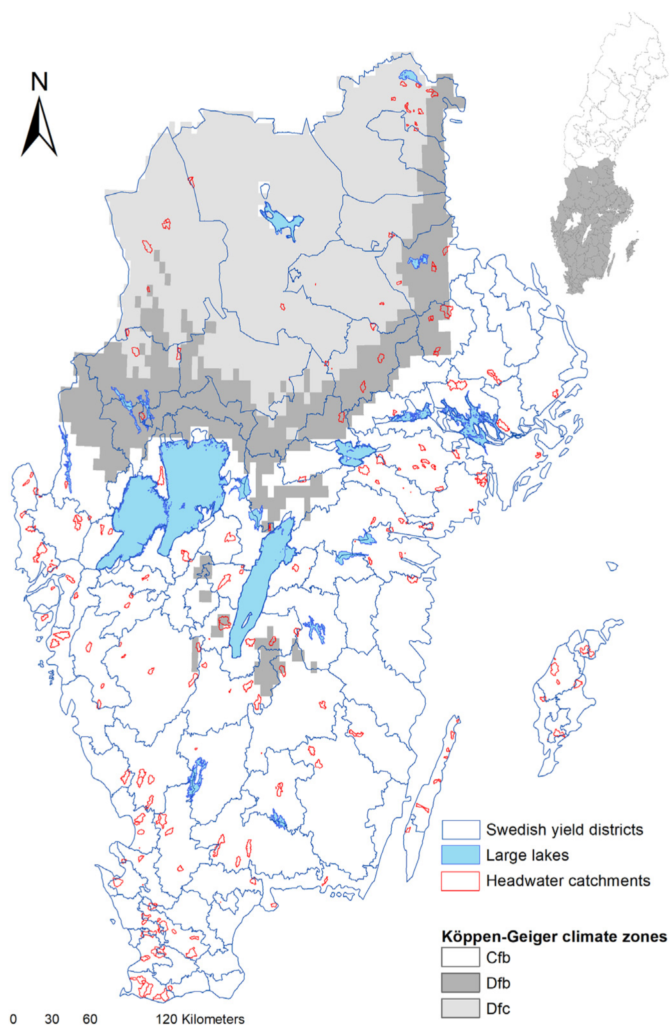

Fig. 1. Map of the southern half of Sweden, showing study catchments and crop yield district borders. The background map shows Köppen-Geiger climate zones (Cfb, warm temperate, fully humid, warm summer; Dfb, snow, fully humid, warm summer; and Dfc, snow, fully humid, cool summer) produced using the downscaling algorithms described by Rubel et al. (2017).

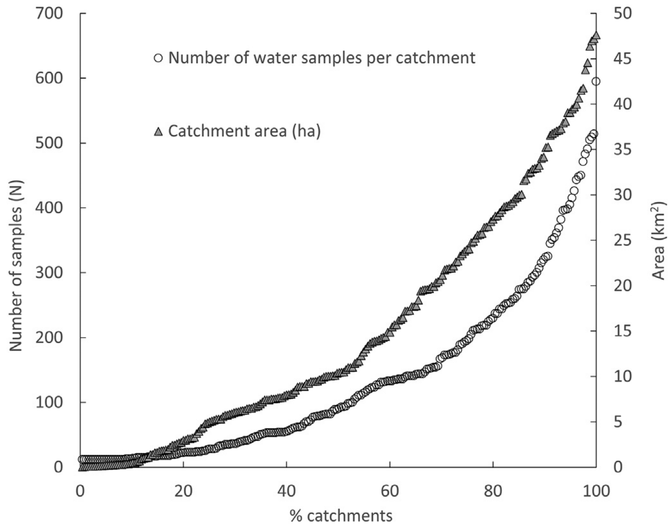

Fig. 2. Distribution of number of water samples per study catchment and of catchments based on their area.

