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Long-term trends in bottom water chemistry of Swedish lakes

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Abstract

Long-term monitoring of lake water is essential for tracking local and long-range effects of anthropogenic pressure and to inform policy aiming at mitigating human environmental impacts. Swedish reference lakes are recovering from acidification; are subject to climate change and increasing inputs of terrestrial dissolved organic matter (DOM). The integrated effects of different environmental pressures alters lake water chemistry and, consequently, affects lake ecosystems. Most time trend analyses have focused on changes in surface water chemistry, whereas less is known about trends in bottom waters. The overall aim of this study was therefore to assess long-term trends (1988-2015) in bottom water chemistry of Swedish reference lakes ($n=13$) in relation to trends in surface waters. The hypothesis was that the prevalent increasing DOM concentrations in northern lakes have exacerbated the depletion of hypolimnetic dissolved oxygen (DO), as a result of DOM induced prolongation of stratification. Consequently, bottom water $\text{NH}_4\text{-N}$ (nitrate reduction to ammonia) and TP (internal loading) were expected to have increased over time in affected lakes. Time trend analysis (Mann-Kendall, $p<0.05$) showed that the yearly median bottom water DO has significantly decreased in 7 lakes. In 6 of these lakes (and 2 additional), surface water total organic carbon (TOC) has increased over time, however, rising TOC concentrations were more prevalent in bottom waters (12 lakes). The results further showed that bottom water nitrogen from ammonia ($\text{NH}_4\text{-N}$) has increased in the 7 lakes with declining DO, whereas bottom water total phosphorus (TP) has increased in 4 of these lakes. In contrast, surface water TP has declined in 7 lakes, which may have masked additional increased internal loading of P. Closer observation of bottom water chemistry revealed that as DO levels dropped, TOC, $\text{NH}_4\text{-N}$ and TP concentrations peaked and were particularly high during periods of sustained anoxia (\geq one year). The results also showed that bottom water Si concentrations have increased in most lakes. In the bottom waters of Brunnsjön, a sustained anoxic period coincided with a 32% step change in Si concentration. In conclusion, the underlying mechanism of the observed rising trends in bottom water TOC, $\text{NH}_4\text{-N}$ and TP are likely a result of prolonged or increased incidence of DO depleted hypolimnia. Clearly, monitoring of bottom waters can reveal important aspects of long-term changes in lake water chemistry. Future research is needed to further assess the long-term effects of brownification and climate change on bottom water DO in northern lakes.

Populärvetenskaplig sammanfattning

Sedan länge är det känt att människan påverkar både den närliggande miljön samt att våra handlingar har globala miljöeffekter på grund av spridning av föroreningar i atmosfären. Långsiktig miljöövervakning av sjöar är en förutsättning för att vi ska kunna upptäcka om och hur mänskliga aktiviteter påverkar sötvatten. Genom att undersöka trender i vattenkemi i sjöar som är minimalt påverkade av lokala störningar kan vi studera globala spridningar av föroreningar. Sverige var länge drabbat av surt regn på grund av utsläpp från förbränning av fossila bränslen. Det sura regnet förorenade både mark och sötvatten. Miljöövervakning möjliggjorde upptäckten av orsaken till försurningen, varefter utsläppen av försurande svavelföreningar reglerades. Sedan dess har sjöar och mark långsamt återhämtat sig från försurningen.

Nu ser vi istället att sjöar på det norra halvklotet har blivit brunare under de senaste årtiondena. Forskning har kopplat detta till att marken återhämtar sig från tidigare försurning, vilket leder till att jordar "läcker" mer organiskt material som transporteras med vatten genom landskapet till nedströms vattendrag och sjöar. En annan teori som har kopplats till den så kallade "brunifieringen" av sjöar och vattendrag är klimatförändringar, eftersom ett våtare klimat också leder till att mer organiskt material sköljs ur jordarna och hamnar i sjöar nedströms. Det ena utesluter inte det andra, eftersom det i naturen är många processer som samverkar. Men, hur är detta relaterat till min studie? Jo, att sjöar blir brunare påverkar hur solens värme fördelas i sjön. Under sommaren är sjöar på våra breddgrader skiktade. Sjöns ytvatten värms upp av solen och ett språngskikt uppstår mellan det varma ytvattnet och det kalla (tyngre) bottenvattnet. Det organiska materialet som gör sjöarna brunare har också förmågan att absorbera solenergi, vilket värmer ytvattnet ytterligare och leder till att det mesta av solens värme stannar i ytvattnet. Brunifieringen kan således leda till varmare ytvatten, vilket i sin tur kan resultera i att skiktningen består under en längre tid, kanske långt in på hösten.

Vad händer i det mörka och kalla bottenvattnet under sommarstagnationen, när det är isolerat från det syrerika varma ytvattnet? I takt med att syret förbrukas av bottenlevande organismer, samtidigt som nytt syre inte tillförs, uppstår syrebrist. Ett syfte med den här studien var att undersöka om syrehalten i bottenvatten har minskat över tid, kanske som ett resultat av att brunifieringen har lett till mer långvarig sommarstagnation. Mikrober som lever på botten av sjöar förbrukar syre och "andas" ut koldioxid när de bryter ner organiskt material, som kontinuerligt tillförs från det överliggande vattnet. Om syret tar slut börjar mikroberna använda andra föreningar än just syre när de förbränner organiskt material. Dessa mikrober "andas" ut andra ämnen. Vid nedbrytningen frigörs också ämnen från det organiska materialet och från sedimentbotten ut i bottenvattnet. Detta påverkar sammansättningen av lösta ämnen i bottenvatten. En annan frågeställning i denna studie var därför att undersöka om halterna av fosfor och ammonium i bottenvatten har ökat över tid, som ett resultat av längre perioder av syrefria botten.

För att svara på frågeställningarna undersöktes trender i bottenvattenkemi mellan 1988 till 2015 i tretton svenska sjöar från Brunnsjön i Emmaboda län, till Abiskojaure i Kiruna kommun. Majoriteten av sjöarna befinner sig dock i södra Sverige. Resultaten visade att syrehalterna i bottenvatten har sjunkit över tid i 7 av 13 sjöar, om man jämför årsmedianvärden. Sex av dessa 7 sjöar har blivit brunare

över tid, vilket stämmer överens med tidigare studier och pekar på att brunifieringen kan ha långsiktigt påverkat syrehalterna i bottenvattnet. Vidare har halterna ammonium i bottenvattnet ökat över tid i just de 7 sjöarna med nedåtgående syrehalter, medan halterna bottenvatten fosfor har ökat i mer än hälften av dessa sjöar. När jag tittade närmare på hur bottenvattenhalten av syre varierade i förhållande till ammonium och fosfor, var det tydligt att när syrenivån sjönk, så sköt ammonium och fosforhalterna i höjden. Vidare upptäcktes att bottenvattnet var syrefritt i flera sjöar under ett helt år, och under dessa perioder var halterna ammonium och fosfor mycket högre än vad som är vanligt. Vad jag inte förväntade att se var att bottenvattenhalterna organiskt kol följde samma mönster. Det vill säga att när syret sjönk, steg halterna organiskt kol, som också var ovanligt förhöjda under de syrefria perioderna. Detta mönster syntes inte i ytvattnet för något av de undersökta ämnena. Vidare visade resultaten att halterna organiskt kol i bottenvattnet har ökat i alla sjöar utan Abiskojaure, medan ytvattenhalterna organiskt kol har ökat i 8 sjöar.

En slutsats som drogs av studien var att minskade bottenvattenhalter av syre över tid är sannolikt den bakomliggande orsaken till den långsiktiga ökningen av organiskt kol, ammonium och fosfor i drabbade bottenvatten. Framtida studier behöver säkerställa denna teori, samt fastställa varför syrehalterna har sjunkit; om det är kopplat till brunifieringen eller uppvärmningen av klimatet – eller en kombination av båda. En annan viktig fråga att svara på är vad detta kan ha för långsiktiga konsekvenser för sjöekosystemen i sig. För att kunna svara på dessa frågor är det av största vikt att miljöövervakningen av både yt- och bottenvattenkemi i svenska sjöar fortgår. Med hjälp av miljöövervakning i alla dess former kan vi upptäcka och förhoppningsvis förhindra både nutida och framtida miljöproblem.

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Abbreviations and glossary

Brownification	process of lakes and rivers becoming browner
Chl α	chlorophyll α
DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter
Epilimnion	top water layer in a stratified lake (extends to the thermocline)
Eutrophic lake	highly productive lake due to high nutrient inputs from catchment area
Hydrous oxide	mineral with a metal and hydroxide and/or oxide component (e.g. γ - Al_2O_3)
Hypolimnion	bottom water layer in a stratified lake (below the thermocline)
Light attenuation	gradual loss of light intensity through a medium (e.g. water)
Mean depth (lake)	lake volume divided by lake surface area
Metalimnion	water layer between epi- and hypolimnion, also called thermocline
$\text{NH}_4\text{-N}$	nitrogen from ammonia, used to estimate ammonia (NH_4^+) levels
Oligotrophic lake	low productive lake due to low nutrient inputs from catchment area
Oligotrophication	process of a lake becoming oligotrophic (due to decreasing P levels)
Oxyhydroxide	mineral with a metal, oxygen and hydroxide component (e.g. α - FeOOH)
P	phosphorus
Phosphate	dissociated forms of phosphoric acid (H_3PO_4), including H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} , the latter anion is only significant at very high pH levels
Redox	reduction-oxidation
Si	dissolved silica, present as silicic acid (H_4SiO_4) at $\text{pH} < 9$
Surface water	refers to the top water layer, sampled 0.5 m below the lakes surface
Thermocline	water layer between epi- and hypolimnion, also called metalimnion
TOC	total organic carbon (most of it is DOC in Swedish lakes)
TP	total phosphorus

1. Introduction

Monitoring lake water chemistry is an essential part of tracking anthropogenically induced environmental change, predicting future challenges for freshwater resource management and mitigating their environmental effects. Lake water chemistry varies naturally and is a signature of the surrounding geology, vegetation and soils. Catchment processes in soils and riparian zones, including weathering of minerals and decomposition of organic matter, produces substances that are exported to streams and lakes. These processes are an essential part of the global cycling of elements, such as carbon, nitrogen and phosphorus (P). Human activities have affected these processes and consequently the composition of dissolved and particulate matter in rivers and lakes. Trends in lake water chemistry portray local and regional pressures acting on the catchment, such as variation in deposition chemistry (Monteith *et al.*, 2007), climate change (Adrian *et al.*, 2009) and changes in land-use or terrestrial vegetation cover (Tanentzap *et al.*, 2008; Larsen *et al.*, 2011).

There is a great body of research about long-term trends in lake water chemistry in the northern hemisphere and the potential drivers of the observed trends (Stoddard *et al.*, 1999; Hongve *et al.*, 2004; Monteith *et al.*, 2007; Futter *et al.*, 2014). Many northern lakes are showing signs of recovery from acidification, such as increasing levels of pH, alkalinity and acid neutralising capacity. The observed recovery is mainly due to decreased acid deposition (Garmo *et al.*, 2014; Driscoll *et al.*, 2016). In addition, increased export of terrestrial dissolved organic matter (DOM) has caused widespread rising dissolved organic carbon (DOC) concentrations in northern temperate lakes and streams (Evans *et al.*, 2006; Monteith *et al.*, 2007). Moreover, rising DOC concentrations increases the vertical light attenuation in the water column, which has a negative impact on lake primary productivity (Thrane *et al.*, 2014) and has been linked to changes in lake temperature and thermocline depth (Tanentzap *et al.*, 2008). Studies have also shown that levels of P in northern lakes have decreased over the past few decades, raising concerns about oligotrophication (Eimers *et al.*, 2009; Arvola *et al.*, 2011; Hu & Huser, 2014; Huser *et al.*, 2018). Nonetheless, eutrophication is still a major concern (Scavia *et al.*, 2014; Andersen *et al.*, 2017). Moreover, internal loading of legacy P from anoxic sediments is an important contributor to surface water P loads. In fact, internal loading is often the main P load to lakes during the period of summer stratification (Nürnberg, 2009). This source of P might be overlooked in time trend studies of lake water chemistry if the bottom waters are not included in monitoring programmes.

To the best of my knowledge, most studies about temporal trends in lakes rely on surface water chemistry data, and less is known about long-term trends in bottom waters (see for instance Futter *et al.*, 2014; Garmo *et al.*, 2014). Moderately deep temperate lakes are thermally stratified during the summer season, and the bottom water layer (hypolimnion) is relatively isolated from the surface layer (epilimnion). The chemical and physical characteristics of surface and bottom waters therefore differ, which consequently affects the everyday life of aquatic organisms. Bottom waters are generally oxygen-depleted but nutrient-rich, whereas surface waters are oxygen-rich but nutrient-depleted. Moreover, hypolimnetic waters are cold and dark, whereas epilimnetic waters are warmer and have better light conditions (Brönmark & Hansson, 2005). Due to this inherent difference, analysis of bottom

water chemistry is an important complement to environmental monitoring and assessment of lake surface waters. A question posed in this study is how the observed long-term trends in surface water chemistry have influenced the bottom waters of the affected lakes. The rising DOC concentrations might have initiated a decreasing trend in bottom water temperatures due to increased light attenuation in the top waters (Tanentzap *et al.*, 2008; Thrane *et al.*, 2014). Moreover, the DOC effect on thermal structure may have prolonged the period of summer stratification and, thus, increased the duration of anoxia in bottom waters (Solomon *et al.*, 2015). Furthermore, chemical reduction reactions prevalent in anoxic conditions affect the composition of dissolved substances in hypolimnion, which influences the cycling of elements in lakes (Wetzel, 2001).

The overall aim of this study was to evaluate long-term time trends in bottom water chemistry in Swedish reference lakes, particularly in relation to dissolved oxygen (DO) concentrations, and to compare the observations to corresponding trends in surface water chemistry. For this purpose, long-term trends and short-term variations in bottom water chemistry (DO, conductivity, nitrogen from ammonia, pH, water temperature, total organic carbon, total phosphorus and dissolved silica) were assessed in 13 Swedish boreal and boreonemoral lakes (0.1 – 2.8 km²). Trends in surface water (0.5 m) chemistry were analysed for comparison. The overall hypothesis was that the prevalent long-term increases in lake water DOC concentrations have exacerbated the depletion of DO in the bottom waters of affected lakes, due to the effects of DOC on lake thermal structure (Solomon *et al.*, 2015). As a consequence of the hypothesised longer duration or more frequent incidence of anoxia, increasing trends in bottom water concentrations of total phosphorus (TP) and ammonia were expected in the affected lakes (Nürnberg, 2009; Zhang *et al.*, 2014). Potential DOC effects on lake thermal structure (Solomon *et al.*, 2015) were evaluated by analysing surface and bottom water temperatures, and the surface water temperatures were assumed to have increased over time.

2. Background

In this chapter, the geology, climate and land-use of the study region (Sweden) is first briefly described. Following this, relevant background knowledge about lakes and the processes governing lake water chemistry is presented. The last section describes recent observations of temporal trends in lake water chemistry of northern lakes.

2.1. Sweden: geology, climate and land-use

Sweden covers 450 000 km², has a long coastline in the east towards the Baltic Sea and the Scandinavian mountain range in the north-west. The country lies on the Fennoscandian Shield, which is a region with old crystalline and metamorphic bedrock. Gneiss, granite, sandstone and marble are common rock types. The soils of Sweden were mainly formed by several periods of glaciation and deglaciation. Therefore, till is the most common soil type and covers around 75% of the land area (SGU, 2017).

The coastal areas in southern Sweden have a warm temperate climate and the natural vegetation is dominated by deciduous forest. The rest of Sweden lies in the cold temperate zone, where boreal forests (taiga) predominate. During the period between 1961 and 1990, the average annual temperatures in Sweden ranged from approximately 7-8°C in the southern coastal regions, to approximately -2°C in the north-western alpine regions. Average annual precipitation generally decreases from the western to eastern borders of the country. The highest average annual precipitation (calculated for 1961-1990) occurred in the north-western alpine regions, where it locally reached 1500-2000 mm per year. The south-western regions are, however, the wettest inhabited areas, with an annual precipitation (1961-1990) of around 1000-1200 mm. In the remaining parts of the country, the average annual precipitation was approximately 500-800 mm per year. During winter, most of the precipitation falls as snow, except for along the southern coastline, where precipitation is dominated by rain (SMHI, 2017b; a).

According to the Swedish Meteorological and Hydrological Institute (SMHI), the average annual temperature in Sweden has risen by approximately 1°C from the 1990s (compared to average during 1961-1990). The increase has been more pronounced during winter in mid- to northern Sweden, where temperatures have risen approximately 2°C. The annual average precipitation has also generally increased throughout Sweden (compared to 1961-1990), and by up to 10% in some regions. This is the case for all seasons except for autumn, during which the precipitation generally has decreased slightly throughout the country. SMHI observed that southern Sweden experienced very intense summer rainfall events during 2003 and 2004, resulting in extensive flooding (SMHI, 2017b).

Two thirds of the Swedish land area are covered by forests (mostly managed), whereas surface waters cover around 9% of the total area and there are nearly 100 000 lakes in the country. The land-use types in percent of total area are presented in Fig. 1 (SCB, 2017).

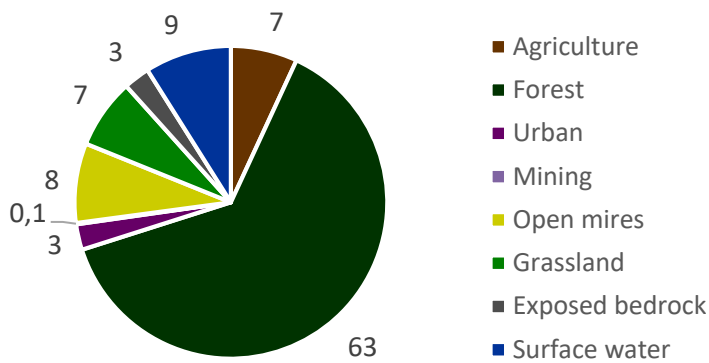


Figure 1. Land-use in percent (%) of the total area of Sweden (SCB, 2017).

2.2. Lakes: stratification, water chemistry and the sediment-water interface

2.2.1. Thermal stratification and vertical distribution of dissolved substances

In most climatic zones, lake surface waters show a pronounced annual temperature cycle reflecting the seasonal variation in climate. Incoming solar radiation drives the temperature cycle and direct thermal contact between lake surfaces and the atmosphere facilitates heat and gas exchange (Boehrer & Schultze, 2008). The attenuation of light in freshwaters is exponential with depth and most of the incoming light energy is absorbed and re-emitted as heat by water, dissolved substances and suspended particles within the first few meters of the lake surface (Brönmark & Hansson, 2005). Wind generated currents distribute the heat in the water column and the depth of heat distribution depends on the available wind energy as well as resistance to mixing due to vertical density differences (Brönmark & Hansson, 2005; Boehrer & Schultze, 2008). Lake stratification and mixing processes are driven by weather conditions, but water density is the central property controlling the stability of stratification (Boehrer & Schultze, 2008). The density of water peaks at 4°C and decreases both with increasing and decreasing temperature. Dissolved substances can also affect water density. In this chapter the annual temperature cycle of moderately deep temperate lakes is described below, starting out with the summer stratification period (Brönmark & Hansson, 2005). This circulation pattern applies for most Swedish lakes, including the studied lakes.

At the start of summer, lake surface water temperature increases and a density gradient is established between the warmer, less dense surface water and the cooler, denser bottom water. The lake begins to stratify, forming an epilimnion (top layer) and a hypolimnion (bottom layer) divided by a sharp temperature gradient called a thermocline. The water layer in between the epi- and hypolimnion is also called metalimnion (Boehrer & Schultze, 2008) (Fig. 2).