($n = 33$) and the water recipient control program at Borgholm municipality ($n = 6$) on the Swedish island of Öland. Catchment delineation was performed based on the 10-m Digital Elevation Model (DEM) and hydrography network data upstream each station for water quality measurements. The majority (216) of stations was non-nested but 19 of the catchments did have an upstream nested measurement station. For each headwater catchment, land use distribution was calculated based on a 10-m grid from national land cover data (Swedish Environmental Protection Agency, 2019). The distribution of geological features was based on the bedrock map of Sweden produced by the Geological Survey of Sweden (SGU, 2016). Based on the digital soil map of Swedish arable topsoils (Söderström and Piikki, 2016), median clay content was calculated for each catchment. Climate differences between selected catchments were considered by accounting for the impact of temperature and precipitation. Mean annual precipitation and temperature for each catchment were calculated from monthly data, based on a 4 km × 4 km precipitation and temperature grid provided by the Swedish Meteorological and Hydrological Institute for the period 1961–1990.

2.2. Soil properties of arable land

Data on soil properties were taken from a comprehensive inventory of topsoil characteristics of Swedish arable land (Djodjic, 2015; Paulsson et al., 2015). This soil monitoring program was performed in 2013 by the Swedish Board of Agriculture, in order to create a better map of Swedish arable soils. It included 12,554 topsoil samples distributed all over southern Sweden, enabling site identification for specific agricultural measures. The following soil analyses were performed: particle size distribution was determined according to ISO 11277 (ISO 11277, 2009); soil pH was determined on dry soil samples mixed with distilled water at a ratio (w/v) of 1:5; and soil organic matter content (SOM) was determined by weight loss on ignition. This arbitrary selection of methods was chosen to keep costs at a minimum, considering that many thousands of soil samples were analyzed. A subset of samples was also analyzed by dry combustion with a Leco Tru-Mac analyzer (LECO, St. Joseph, MI) for comparison and to correct for clay content in loss of ignition values. Following extraction with ammonium acetate lactate (AL) according to Egnér et al. (1960), concentrations of phosphorus (P-AL), potassium (K-AL), magnesium (Mg-AL), calcium (Ca-AL), iron (Fe-AL), and aluminum (Al-AL) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES),. Phosphorus sorption capacity (PSC-AL) was calculated as the sum of Al-AL and Fe-AL on a molar basis. Degree of P saturation (DPS) was then calculated as the ratio between P-AL and PSC-AL (Ulén, 2006). Despite the large number of soil samples in the survey, the data density with approximately one sample per 200 ha arable land (Djodjic, 2015) was still too low to give a sufficient number of samples per small headwater catchment. Therefore, the average values obtained for different soil properties were calculated for larger crop yield districts (Fig. 1). Yield statistics were introduced in Sweden in 1961, and by 1989 there were 106 crop yield survey districts (SCB, 2016). In this study, 88 yield survey districts with available soil inventory data were selected. Kirchmann et al. (2020) used data on soil properties for yield districts to study correlations with standard crop yields (SCB, 2016) derived from a regression model providing yield trends for each crop over 15 years (2000–2015). Due to the lack of specific data on soil properties for each small headwater catchment, the average values of soil properties for each yield district were assumed to be representative for all headwater catchments within a given yield district.

2.3. Water quality data

The Department of Aquatic Sciences and Assessment (SLU) is a data host for a number of environmental water quality monitoring programs (Fölster et al., 2014). In this study, all water courses with catchment area smaller than 50 km^2 were identified and extracted from the database. The data originated from 13 different subprograms within the Freshwater program. Thereafter, all objects with at least 12 recorded measurements of nutrient variables (TP, DP, TN, and DN) in the period 2000–2019 were chosen for further analyses. These were complemented with corresponding data on nutrient concentrations from the “Agricultural Monitoring Programme” (Kyllmar et al., 2014), which consists of 21 small catchments dominated by agriculture, together with data from 12 arable fields from the monitoring program “Observation fields on arable land” (Djodjic and Bergström, 2005; Linefur et al., 2017). Finally, data from six small catchments included in the water recipient control program in Borgholm municipality on the island of Öland were also added to the dataset.

Water samples were analyzed at a water laboratory certified by the Swedish Board for Accreditation and Conformity Assessment (SWEDAC), following Swedish Standard Methods. Total P was analyzed on unfiltered samples after digestion in acid persulfate solution, while DP was measured after filtration with a 0.2-μm pore diameter filter (Scheleicher and Schüll GmbH, Dassel, Germany). Particulate P (PP) was calculated as the difference between TP and DP. For analyses of TN, water samples were treated with hydrochloric acid. The N content was measured through chemoluminescence after catalytic oxidation into nitrogen oxides.

2.4. Statistical analyses

All variables were tested for normality and, if non-normal distribution was shown, they were $\log_{10}$-transformed prior to further analyses. For each catchment, median values of nutrient concentrations (DP, TP, PP, DN, TN) were calculated. Principal component analysis (PCA) (JMP 13.0.0, SAS Institute, Cary, NC) was performed to identify possible clustering. To reduce the total number of variables, the bedrock categories were based on their origin grouped into sedimentary, igneous, and metamorphic, and the distribution of these bedrock categories for each catchment was included in the PCA. Thereafter, linear regression fit was calculated between water nutrient concentrations and catchment characteristics. The R^2-values of the linear fit and corresponding p-values were calculated to study the percentage of dependent variables, i.e., nutrient concentrations, explained by independent variables, i.e., catchment characteristics. Thereafter, multiple linear regression was performed to explore the degree to which different combinations of variables explained the variance in the water quality variables studied.

Only statistically significant variables ($p < 0.05$) were included in the multiple linear regressions for each water quality parameter.

To explore the correlations between parent geology and soil properties, each soil sample from the soil survey data was spatially connected to the bedrock map of Sweden and the corresponding geological category was identified. Based on soil properties, bedrock categories were clustered into three geological groups with comparable values of soil properties. Analysis of variance (ANOVA) was performed to test for statistically significant differences between the groups and Tukey-Kramer Honestly Significant Difference (HSD) test to perform multiple comparisons of group means. Thereafter, the distribution of the new geological groups within each of the study catchments was calculated in Arc GIS. Based on this, all catchments were divided into two groups, sensitive and non-sensitive. To study possible differences in water nutrient concentrations between catchments with sensitive and non-sensitive geological groups, two different statistical analyses were performed. First, ANOVA was performed to study the differences in means. Second, since proportion of agricultural land had a strong impact on nutrient concentrations, interaction effects of geological group on the intercepts and slopes of the linear regressions for proportion of arable land and water nutrient fractions were also analyzed.

3. Results

The population of 235 catchments was not normally distributed with regard to catchment size or number of existing water sample analyses per catchment (Fig. 2). The mean catchment size was 14.9 km^2 and the median size 10.4 km^2, indicating a skewed distribution towards smaller catchments.

The mean number of available water analyses per catchment was 134, whereas the median was 91, once again indicating large numbers of catchments with fewer available water analyses. However, the correlation between catchment size and number of samples per catchment was slightly negative but rather weak ($R^2 = 0.016$, $p < 0.05$).

The PCA results (Fig. 3) showed that all water quality parameters were positively correlated with the proportion of arable land in the catchment and, to a smaller degree, the proportion of open land. All water quality parameters were negatively correlated with the proportions of other land use categories (forest, wetland and water). As for the soil properties, different P fractions were negatively correlated with both PSC and Al-AL. Interestingly, soil pH, Ca-AL, and even content of P-AL in soil and DPS had a more strongly positive correlation to TN and DN than to P fractions in water samples. The correlations with geology were generally weak or non-significant, with only the total percentage of sedimentary rock in the catchment being placed close to the cluster of water quality parameters. However, the proportion of sedimentary bedrock in the catchment was correlated with a number of important soil properties, with a positive correlation with P-AL, DPS, and pH and a negative correlation with Al-AL and PSC.

The results of the bivariate linear regression analysis are presented in Table 1. These results were in line with the results of the PCA. Proportion of arable land was the strongest explanatory variable for all water quality parameters, but many other catchment properties were highly significantly correlated with water chemistry.