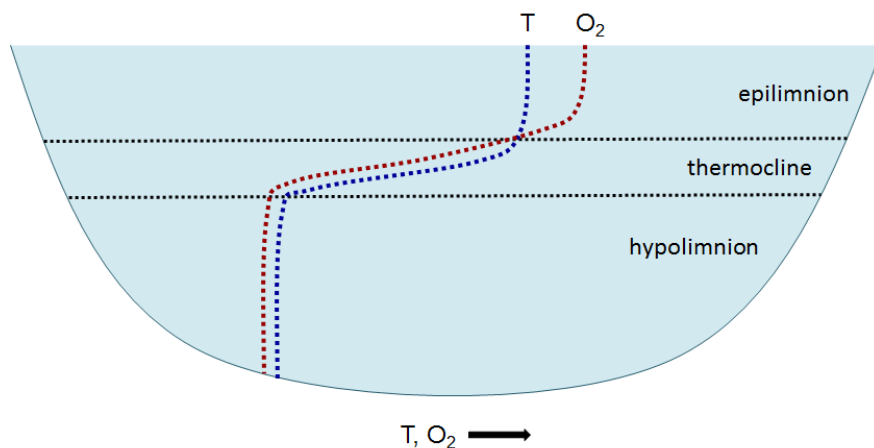


Figure 2. Schematic illustration of a lake with oxygen depleted hypolimnion during summer season thermal stratification.

During the stratification period, wind generated currents distribute heat, oxygen and other substances in the epilimnion. The hypolimnion is however relatively isolated from the oxygen rich top layer, and settling of dead organism and particles is the main external input of matter to bottom waters. The thickness of the epilimnion varies throughout the season, starting out as a thin layer formed in late spring and increasing due to wind action throughout summer (Boehrer & Schultze, 2008). As the year proceeds to autumn, the incoming solar energy decreases and the lake surface starts to cool down. The epilimnetic temperature decreases and the density induced resistance to mixing gradually declines. Eventually, wind generated currents homogenize the whole water column into one layer (mixolimnion) (Brönmark & Hansson, 2005; Boehrer & Schultze, 2008).

Towards winter, the intensity of incoming solar radiation decreases and freshwaters becomes cooler. When lake water temperatures reach 4°C the lake will begin to stratify again, but inversely, with a cooler surface layer and a 4°C bottom layer. The density difference is however small around this temperature range and the resistance to mixing is minor. Eventually, an ice-cover develops, increases in thickness, and seals the lake from wind induced mixing. Towards spring, solar energy increases again and the thickness of the ice-cover declines. Finally, the ice breaks and the lake is exposed to wind induced mixing again, which causes the lake to turnover completely (Brönmark & Hansson, 2005).

Lakes can be classified according to their circulation pattern. Holomictic lakes recirculate at least once per year and can be divided into subclasses, for instance monomictic, dimictic and polymictic, indicating the time and frequency of circulation events. Dimictic lakes have the circulation pattern described above. There are also amictic lakes, which do not experience deep water recirculation. This class usually includes permanently ice-covered lakes. Furthermore, some lakes only experience partial deep water recirculation and are called meromictic (Boehrer & Schultze, 2008). Most lakes in Sweden are dimictic, i.e. they overturn in spring following ice-melt, are thermally stratified during summer, recirculate again in autumn and stratify in winter when the ice-cover acts as a wind barrier. There is however a latitudinal difference in the annual stratification cycle of Swedish lakes.

The vertical and temporal distributions of dissolved and particulate substances in lakes are largely influenced by the seasonal circulation pattern. When the lake water column is homogenised during spring and autumn turnover events, the vertical distribution of substances is generally uniform.

However, as lakes begin to stratify, the chemical composition of epilimnion and hypolimnion starts to differentiate. In bottom waters, oxygen levels decline, whereas the composition of several other major dissolved elements begins to increase (Wetzel, 2001; Brönmark & Hansson, 2005). The dynamics of DO in lakes governs the distribution and productivity of many aquatic organisms, as oxygen is vital for aerobic metabolism. Furthermore, DO levels influence the solubility of several inorganic compounds by affecting redox conditions. DO is also produced in lakes via photosynthesis, and consumed via biological and chemical oxidation processes. The balance between photosynthesis and oxidation processes also influences the dynamics of DO in lakes (Wetzel, 2001).

The vertical distribution of temperature and oxygen during thermal stratification varies with lake productivity. In extremely unproductive lakes, oxygen concentrations with depth are mainly regulated by physical processes (e.g. temperature). However, generally during thermal stratification, biological oxidation of organic matter consumes hypolimnetic oxygen. Since there is no renewal from photosynthesis, diffusion or circulation (as in epilimnion), oxygen levels are gradually depleted (Fig. 2). The rate of oxygen consumption in the hypolimnion depends on the input of organic matter from the upper water layers and temperature. Hypolimnetic oxygen levels in eutrophic lakes are rapidly depleted due to high input of organic matter. Plant and animal respiration contributes to the oxygen depletion, however, bacterial respiration in the water column and at the sediment-water interface is more important. Since organic matter accumulates at the bottom of lakes due to gravitational forces, bacterial decomposition is greatest at the sediment-water interface and this region rapidly becomes anoxic during summer stratification. Highly eutrophic lakes can develop anoxia throughout hypolimnion within a few weeks (Wetzel, 2001).

Dissolved substances may also affect the circulation pattern in lakes. For instance, DOM absorbs incoming sun light and re-emits the energy as heat, which increases light attenuation and temperatures in the top water layers in lakes. This translates into less light and less heat reaching bottom waters, which enhances the temperature difference between surface and bottom waters and strengthens the stability of stratification (reviewed in Solomon *et al.*, 2015).

2.2.2. Lake water chemistry and catchment influences

The movement of water and materials from land to freshwater recipients connects terrestrial and aquatic ecosystems within a catchment (Likens & Bormann, 1974). The composition of lake water is therefore regulated by catchment geology, soil composition and vegetation cover. Moreover, regional climate, hydrology and atmospheric deposition chemistry also plays a key role in shaping the characteristics of lakes (Wetzel, 2001; Brönmark & Hansson, 2005). The chemical composition of precipitation changes as it percolates through soils, as a result of chemical and biological processes, such as degradation of organic materials and weathering (Wetzel, 2001). Weathering of minerals and chemical exchange reactions releases ions, such as Ca^{2+} , Mg^{2+} , K^+ and Na^+ , that are transported with anionic counter ions (i.e. SO_4^{2-} and NO_3^-) to lakes (Eriksson *et al.*, 2011). Major components of biota, such as carbon, nitrogen and phosphorus, are also transported to downstream lakes via the movement of water. In large catchments, infiltrating rainwater has a longer distance to cross before reaching the lake recipient and will hence accumulate more substances. A large catchment to lake area ratio, thus, results in a more pronounced catchment influence on the chemical composition of the lakes within (Wetzel, 2001; Brönmark & Hansson, 2005).

The flux of carbon to and within lakes includes particulate and dissolved inorganic carbon (PIC and DIC), as well as particulate and dissolved organic carbon (POC and DOC). DIC includes the constituents of the carbonate system: dissolved carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). DIC is derived from mineral weathering, atmospheric CO_2 as well as aquatic and terrestrial respiratory production of CO_2 . When precipitation, containing dissolved CO_2 and carbonic acid, infiltrates through catchment soils the water is enriched with microbial and plant derived CO_2 . This generates more carbonic acid, which participates in mineral weathering processes and influences the chemical composition of freshwater recipients. Furthermore, the constituents of the carbonate system are involved in chemical equilibrium processes, which largely regulate the buffering capacity and pH of freshwaters as well as the availability of DIC for photosynthesis (Wetzel, 2001).

Natural waters have the capacity to withstand acidification by the buffering mechanisms of dissolved substances, usually weak acid anions, which can neutralise H^+ . Due to the high solubility and occurrence of CO_2 in waters and the prevalence of carbonates as primary minerals throughout the world, the carbonate system is the major buffering mechanism in freshwaters. The buffering capacity of water is termed *alkalinity* (Wetzel, 2001). Measuring alkalinity provides an indication of the risk of a lake to become acidified. Lakes that have alkalinity levels above 0.5 meq l^{-1} are considered to have a very good buffering capacity, whereas lakes that have alkalinities of less than 0.01 meq l^{-1} have very low or no capacity to buffer inputs of acidifying substances (Brönmark & Hansson, 2005). In freshwaters with low DIC concentrations, dissolved organic anions from DOM can add alkalinity. There are also substances that impart acidity to freshwaters, including organic acids, mineral acids and CO_2 . The combined effect of substances that add acidity or alkalinity determines the actual pH and buffering capacity of lake water (Wetzel, 2001).

Lake ecosystems are dependent on the input of energy in the form of organic matter, which is either produced within the lake (autochthonous) or imported from terrestrial sources (allochthonous). Autochthonous OM is produced by photosynthesizing aquatic organisms, such as algae, cyanobacteria and macrophytes, which fix atmospheric CO_2 and transform it into biomass. Allochthonous organic matter is produced by terrestrial plants within the catchment and transported to lake recipients (Wetzel, 2001). Although organic matter includes both living and non-living organic components in soil and aquatic ecosystems, the living components, such as algae and bacteria, are of very small quantity. Nonetheless, microorganisms are of importance for mediating the energy and carbon fluxes in lakes through decomposition of organic materials. Organic matter mainly consists of dissolved and particulate organic carbon compounds that can be divided into humic and non-humic substances. Non-humic substances include carbohydrates, proteins, lipids, pigments and other low-molecular-weight labile organic substances. The turnover of non-humic substances is fast and the instantaneous concentrations in lakes are usually low. Humic substances are dark-coloured (yellow to brown), heterogeneous and high-molecular-weight degradation products that are recalcitrant to further biological degradation. Due to their stability, humic substances accumulate in soils and waters and form most of the organic matter present therein (70-80%) (Wetzel, 2001). Humic substances give lakes a brownish colour, attenuate light and affect lake water pH through their organic acid components. In catchments dominated by coniferous forests (i.e. the majority of Swedish forested catchments), the high lignin content in leaf litter results in slow degradation rates and subsequent accumulation of humic substances in soil and lake recipients (Brönmark & Hansson, 2005; Porcal *et al.*, 2009).