Calculation of multiple regression equations revealed other variables that could be combined with proportion of arable land to further explain

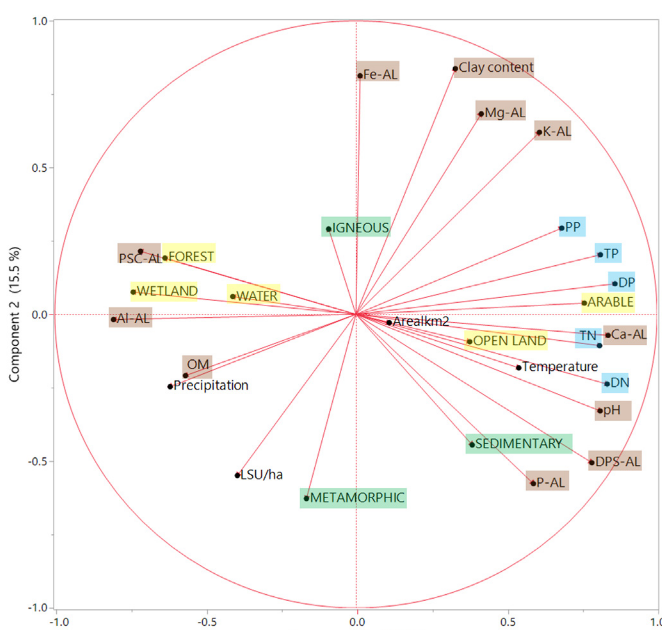

Fig. 3. Principal component analysis (PCA) plot of correlations between water quality parameters (blue), bedrock distribution (green), land use distribution (yellow) and soil properties (brown), as well as temperature, precipitation, catchment area, and animal density (livestock units per hectare arable land (LSU/ha)).

Table 1
Coefficient of determination (R^2) of linear fit between water quality parameters (columns) and different catchment properties (rows).

	DP	PP	TP	DN	TN
Area	0.04**	0.01*	0.03**	0.02*	0
Precipitation	0.23***	0.17***	0.23***	0.08***	0.17***
Temperature	0.25***	0.17***	0.25***	0.39***	0.21***
pH	0.29***	0.06***	0.18***	0.38***	0.33***
Organic matter	0.16***	0.08***	0.12***	0.11***	0.11***
P-AL	0.18***	0.08***	0.14***	0.45***	0.31***
K-AL	0.25***	0.28***	0.28***	0.14***	0.17***
Mg-AL	0.13***	0.13***	0.15***	0.02*	0.04**
Ca-AL	0.34***	0.12***	0.26***	0.32***	0.29***
Al-AL	0.33***	0.11***	0.24***	0.21***	0.21***
Fe-AL	0.001	0.07***	0.02*	0	0
DPS-AL	0.31***	0.09***	0.22***	0.46***	0.39***
PSC-AL	0.24***	0.04**	0.15***	0.17***	0.15***
Livestock density	0.09***	0.07***	0.08***	0.16*	0
Wetland	0.33***	0.14***	0.24***	0.42***	0.30***
Open	0.18***	0.15***	0.20***	0.14***	0.04**
Water	0.16***	0.07***	0.12***	0.15***	0.16***
Forest	0.28***	0.14***	0.21***	0.44***	0.46***
Arable	0.51***	0.32***	0.45***	0.64***	0.54***
Clay content	0.12***	0.24***	0.19***	0	0.03*
Sedimentary	0.03*	0	0	0.12**	0.05
Metamorphic	0.01	0	0	0	0
Igneous	0	0	0	0.01	0

Level of significance: *$p < 0.05$; **$p < 0.01$ and ***$p < 0.001$. Grey background indicates negative correlation. DP = dissolved phosphorus, PP = particulate P, TP = total P, DN = dissolved nitrogen, TN = total N.

the variance in concentrations of different nutrient fractions between catchments. The highest coefficient of determination (R^2) was recorded for DN (0.77) with four explanatory variables (Table 2). The lowest R^2 value was recorded for PP (0.41), based on only two statistically significant explanatory variables, proportion of arable land and clay content. Two different multiple regression equations were obtained for DP (Table 2). In the first of these, as for all other variables, only variables describing catchment properties were included, resulting in $R^2 = 0.59$. In the second equation, PP concentration was included as an additional explanatory variable for DP, increasing the R^2 value to 0.76 (Table 2).