Algae assimilate P in the form of phosphate, which is incorporated in biomass and passed along the food chain. P concentrations in freshwaters are often measured as total phosphorus (TP), which constitutes both the organic and inorganic fractions and is commonly used as an estimate of lake productivity (Brönmark & Hansson, 2005). The organic fraction of TP is predominant, and most of the total organic P occurs as particulate organic P (approximately 70% or more), whereas the rest is dissolved or colloidal organic P. The percentage of TP present as inorganic soluble P (phosphate) is usually very low (Wetzel, 2001). In most lakes that are minimally affected by anthropogenic sources of P, TP concentrations are between 1 and 100 $\mu\text{g l}^{-1}$ (Brönmark & Hansson, 2005). However, as a result of regional geology, the variations in TP concentrations are high. In high altitude lakes surrounded by crystalline bedrock, P levels are generally the lowest, whereas P levels increase towards lowland lakes enclosed by sedimentary rock deposits. Moreover, TP levels tend to be higher in lakes rich in organic matter, as organic matter contains P (Wetzel, 2001). The amount of P in lakes is also influenced by point and diffuse anthropogenic sources as well as internal loading from sediments (Nürnberg, 2009). Due to human impact from mainly agriculture, urban storm water, and wastewater effluents, many lakes have substantially elevated levels of P. The amount of P in lakes is generally positively related to lake productivity, and increased inputs of P have resulted in widespread eutrophication of lakes (Brönmark & Hansson, 2005).

From the above introduction to lake water chemistry and catchment influences it should be evident that the composition of substances in lake water is a result of multiple mechanisms and processes occurring within the lake and the surrounding catchment. When studying temporal trends in lake water chemistry, it is therefore not straightforward to determine the main drivers behind any observed trends. In bottom waters, reactions occurring at the sediment-water interface largely influence the composition of dissolved substances in hypolimnion and subsequently the whole lake.

2.2.3. The sediment-water interface

Particulate inorganic and organic substances eventually sink to the bottom of lakes, which enables enrichment of nutrients and other substances in the sediment. Sediment consists of a solid phase as well as the pore water. The solid phase contains i) organic matter, ii) minerals and ii) an inorganic constituent of biological origin, including diatom cell walls and calcium carbonates. Decomposition of organic matter predominantly occurs at the sediment-water interface. Consequently, nutrient levels are generally higher in the water overlying sediments compared to the water column (Wetzel, 2001; Brönmark & Hansson, 2005). Sediment mineral particles have a large and active surface area where chemical reactions take place. The processes occurring at the sediment-water interface are important in regulating the composition of dissolved substances in lakes. These processes include ion-exchange reactions between cations and negatively charged surfaces of clay particles, weathering reactions as well as adsorption-desorption reactions. For instance, dissolved silica (Si), phosphate and anions of organic acids can specifically adsorb to hydrous oxide surfaces and, thus, compete for the same sorption sites (Stumm & Morgan, 1981). Several of the substances that are assessed within this study (organic carbon, TP and Si) are therefore interconnected via the adsorption-desorption dynamics of their constituents (in addition to other relationships).

As a consequence of continuous decomposition of organic matter at the sediment-water interface, DO is depleted in the bottom waters during thermal stratification. Under anaerobic conditions, further decomposition of organic matter requires alternative electron acceptors, including nitrate (NO_3^-) and

Fe(III) (in e.g. Fe(III) hydrous oxides). Reduction of NO_3^- produces N_2 or ammonia (NH_4^+), whereas dissimilatory reduction of Fe(III) generates Fe^{2+} . The vertical distribution of NH_4^+ in stratified conditions is opposite that of oxygen: epilimnetic NH_4^+ levels are low, whereas NH_4^+ concentrations increase towards hypolimnion and the sediment (Wetzel, 2001). It is important to note that reductive dissolution of Fe(III) does not only release Fe^{2+} into the overlying water, but also other compounds associated with Fe(III) hydrous oxides, including organic carbon (Skoog & Arias-Esquivel, 2009), phosphate (Nürnberg, 2009) or Si (Kato, 1969; Siipola *et al.*, 2016).

The exchange of P across the sediment-water interface plays an important role in the cycling of P in lakes and is regulated by sorption processes, redox conditions as well as biological activity (Wetzel, 2001). P is deposited into lake sediments by multiple mechanisms, including sedimentation of catchment derived P minerals and of P incorporated in organic matter. Adsorption and co-precipitation of phosphate with inorganic compounds are also major contributors to sediment P loading. Phosphate can adsorb to positively charged edges of clay minerals and hydrous oxides (e.g. Fe(III) oxyhydroxide), or co-precipitate with Fe or Al (Wetzel, 2001). Release of P from sediments is commonly referred to as internal loading of P and is often the main P load to lakes during summer. Internal loading of P is defined as P released from sediment surfaces and transported into the overlying water. The main mechanism responsible for the P release is dissimilatory reduction of Fe(III) oxyhydroxide. When Fe(III) is reduced to the soluble Fe^{2+} , associated phosphate is released into the pore water and can be transported to the overlying water by diffusion or bioturbation (Nürnberg, 2009). Reduction of Fe(III) also affects the alkalinity of hypolimnion by consuming H^+ (Dillon *et al.*, 1997). As in the case of phosphate, Si can adsorb to the surfaces of hydrous oxides (such as Fe(III) oxyhydroxides). In natural waters below pH 9, Si is primarily present as silicic acid (H_4SiO_4). Adsorption of phosphate and Si to hydrous oxides is accompanied by a release of protons into the surrounding water (Stumm & Morgan, 1981).

2.3. Time trends in DOC and P concentrations in northern lakes

This chapter presents long-term time trends in lake surface water DOC concentrations in Europe and North America as well as recently reported long-term trends in lake surface water P concentrations in Sweden. Potential drivers of the reported trends is also described.

2.3.1. Trends in DOC concentrations

Over the past 30 years, DOC concentrations in northern lakes and streams have increased (Monteith *et al.*, 2007; Erlandsson *et al.*, 2008; Futter *et al.*, 2014). Proposed drivers of the rising DOC concentrations include climate change (Hongve *et al.*, 2004) and recovery from acidification (Evans *et al.*, 2006; Monteith *et al.*, 2007). Much of the organic carbon in lakes is terrestrially derived and mainly imported as DOC. Wetlands and littoral land-water interfaces are highly productive and constitute an important source of DOC (Wetzel, 2001).

Different aspects of a changing climate can influence DOC export from catchments to streams and lakes. Climate change scenarios predict a future with either warmer and wetter, or warmer and drier conditions in the northern temperate regions. Rising temperatures may result in shorter periods of frozen soils and increased soil temperatures, which would lead to higher decomposition rates of organ-

ic matter. If more DOC is produced within a catchment, the terrestrial DOC export to lakes and streams may increase. Moreover, rising DOC concentrations in lakes have also been linked to climate change mediated effects on runoff due to changes in precipitation patterns. The intensity and duration of precipitation affects the flow of water through catchments and, consequently, the concentrations and loads of DOM into lakes and streams (Porcal *et al.*, 2009 and references therein).

Several studies have shown that increasing levels of DOC in northern lakes and streams can be ascribed to recovery from acidification (Evans *et al.*, 2006; Monteith *et al.*, 2007). Acid deposition has decreased over the past decades in Europe and North America, as a response to decreased emissions of sulphur (mainly) and nitrogen oxides (Driscoll *et al.*, 2016; Rogora *et al.*, 2016). In parallel to the decline in acid deposition, studies have observed several indications of soil and surface water recovery from acidification (Löfgren *et al.*, 2011; Futter *et al.*, 2014; Garmo *et al.*, 2014). Pronounced recovery has in particular been observed in lakes in acid-sensitive regions (Kopáček *et al.*, 2015). However, in acid-sensitive Swedish lakes, the recovery has been slow (Futter *et al.*, 2014).

Sobek *et al.* (2007) performed a large scale study of the patterns and regulations of DOC in 7 500 lakes, covering a wide climatic gradient in mainly the northern hemisphere. The median DOC concentration in the assessed lakes was 5.71 mg l⁻¹ and in 87% of the lakes, DOC concentrations were between 1 and 20 mg l⁻¹. A partial least square regression analysis demonstrated that DOC concentrations in lakes were highly influenced by terrestrial land cover. For instance, DOC levels were positively correlated with “conifer boreal forest” and negatively correlated with “bare desert”. Lake DOC levels were also positively related to conductivity, soil carbon density and soil C:N ratio. The study also demonstrated that high levels of precipitation, mean annual runoff and high altitude corresponds to low DOC levels in lakes (Sobek *et al.*, 2007).

There are several potential consequences of increased concentrations of DOM in lakes. Since DOM absorbs sunlight, higher concentrations increase vertical light attenuation, resulting in less light energy available to heat bottom waters (reviewed in Solomon *et al.*, 2015). Tanentzap *et al.*, (2008) reported long-term cooling of whole-lake average temperatures in Clearwater Lake, Canada, despite indication of climate warming. The whole-lake cooling was a result of a rising thermocline depth and decreased hypolimnetic water temperatures. Modelling results showed that the main drivers of the rising thermocline depth were reductions in wind speed, due to forest regrowth, and increased DOC concentrations. Moreover, the results showed that the cooling of hypolimnetic waters was caused by substantial increases in vertical light attenuation, itself a result of increased DOC concentration in Clearwater Lake (Tanentzap *et al.*, 2008). Increased DOM concentrations and absorption of light energy in top waters of lakes may also result in warming of the epilimnion, which would influence thermal stratification. Moreover, warmer surface waters might result in earlier onset and longer duration of the summer stratification period (Solomon *et al.*, 2015). This may in turn exacerbate already oxygen poor conditions in hypolimnion and result in longer periods of anoxia in the affected lakes.