Evaluation of soil properties per bedrock category revealed some differences in important soil properties between different geological formations (Table S1). In general, most, but not all, sedimentary bedrock categories showed higher pH and P-AL values, and lower Al-AL values. These areas were classified in geological group 1. However, some of the sedimentary bedrock categories (e.g., wacke, quartz arenite, arenite, kaolin) with very low or very high clay content differed from this pattern, and were therefore classified in geological group 2 (Table 3). Finally, all other bedrock categories (igneous and metamorphic) were classified in geological group 3. The results of ANOVA per geological group showed that group 1 was significantly different from the other two groups for most of the soil properties assessed (Table 3).

In particular, geological group 1 had significantly higher ($p < 0.05$) pH, P-AL, Ca-AL, and DPS-AL, and significantly lower ($p < 0.05$) Al-AL, Fe-AL, clay content, and PSC-AL, than groups 2 and 3 (Table 3). Some of these soil properties, together with proportion of arable land, were indicated by multiple regression as the most important variables explaining the variance in water nutrient fractions. Therefore, presence of geological group 1 was used to categorize a catchment as potentially sensitive and the area of this geological group was calculated for each catchment. Of the 235 catchments in the dataset, 176 catchments were found to be non-sensitive catchments, with no occurrence of geological group 1. In the remaining 59 catchments, there was at least some occurrence of the bedrock categories in geological group 1 (minimum 0.1%, mean 44.9%, maximum 99.1%).

The ANOVA results showed that the mean values of all water nutrient fractions (TP, DP, PP, TN, DN) in catchments with some occurrence of the sensitive geological group 1 were significantly higher ($p < 0.001$) than the mean values in non-sensitive catchments. In addition, tests of the interaction effects for two groups of catchments showed that both the intercept and the slope of the regression line between proportion of arable land and water nutrient fractions were significantly different ($p < 0.001$) for DN, DP, and TP (Fig. 4). The interaction effect was not significantly different for TN (Fig. 4) and PP (data not shown). It is worth noting that the intercept of DP, TP, and DN was higher for the sensitive catchments, whereas the slope of regression was lower (Fig. 4).

Based on these results, all areas of Sweden with arable land on bedrock categories included in the sensitive group (geological group 1; Table S1) were mapped (Fig. 5). According to this mapping, around 688,300 ha, or approximately 25% of Swedish arable land, are situated on sensitive geological bedrock with a risk of higher nutrient losses, especially losses of DP and DN.

Table 2
Multiple regression equations and coefficient of determination (R^2) for different water quality parameters. DP = dissolved phosphorus, PP = particulate P, TP = total P, DN = dissolved nitrogen, TN = total N.

Equation	R^2
DP = 2.734 + 0.39*Arable%-0.764*Al-AL	0.59
DP = 1.98 + 0.20*Arable-0.70*Al-AL + 0.58*PP	0.76
PP = 0.52 + 0.27*Arable+0.46*Clay	0.41
TP = 0.79 + 0.31*Arable+0.71*K-AL-0.37*Al-AL	0.55
DN = 0.73 + 0.45*Arable-0.22*Forest-0.14*Wetland+1.06*P-AL	0.77
TN = 2.87 + 0.26*Arable-0.26*Forest+0.38*DPS-AL	0.61

Table 3
Number (n) of soil samples and mean values of soil parameters in geological groups 1, 2, and 3. Values within rows followed by different letters (A-C) are significantly different ($p < 0.05$) according to Tukey-Kramer HSD test.