2.3.2. Trends in P concentrations

Studies have shown that P concentrations in lakes and streams in the northern hemisphere are declining and this process is referred to as oligotrophication (Eimers *et al.*, 2009; Arvola *et al.*, 2011; Hu & Huser, 2014; Huser *et al.*, 2018). In a current study using monitoring data from the Swedish Trend Lakes (n=81), possible drivers of the observed declining surface water TP concentrations were assessed (Huser *et al.*, 2018). The results showed that in more than half of the analysed lakes (n=42), the surface

water TP concentrations had declined between 1988 and 2013, whereas total organic carbon (TOC, of which >95% is DOC in boreal lakes (Gadmar *et al.*, 2002)) concentrations had increased in 70% of the studied lakes. Because organic matter in northern lakes is largely catchment derived, and DOM is the main vector for P transport (Baldwin, 2013; as in Huser *et al.*, 2018), the authors argued that P levels in terrestrially derived DOM might be decreasing (Huser *et al.*, 2018). To determine the main drivers of the observed TP trends, Huser *et al.* (2018) performed stepwise multiple linear regression. In the final model, three parameters were included and explained 74% of the variation in surface water TP trends. The variables were i) change in TOC over time (Δ TOC, 59% variation explained), ii) average catchment soil aluminium to P ratio (Al:P, 8% variation explained) and iii) change in pH over time (Δ pH, 7% variation explained). According to the authors, the influence of catchment Al:P indicates that soil binding capacity of P might be connected to the observed declining P trends (Huser *et al.*, 2018). The authors further discussed that since DOC release from soils has previously been correlated with increased P sorption (in Giesler *et al.*, 2005), the catchment P export might have been limited due to increased DOC export in the study area. Furthermore, the influence of Δ pH was most likely connected to decreased solubility and transport of P binding minerals (hydrrous oxides) to lakes, itself a result of soil recovery from acidification. Interestingly, no relationship was observed between the modelled declining trends in P deposition and changes in lake water TP concentrations. Thus, the authors concluded that the declining TP concentrations in the surface waters of the study lakes can be attributed to changes in watershed processes and climate, which affect P sorption and transport to lakes (Huser *et al.*, 2018).

3. Materials and Methods

3.1. Lake and catchment information

The 13 study lakes are small (0.1 – 2.8 km²) boreal and boreonemoral lakes located between 56.6° and 68.3° N (Fig. 3, Table 1, 2). The lakes almost cover the entire latitudinal extent of Sweden and are unaffected by local anthropogenic disturbance other than forestry. There is however a strong focus on the southern region (10 out of 13 lakes), where the lakes also cover the longitudinal climatic difference with increasing annual precipitation from east to west. Moreover, the Swedish west coast and the southern region was historically more heavily affected by acid rain (Moldan *et al.*, 2013).



Figure 3. Map of Sweden displaying the locations of the studied lakes.

Table 1. Lake coordinates in SWEREF TM 99 and WGS84 formats.

Lake	SWEREF TM 99		WGS84	
	N	E	N	E
Abiskojaure	7580297	649260	68.30°	18.62°
Allgjuttern	6423705	564394	57.95°	16.09°
Brunnsjön	6272735	544546	56.60°	15.73°
Fiolen	6326806	471568	57.08°	14.53°
Fräcksjön	6449472	334111	58.16°	12.18°
Härsvatten	6435278	324786	58.02°	12.03°
Remmarsjön	7086383	660281	63.87°	18.26°
Rotehogstjärnet	6524276	304669	58.81°	11.62°
Stora Skärsjön	6282846	381812	56.67°	13.07°
Stensjön	6835462	584002	61.64°	16.59°
Stora Envättern	6555399	634249	59.12°	17.34°
Älgsjön	6552173	578856	59.10°	16.38°
Övre Skärsjön	6634470	530705	59.85°	15.55°

All study lakes except for Härsvatten are included in the Swedish national monitoring project “Trend Lakes”. The Trend Lakes project is a part of the Swedish national monitoring of freshwaters, run by the Swedish Agency for Marine and Water Management (SwAM) and performed by SLU. The overall objectives of the Trend Lakes project are to describe the state and large-scale changes in the Swedish aquatic environment, and to provide a basis for assessing threats and possible measures. The lakes included are a representative sample of Swedish lakes unaffected by local emissions or intensive land-use (other than forestry). Härsvatten is a reference lake in the ISELAW (Integrated studies of the effects of liming acidified waters) project, which aims at investigating the long-term effects of liming in lakes and rivers, as well as developing the liming operations (Fölster *et al.*, 2014).

The lake areas range from 0.1 to 2.8 km², whereas the maximum depths range between 7.7 m and 40.7 m (Table 2). Abiskojaure is the largest lake in the dataset, both by lake area and volume. The smallest lakes by area are Brunnsjön, Rotehogstjärnet and Härsvatten. Further details about lake morphology are listed in Table 2. A previous characterisation of the lakes assessed in this study showed that the estimated proportions hypolimnetic lake volume (% of total volume) and hypolimnetic sediment area (% of total sediment area) varied substantially (Fig. 4) (Persson, 1996). According to the previous study, Allgjuttern, Brunnsjön and Fräcksjön have the largest shares of hypolimnetic lake volume and sediment area. The smallest hypolimnetic volume and sediment area was estimated to be 1% for both characteristics in Fiolen (Persson, 1996).

Table 2. Lake morphometry, including area, volume, maximum depth (z) and mean depth (z) as well as altitudes (meters above sea level) (Persson, 1996). Grey = maximum values, green = minimum values.

Lake	Area (km ²)	Vol (Mm ³)	Max z (m)	Mean z (m)	m a.s.l.
Abiskojaure	2.838	31*	35	11*	487.5
Allgjuttern	0.185	2.096	40.7	11.4	126.3
Brunnsjön	0.107	0.571	10.6	5.3	98.4
Fiolen	1.637	6.21	10.5	3.8	226
Fräcksjön	0.276	1.624	14.5	6.0	58
Härsvatten	0.180	1.008	26.2	5.7	130
Remmarsjön	1.364	7.017	14.4	5.2	234.1
Rotehogstjärnet	0.168	0.571	9.4	3.4	120.5
Stora Skärsjön	0.313	1.172	11.5	3.8	60
Stensjön	0.569	2.407	8.5	4.2	268
Stora Envättern	0.373	1.847	11.2	5	62
Älgsjön	0.357	1.31	7.7	3.7	39
Övre Skärsjön	1.728	9.907	32	5.7	218.7

* Estimated values (Persson, 1996).

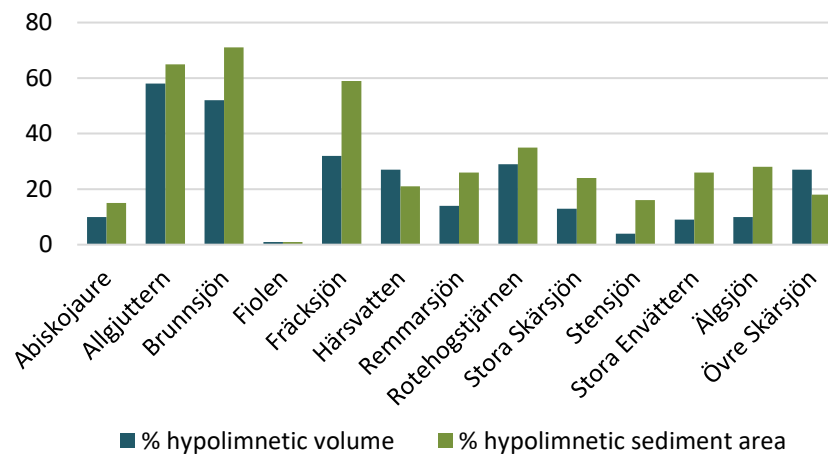


Figure 4. Estimated proportions hypolimnetic lake volume (% of total lake volume) and hypolimnetic sediment area (% of total sediment area) (Persson, 1996).

Most of the study lakes are oligotrophic, whereas 3 lakes are mesotrophic (based on mean surface water TP, 2013-2015, Table 3) (Swedish EPA, 2000). Älgsjön is the only eutrophic lake in the dataset and had the highest mean chlorophyll *a* concentration during this period. Abiskojaure is the clearest lake with the lowest levels of nutrients, chlorophyll *a* and TOC, whereas Brunnsjön is the most humic lake, with the highest levels of TOC and total nitrogen (Table 3).

Table 3. Mean surface water levels of absorbance (Abs F, filtered, 420 nm/5 cm), chlorophyll *a* (chl *a*), total nitrogen (TN), total organic carbon (TOC) and total phosphorus (TP) calculated for 2013–2015. Trophic status and weather the lake is humic or clear is also stated. O = oligotrophic, M = mesotrophic and E = eutrophic. H = humic and C = clear. Grey = maximum values, green = minimum values.

Lake	Abs F	Chl <i>a</i> ($\mu\text{g l}^{-1}$)	TN ($\mu\text{g l}^{-1}$)	TOC (mg l^{-1})	TP ($\mu\text{g l}^{-1}$)	Trophic status ¹	Humic/ Clear ²
Abiskojaure	0.013	0.76	96	1.4	3.9	O	C
Allgjuttern	0.056	2.3	308	7.4	4.3	O	C
Brunnsjön	0.477	3.5	828	22.8	13.4	M	H
Fiolen	0.066	5.9	505	8.2	12.7	M	H
Fräcksjön	0.149	4.1	432	11.5	9.9	O	H
Härsvatten	0.036	2.3	360	4.4	4.0	O	C
Remmarsjön	0.172	2.2	266	9.3	8.5	O	H
Rotehogstjärnet	0.275	12.2	476	14.1	13.9	M	H
Stora Skärsjön	0.049	3.9	294	4.5	7.9	O	C
Stensjön	0.127	2.6	244	8.0	6.5	O	H
Stora Envättern	0.087	3.3	408	11.1	6.9	O	H
Älgsjön	0.311	14.2	776	21.5	25.5	E	H
Övre Skärsjön	0.204	2.3	376	10.4	6.3	O	H

¹ Based on mean TP concentrations in lake surface waters 2013–2015. TP $\leq 12.5 \mu\text{g l}^{-1}$ = O, TP between 12.5 – 25 $\mu\text{g l}^{-1}$ = M, TP between 25 – 100 $\mu\text{g l}^{-1}$ = E (Swedish EPA, 2000).

² Based on mean absorbance (filtered, 420 nm/5 cm) in lake surface waters 2013–2015. Absorbance ≤ 0.06 = clear, absorbance > 0.06 = humic (Swedish EPA, 2007).

Forests are the predominant land cover in the catchment areas of all studied lakes (48-92%), except for Abiskojaure (8%) (Table 4). In most of the catchments there are no urban areas, and agriculture only covers a substantial percentage of the Fiolen catchment area (12%). Freshwater is a substantial share of the area in several lake catchments, especially for Fiolen (29%). The catchment land cover data was provided by Fölster¹ and originates from Swedish Land Cover Data (Svenska Marktäckedata), which is based on the EU classification system for CORINE land cover (Table 4).