	Geological group		
	1	2	3
n	3449	557	8590
pH	7.0 A	6.2 B	6.2 B
Organic material	0.61 B	0.63 B	0.68 A
Clay content	1.12 C	1.47 A	1.25 B
P-AL	1.94 A	1.67 C	1.71 B
K-AL	2.02 B	2.17 A	2.03 B
Mg-AL	2.00 C	2.24 A	2.09 B
Ca-AL	3.49 A	3.25 B	3.17 C
Al-AL	2.29 C	2.51 B	2.56 A
Fe-AL	2.50 B	2.65 A	2.64 A
DPS-AL	1.31 A	0.85 B	0.86 B
PSC-AL	1.13 C	1.33 B	1.36 A

4. Discussion

The proportion of arable land in the catchment was the single strongest factor influencing the nutrient concentrations in water in 235 headwater catchments in the southern half of Sweden. This is in line with previous findings elsewhere (Beaulac and Reckhow, 1982; Foley et al., 2005; Bol et al., 2018). The correlation with proportion of agricultural land was stronger for the soluble forms of nutrients (DP and DN) than for the total concentrations (TP and TN). Based on long-term measurements of water quality in Sweden (Kyllmar et al., 2014), DN is the dominant form of N in water in small catchments dominated by agriculture (on average 77%), but DP constitutes on average only 35% of TP.

Beside the proportion of arable land, DP concentrations were strongly and negatively correlated with soil content of Al and proportion of wetland area in the catchment. Both Al and Fe content in soil are often indicated as important factors for P sorption (Schoumans and Groenedijk, 2000; Börling, 2003; Ulén, 2006), but in this study only the correlation with Al content was significant. Eriksson et al. (2013) showed that phosphate sorbed on iron (Fe) (hydr)oxides was a dominant P species in clay fractions in unfertilized soil, but that after long-term fertilization, P accumulated mainly as P adsorbed to Al (hydr)oxides. The Al-AL content in the geologically sensitive group of sedimentary bedrock was significantly lower than in the other two groups (Table 3). Phosphorus content in soil measured as P-AL was more strongly correlated to DP ($R^2 = 0.18$, Table 1) than PP ($R^2 = 0.08$), but the correlation was still weak. Previous studies have also found it difficult to disaggregate the influence of soil P content on P export found at the plot and field scale to a larger, catchment scale (Haygarth et al., 2012; Sandström et al., 2020). Interestingly, including the concentration of PP as an independent variable in the multiple regression equation to describe concentration of DP, together with proportion of arable land and Al-AL, significantly increased the coefficient of determination, from $R^2 = 0.59$ to $R^2 = 0.76$ (Table 2). Conceptually, this could be interpreted as two sources of DP: one connected to mobilization of soil particles and PP, and following release of DP from soil particles in the water phase; and the second governed by soil sorption capacity (PSC, Al-AL) determining the release of DP from the bulk soil, independently of PP mobilization.

The concentration of PP and the proportion of arable land were most strongly correlated with clay content and K-AL (Table 1). However, the clay content and K-AL are also strongly correlated ($R^2 = 0.56$, $p = 0.001$). Positive correlations between clay content and losses of P have been reported previously by Kyllmar et al. (2014) and Sandström et al. (2020), as mobilization of soil particles as carriers of PP is dependent on soil clay content (Withers et al., 2007). Beaulac and Reckhow (1982) concluded that clay soils characterized by high nutrient adsorption capacity, high erodibility, and low infiltration capacity may be sensitive to nutrient export via runoff.

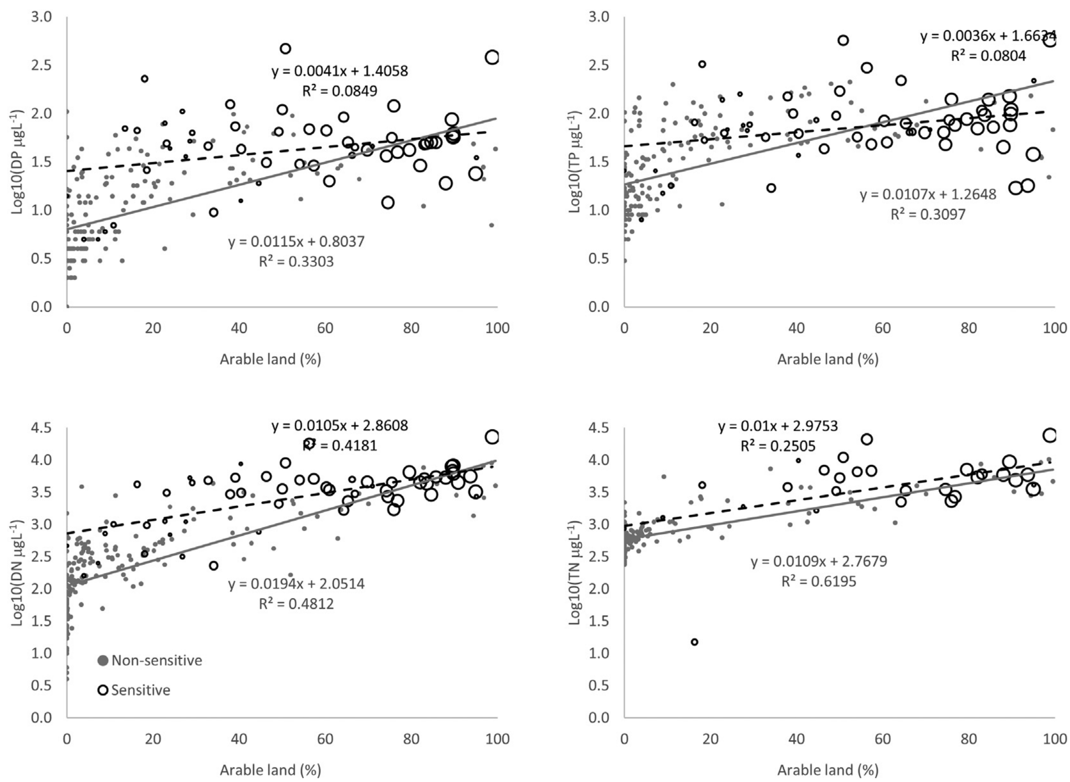

Fig. 4. Linear regression between proportion of arable land (%) in a catchment and dissolved phosphorus (DP), total P (TP), dissolved nitrogen (DN), and total N (TN) for catchments with geologically sensitive and non-sensitive bedrock categories. For sensitive catchments, circle size is proportional to the percentage of geologically sensitive area in the catchment.

It is interesting that the multiple regression equations for both DN and TN (Table 2) unexpectedly included some soil properties which are usually used to describe soil P status, namely soil P content, P-AL, and DPS. It is difficult to find a direct link between these properties and N losses, and an indirect link is more likely. Areas with high soil P status, and thereby high DPS, are also areas with intensive agricultural production and high crop yields (Kirchmann et al., 2020), and presumably receive high N fertilizer/manure applications, leading to high N losses. The assumption made in this study that the soil properties for a given larger yield district are representative for a smaller headwater catchment introduces uncertainties in interpretation of the results. However, although the main criterion for delineation of crop yield districts in Sweden is similarity in yields, other properties such as climate, soil type, topography, and cultivation type are also taken into consideration (Statistics Sweden, 2020).

Mapping of sensitive areas for nutrient losses based on the geological map of Sweden and the correlations to certain soil properties revealed that catchments with more arable land on sedimentary rock have significantly higher nutrient losses, especially as dissolved fractions. Dillon and Kirchner (1975) found significantly higher P export from sedimentary catchments compared with the corresponding igneous mixed catchments for both predominantly forested catchments and mixed (forest and pasture) catchments. Low P concentrations were found in silica-rich, iron-poor igneous rocks such as granite and rhyolite (Porder and Ramachandran, 2013), which are frequently occurring parent material of the soil samples included in our study (Table S1). Additionally, the soils in the sedimentary rock catchments were found to be characterized by high pH and Ca-AL, and low clay content and Al-AL. As seen in Fig. 4, these catchments tended to have higher nutrient concentrations at lower percentages of arable land, whereas these differences disappeared at approximately 80% arable land in the catchment. There are two main implications of these results. First, there is a need to acknowledge these sensitive areas and raise awareness about the increased risks of high nutrient losses from arable land in these catchments. Second, the EU Water Framework Directive requires environmental goals to deviate only slightly from background or reference conditions (Bol et al., 2018). From the intercept values of the regression equations in Fig. 4, where there is no arable land in the catchments, it is clear that sensitive areas had significantly higher nutrient concentrations in water than non-sensitive areas, even under reference conditions. Applying these intercept values with no arable land as the baseline or reference condition, and imposing the lower intercept values from non-sensitive areas on sensitive catchments as a reference value, might lead to unattainable environmental goals.