¹ Jens Fölster, Head of Geochemistry and hydrology unit, Department of Aquatic Sciences and Assessment, SLU, land-use data was produced 2014 and sent via e-mail 2017-09-18.

Table 4. The catchment areas of the studied lakes and land cover in percent of the catchment area (aggregated from Swedish Land Cover Data, provided by Fölster, Department of Aquatic Sciences and Assessment, SLU).

Lake	Catchment (km ²)	Forest (%)	Mire (%)	Water (%)	Urban (%)	Agric. (%)	Pasture (%)	Other* (%)
Abiskojaure	370	8.0	0.29	4.1	0	0	0	88
Allgjuttern	1.13	84	1.3	15	0	0	0	0
Brunnsjön	3.42	92	4.1	3.1	0	0	0.51	0
Fiolen	5.45	48	4.8	29	0	12	5.6	0
Fräcksjön	4.59	87	4.2	6.1	1.8	0	0.76	0
Härsvatten	1.94	75	5.5	19	0	0	0	0
Remmarsjön	126	82	14	3.8	0.12	0.21	0.34	0
Rotehogstjärnet	3.58	78	16	4.5	0	0.91	0	0
Stora Skärsjön	2.64	75	8.9	16	0	0	0	0
Stensjön	3.09	66	16	18	0	0	0	0
Stora Envättern	1.43	59	14	27	0	0	0	0
Älgsjön	5.04	84	5.3	6.2	0	0.050	4.4	0
Övre Skärsjön	8.76	71	8.3	20	0	0.37	0.34	0

* Mainly other vegetation cover or sparsely vegetated land, including exposed bedrock.

3.2. Laboratory methods

The water chemical analyses were performed by the Geochemical laboratory at the Department of Aquatic Sciences and Assessment at SLU, using SWEDAC accredited methods. Current methods are listed in Table A1 in Appendix A, whereas further details including older methods are available on the SLU Geochemical Laboratory website:

<https://www.slu.se/vatten-miljo/vattenanalyser>

When changing chemical analysis methods (or instruments), the staff at the Geochemical laboratory performs quality control procedures to assess the reliability and comparability of the new methods and to renew the accreditation. For instance, the new and past methods are used in parallel for a period of time and statistical analyses are performed to determine the comparability of the methods. Further information about the water chemical analysis and quality assurance are available at the webpage above.

Within this study, lake water TOC data and trends are considered to represent concentrations and changes in DOC, as generally >95% of the organic carbon in boreal lake water is dissolved (Gadmar *et al.*, 2002).

3.3. Data collection and treatment

For the purpose of this study, Swedish reference lakes with long-term and active bottom water sampling were considered to be suitable candidates. An additional criterion was consistent measurements of DO. Initially, monitoring data from all Swedish reference lakes included in national and regional monitoring programmes was downloaded. After examination of the sampling depths, active sampling period and DO data, 13 lakes were chosen as suitable candidates (Table 5). The water

chemistry data was downloaded from a database managed by SLU (<http://miljodata.slu.se/mvm/>) and the data treatment was performed using Microsoft Access, Microsoft Excel and JMP (SAS Institute Inc.).

Table 5. The studied lakes, total number of samples, sampling period and years as well as mean yearly sampling frequency. From 2013, Härsvatten was only sampled 4 times per year in general.

Lake	Samples	Period	Years	Frequency
Abiskojaure	132	1988-2015	28	5
Allgjuttern	215	1988-2015	28	8
Brunnsjön	217	1988-2015	28	8
Fiolen	220	1988-2015	28	8
Fräcksjön	184	1988-2011	24	8
Härsvatten	202	1988-2015	28	7
Remmarsjön	212	1988-2015	28	8
Rotehogstjärnet	217	1988-2015	28	8
Stora Skärsjön	216	1988-2015	28	8
Stensjön	210	1988-2015	28	8
Stora Envättern	218	1988-2015	28	8
Älgsjön	111	1997-2011	15	7
Övre Skärsjön	211	1988-2015	28	8

The water chemistry data from the 13 study lakes was separated into two datasets containing i) surface water samples (0.5 m) or ii) bottom water samples, from the same sampling date. According to sampling procedures, bottom water samples were sampled one meter above the sediment level. The bottom water sampling depths of certain lakes varied slightly with time. In order to eliminate the potential influence of a changing sampling depth to time trends in water chemistry, outliers were examined. For each lake, the sampling depths of the bottom water measurements were compared with the mean bottom water sampling depth of the respective lake. If a sampling depth was more than two standard deviation units from the respective lake mean, it was marked as a potential outlier. Visual inspection of lake by lake time series plots of DO concentrations showed no difference between the general temporal pattern and the potential outliers. Therefore, most of the potential outliers were kept in the dataset, except for a few that were considered too shallow (in total 14 samples).

In order to evaluate trends in yearly minimum, median and maximum DO concentrations, some values were removed from the dataset, since lack of DO measurements resulted in the same minimum, median and maximum values in these cases. Data points for 1988 were removed for Abiskojaure, Stora Skärsjön and Stensjön. Furthermore, Härsvatten was not assessed after 2012, when the sampling frequency changed from 8 to 3 samples per year in 2013, and then to 4 samples per year. This change obscured several temporal patterns. Moreover, DO was only reported once in Härsvatten 2014. For the same reason, Härsvatten was only analysed until and including 2012 when assessing minimum, median and maximum water temperatures.

3.3.1. Identification of outliers

After visual inspection of time series plots displaying the parameters of interest in this study it was suspected that some extreme values were likely false (see for instance Fig. 5). Different methods were

therefore tested in order to find a suitable way of identifying and removing outliers. However, none of the methods applied was considered satisfactory for this dataset. All measurements were consequently included in further analysis. The methods evaluated and their insufficiency will be described in this section in order to justify keeping all measurements in the dataset.

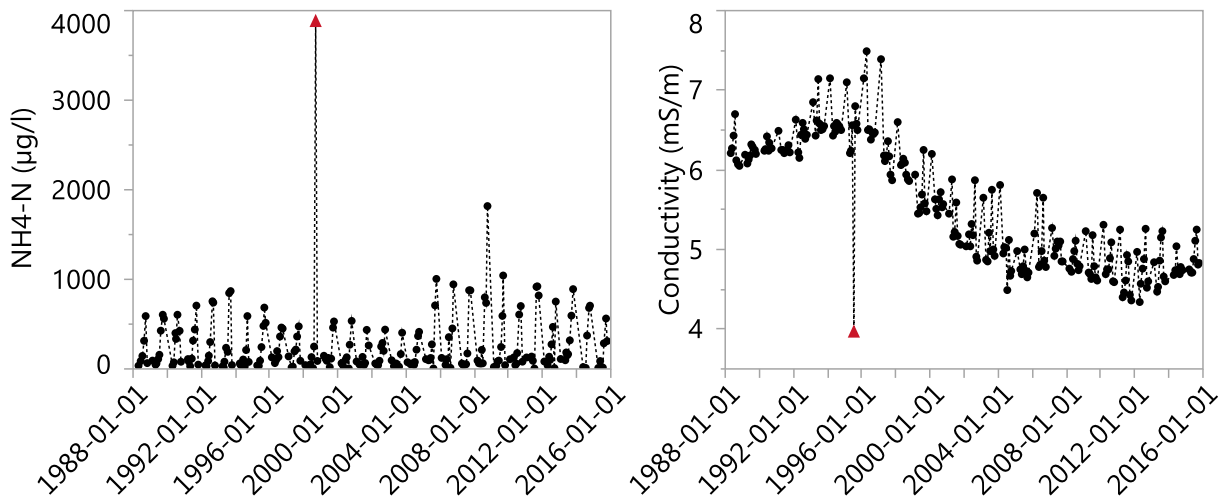


Figure 5. Example of suspected false extreme values (red triangles). The plots display concentrations of nitrogen from ammonia (NH₄-N) in the bottom waters of Stora Skärsjön (left) and conductivity levels in the bottom waters of Fiolen (right).

For the first method (referred to as method $\text{mean} \pm \text{SD}$) tested, measurements from all parameters of interest were first log transformed (\log_{10}). Then, if a value was more than two standard deviation units from the \log_{10} parameter mean of the respective lake, it was marked as a potential outlier. After visual inspection it was apparent that most of the identified outliers were likely not false extreme values, since they followed the general temporal pattern and were accompanied by several adjacent values. Using three standard deviation units as a condition was not satisfactory in all cases neither for this dataset (Fig. 6).

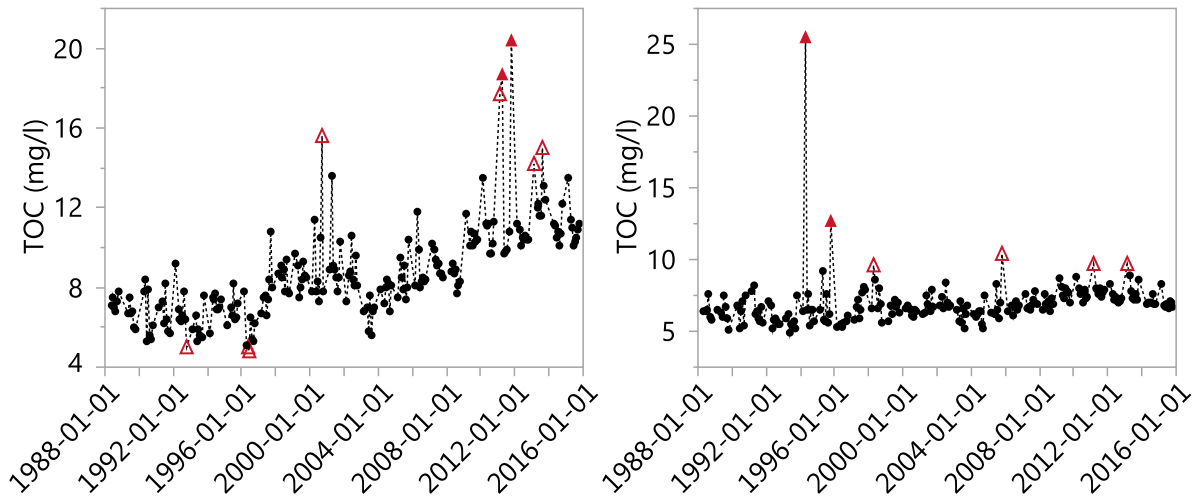


Figure 6. Example of method $\text{mean} \pm \text{SD}$, used to identify potential outliers. The plots display total organic carbon (TOC) concentrations in the bottom waters of Övre Skärsjön (left) and Allgjuttern (right). The outliers were values (log transformed) more than two standard deviation units (open red triangles) or three standard deviation units (red triangles) from the \log_{10} parameter mean.