5. Conclusions

Based on long-term average nutrient concentrations in stream water in a population of 235 headwater catchments in southern Sweden and the corresponding catchment characteristics, we found that:

- Proportion of agricultural land in the catchment had the strongest influence on all investigated nutrient forms in stream water in headwater catchments. Increasing proportion of arable land was associated with increased nutrient concentrations in water.
- Increasing share of forest and water/wetlands in the catchment had the opposite effect, resulting in lower nutrient concentrations in stream water in headwater catchments.
- Geology had a strong impact on soil properties, which in turn influenced water quality. Similar patterns in a range of soil properties governing nutrient concentrations in headwaters are linked to catchment geology and can be used to trace sensitive areas.
- Mapping of sensitive areas is necessary to better protect water quality and to assign representative reference values for the EU Water Framework Directive.

The next step in disentangling the relationships between catchment properties and nutrient losses is to study in detail similarities

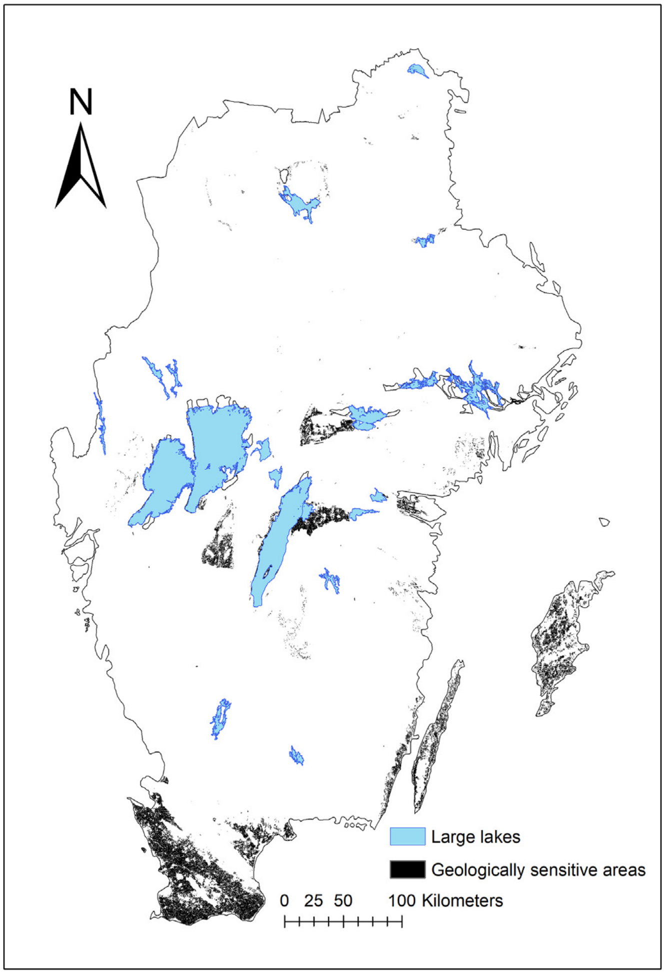

Fig. 5. Map of the southern half of Sweden showing geologically sensitive areas for nutrient losses.

and differences in nutrient pools and behavior in sensitive and non-sensitive areas. The knowledge obtained could help tailor abatement strategies and set reasonable goals that take into consideration differences in sensitivity to nutrient losses.

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CRediT authorship contribution statement

Faruk Djodjic: Conceptualization, formal analysis, writing original draft, review and editing, funding acquisition and project administration. **Magdalena Bieroza:** writing - review and editing. **Lars Bergström:** writing - review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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