In view of this, a second method was tested (referred to as method PCT99-dif). In this method, the outliers were identified by calculating and adding up the absolute difference between the measurement of interest (x_n) and the previous ($x_{(n-1)}$) and subsequent ($x_{(n+1)}$) measurement. The summed absolute difference ($|x_n - x_{(n-1)}| + |x_n - x_{(n+1)}|$) calculated for each sample was compared with the 99th percentile of the summed absolute difference calculated for each lake. If $|x_n - x_{(n-1)}| + |x_n - x_{(n+1)}|$ was larger than the 99th percentile (per parameter and lake), the sample was identified as a potential outlier. See Figs. 6 and 7 for a comparison of method $\text{mean} \pm \text{SD}$ and method PCT99-dif.

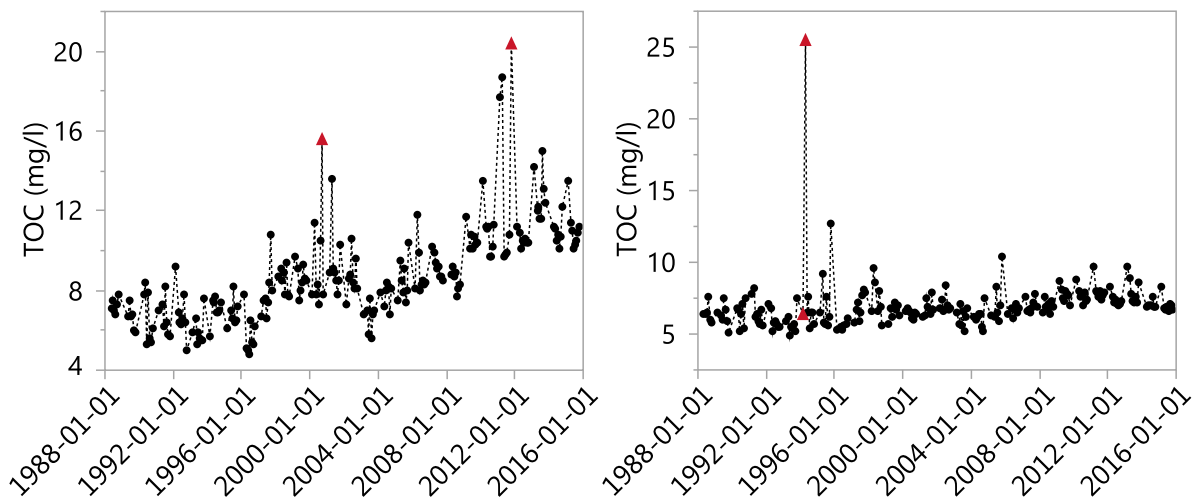


Figure 7. Example of method PCT99-dif, used to identify potential outliers. The plots display total organic carbon (TOC) concentrations in the bottom waters of Övre Skärsjön (left) and Allgjuttern (right). The outliers (red triangles) are samples for which the absolute difference between the sample (x_n) and adjacent measurements, i.e. $|x_n - x_{(n-1)}| + |x_n - x_{(n+1)}|$, was larger than the 99th percentile.

One adverse outcome of method PCT99-dif was that some measurements sampled prior or after extreme values were falsely marked as outliers, although the values followed the general pattern (as in Allgjuttern, Fig. 7). Therefore, an *additional* condition was used in the final method tested (referred to as method PCT99-dif & max/min-dif). First the maximum value of either $|x_n - x_{(n-1)}|$ or $|x_n - x_{(n+1)}|$ was identified and divided by the minimum value of either $|x_n - x_{(n-1)}|$ or $|x_n - x_{(n+1)}|$ (max/min-dif). Provided that the summed added difference is large (condition from method PCT99-dif), max/min-dif should be approximately 1 for extreme values and >1 to $>>1$ for adjacent “true” measurements. Hence, if the condition from method PCT99-dif was fulfilled, and if max/min-dif was <2 , the value was marked as an outlier and evaluated. For the TOC concentration time series data, this method was suitable for the temporal pattern in for instance Allgjuttern (Fig. 8). In the case of Övre Skärsjön, the same TOC outliers were chosen with the added criterion as for method PCT99-dif (Figs. 7, 8).

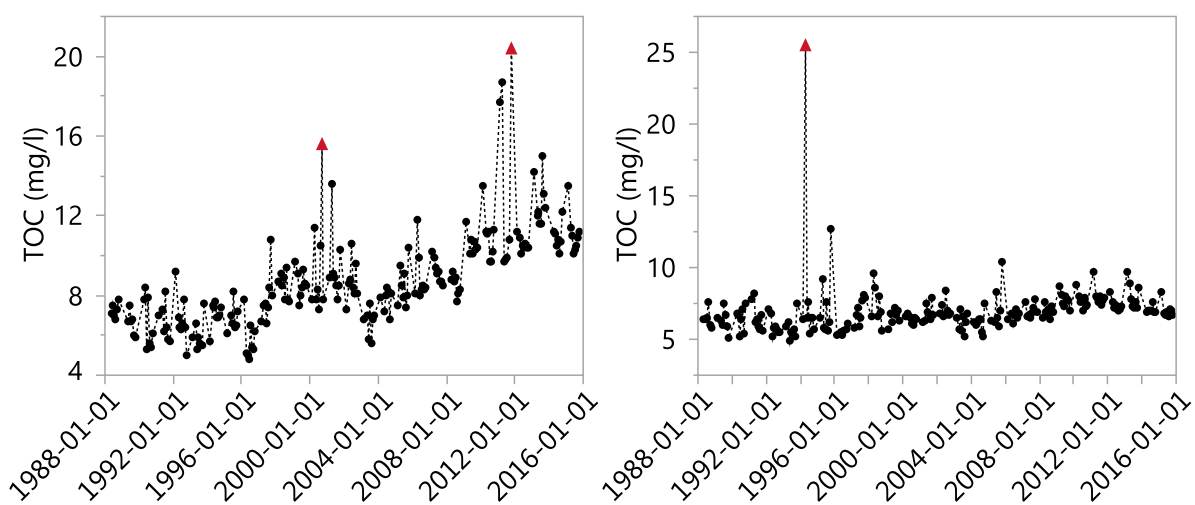


Figure 8. Example of method PCT99-dif & max/min-dif, used to identify potential outliers. The plots display total organic carbon (TOC) concentrations in the bottom waters of Övre Skärsjön (left) and Allgjuttern (right). The outliers (red triangles) were identified by two conditions: 1) samples for which the absolute difference between the sample (x_n) and adjacent measurements, i.e. $|x_n - x_{(n-1)}| + |x_n - x_{(n+1)}|$, was larger than the 99th percentile, and 2) samples for which the ratio between the maximum and minimum of either $|x_n - x_{(n-1)}|$ or $|x_n - x_{(n+1)}|$ was <2 .

After evaluation of the values identified as outliers by method PCT99-dif & max/min-dif, it was evident that the method had limitations. Due to dilution and concentration effects, high variations between adjacent measurements are not improbable when conditions in the bottom waters change from a mixed water layer (during late autumn and spring turnover) to stratified bottom waters (summer and winter thermal stratification). Several identified outliers were likely only portraying this effect. For instance, two samples in Allgjuttern were identified as outliers in the nitrogen from ammonia ($\text{NH}_4\text{-N}$) time series data (Fig. 9). The identified outliers were the first measurement of the respective year (in February and March), and in both cases the previous measurements were sampled in autumn, whereas the subsequent measurements were sampled in spring. A mere visual inspection of the $\text{NH}_4\text{-N}$ time series plots showed that the variations in $\text{NH}_4\text{-N}$ concentrations were also high in other cases in

between measurements. Moreover, Allgjøttjern DO time series plots display the seasonal shift in DO concentrations between these measurements, which further confirms the observation (Fig. 9).

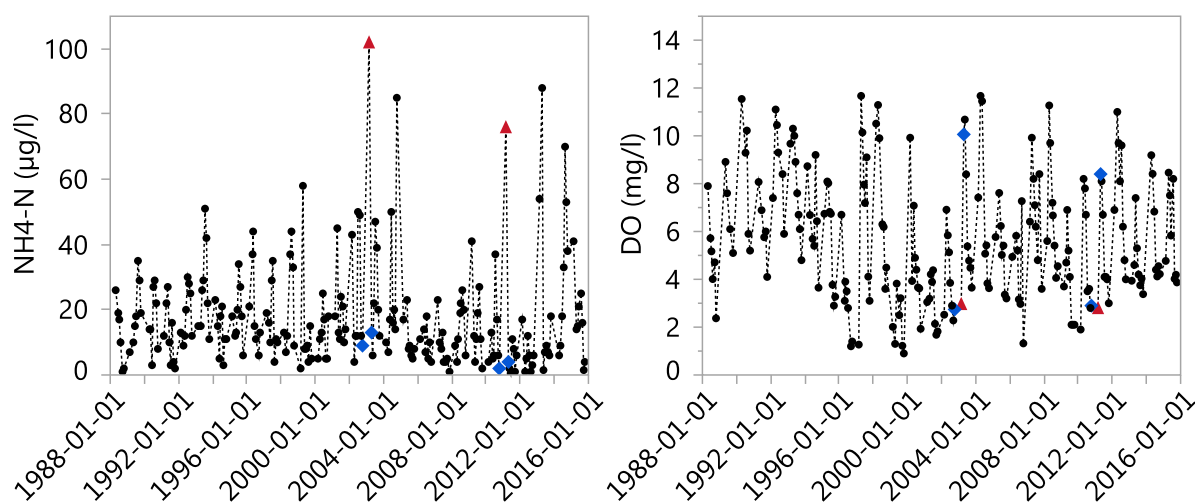


Figure 9. Example of outliers that likely represent true large variation in bottom water concentrations of dissolved substances, as conditions change from stratified to mixed water. The plots display nitrogen from ammonia ($\text{NH}_4\text{-N}$, left) and dissolved oxygen (DO, right) concentrations in the bottom waters of Allgjøttjern. The red triangles are $\text{NH}_4\text{-N}$ outliers identified by method PCT99-dif & max/min-dif, and the blue diamonds are adjacent measurements. The DO plot shows the difference in DO levels between stratified (red triangle, winter stratification) and mixed (subsequent blue diamond, spring turnover) conditions.

Due to the above mentioned limitations and other similar cases observed, all measurements were kept in the dataset in order not to fail observing important events and variations in bottom water chemistry.

3.3.2. Statistical methods

The Mann-Kendall (MK) trend test was used to assess if the concentrations of selected parameters (e.g. TOC, DO, TP) have statistically significantly changed over time in the studied lakes. Significant(ly) is henceforth used when stating “statistical significance” at a significance level of 0.05. Time trends were assessed for i) surface water levels of absorbance (filtered, 420 nm/5 cm), alkalinity, chlorophyll α , conductivity, DO, $\text{NH}_4\text{-N}$, pH, Si, sulphate (SO_4^{2-}), water temperature, TOC and TP, as well as ii) bottom water levels of conductivity, DO, $\text{NH}_4\text{-N}$, pH, Si, water temperature, TOC and TP. In order to further analyse bottom water oxygen levels and temperatures, MK trend tests were performed for time series data of yearly minimum, median and maximum DO concentrations and water temperatures. Furthermore, to evaluate if there were any significant monthly trends in surface and bottom water temperatures, seasonal (by month) MK trend tests of monotonic trends were also performed.

MK is a rank-based non-parametric test for significance of Kendall's rank correlation coefficient τ (τ). No assumption of normality is required, however, the Y variables should not be serially correlated and the spread of the distribution must remain constant. The test is performed by calculating Kendall's S

statistic from the Y and X data pairs. If S is significantly different from zero, the null hypothesis (H_0) of no trend is rejected. To obtain the ranks of data, the following procedure is performed:

All data pairs are first ordered by increasing time (T). If the Y-values increase more often than decrease over time, there is a positive correlation (trend) between Y and T. Similarly, if the Y values decrease more often than increase with T, there is a declining trend in Y. If the Y-values increase and decrease roughly the same number of times, there is no correlation with T. A two-sided hypothesis test evaluates the following statements for the null hypothesis (H_0) and the alternative hypothesis (H_1):

H_0 : no correlation exists between Y and T ($\tau = 0$), i.e. there is no monotonic trend

H_1 : Y and T are correlated ($\tau \neq 0$), i.e. there is a monotonic trend

To compute the test statistic Kendall's S, the number of Y-T data pairs where Y declines as T increases (discordant pairs, M) is calculated. Next, the number of Y-T data pairs, where Y increases as T increases (concordant pairs, P) is calculated. Following this, the test statistic is calculated by subtracting the number of discordant pairs (M) from the number of concordant pairs (P):

$$S = P - M$$

The number of possible comparisons among the n data pairs are $n(n-1)/2$. If all Y's increase over time, $S = n(n-1)/2$. Similarly, if all Y's decrease as T increases $S = -n(n-1)/2$. Following this, by dividing S with $n(n-1)/2$, a value between -1 and +1 is obtained, and this value is called Kendall's τ .

$$\tau = \frac{S}{n(n-1)/2}$$

Finally, in order to test for significance of τ , Kendall's S is standardised, as is common procedure in hypothesis testing, and the standardised test statistic (which can be approximated by a normal distribution if $n > 10$) is used to determine the p-value. If the p-value is less than the significance level (α), the null hypothesis of no trend is rejected.

In order to estimate the yearly increase or decline in lake water concentrations for the significant trends, Theil-Sen slope estimates were calculated. To calculate the Theil-Sen slope, each Y-T data pair of a time series is compared with all other Y-T data pairs, and for each of the comparisons a slope ($\Delta Y/\Delta T$) is calculated. A dataset containing n Y-T pairs will result in $n(n-1)/2$ slopes. The Theil-Sen slope is the median of all possible pairwise slopes (Helsel & Hirsch, 1992).

The MK trend tests and the calculations of Theil-Sen slopes were performed using SK-Theil, which is a Visual Basic Excel program developed by Grimvall (1998) and further extended and modified by Fölster and Seibert (2003).

3.3.3. Additional calculations

The yearly rate (%) of change in concentrations of the assessed water chemical parameters with statistically significant trends (Mann-Kendall, $p < 0.05$) was estimated by dividing the Theil-Sen slopes with the median concentration of the respective parameter for each lake and over the study period (Tables 15, 16). The significant trends were also averaged by parameter for surface and bottom waters separately.

To assess when (i.e. which month) the maximum concentrations of TOC, TP, NH₄-N and Si generally occurred in each study lake, the following calculations were performed: First, the yearly maximum concentration of TOC, TP, NH₄-N and Si was identified for each lake and for the whole study period. Then, the number of samples with the yearly maximum values were summed up by sampling month and lake (Fig. 12). Following this, in order to find out when the maximum concentrations of the selected parameters generally occurred for the whole body of lakes, the number of samples with the maximum yearly values were summed up by month and divided by the total number of samples (with the maximum yearly values). This resulted in a fraction stating the overall monthly share of the yearly maximum values for the parameters of interest (Fig. 11, left). Furthermore, to enable an unbiased assessment of the occurrence of maximum concentrations, the overall monthly sampling frequency relative to the month with the highest number of samples (June) was also calculated (Fig. 11, right).

4. Results

4.1. Overview of lake water chemistry

In this chapter, an overview of lake water chemistry in the studied lakes as well as the differences in concentrations between surface and bottom waters is presented. The median surface water pH (over the whole study period) ranged between pH 4.7 in the acidified lake Härsvatten, to 7.1 in the northern lake Abiskojaure (Table 6). In 12 out of 13 lakes, median pH levels were lower in the bottom waters compared to surface waters. This is consistent with that CO₂ consuming photosynthesis generally is absent in the bottom waters (of sufficiently deep lakes), as opposed to the surface waters. However, CO₂ producing (i.e. acidity generating) respiratory processes are prevalent throughout the lake, and especially at the sediment-water interface (Wetzel, 2001). Other lakes with the lowest median surface water pH levels in this dataset include Rotehogstjärnet (pH 5.4) and Brunnsjön (pH 5.5) (Table 6). Rotehogstjärnet lies in south-western Sweden, an area heavily affected by historic acid deposition, whereas Brunnsjön is situated in a south eastern area which was also strongly acidified (Moldan *et al.*, 2013). Moreover, both Brunnsjön and Rotehogstjärnet are humic lakes (Table 3).

The median TOC concentrations ranged from 1.4 mg l⁻¹ throughout the clear lake Abiskojaure, to 19 mg l⁻¹ in the surface water and 20.2 mg l⁻¹ in the bottom water of the brown lake Brunnsjön (Table 6). Abiskojaure also had the lowest median TP levels in both the surface (4 mg l⁻¹) and bottom (5 mg l⁻¹) waters, as well as the lowermost NH₄-N levels in the bottom waters (7 mg l⁻¹). Moreover, Abiskojaure was the clearest lake in the dataset (Table 3) and had the highest median DO levels observed over the study period (1988-2015). At the other end of the range, Brunnsjön was the most humic lake (Table 3) and had the lowermost median surface water DO levels 8.6 mg l⁻¹ throughout the period of observation (1988-2015) (Table 6). The two lakes with the lowest median bottom water DO levels were Älgsjön (1.6 mg l⁻¹) and Stora Skärsjön (1.7 mg l⁻¹). Älgsjön is also a humic lake with the second highest median surface water TOC level (18.1 mg l⁻¹), whereas Stora Skärsjön is a clear lake with comparatively low median surface water TOC levels (4.4 mg l⁻¹) (Table 6).

The differences between surface and bottom water levels of the herein assessed water chemical parameters were highest in the case of NH₄-N concentrations (Table 6). Ratios between bottom and surface water NH₄-N were particularly high for Stora Skärsjön (940%) and Stora Envättern (720%) (Table 7). Similarly, both the median TP and Si levels were always higher in the bottom waters compared to surface waters, however, the ratios were not as high as in the case of NH₄-N. The highest bottom:surface TP ratio was observed in Härsvatten (225%), whereas the highest bottom:surface Si ratio was observed in Stora Envättern (255%) (Table 7).

Table 6. Median surface (s) and bottom (b) water levels of dissolved oxygen (DO), nitrogen from ammonia (NH₄-N), pH, dissolved silica (Si), water temperature (temp), total organic carbon (TOC) and total phosphorus (TP) over the period of observation (Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015).

Lake	DO		NH ₄ -N		pH		Si		Temp		TOC		TP	
	(mg l ⁻¹) s	(mg l ⁻¹) b	(µg l ⁻¹) s	(µg l ⁻¹) b	s	b	(mg l ⁻¹) s	(mg l ⁻¹) b	(°C) s	(°C) b	(mg l ⁻¹) s	(mg l ⁻¹) b	(µg l ⁻¹) s	(µg l ⁻¹) b
Abiskojaure	11.5	11.5	7.5	7	7.1	7.0	0.6	0.64	7.4	6.7	1.4	1.4	4	5
Allgjuttern	9.4	5.2	7	13	6.6	6.0	1.2	1.7	14.8	4.2	7.3	6.8	6	10
Brunnsjön	8.6	3.0	25	100	5.5	5.3	4.3	5.3	14.9	4.7	19	20.2	12	17
Fiolen	9.9	8.3	15	22	6.6	6.3	0.2	0.3	14	11.7	7.1	6.9	11	12
Fräcksjön	9.8	4.4	12	36	6.4	5.9	2.1	2.8	14.2	4.9	8.9	8.9	10	12
Härsvatten	10.2	4.8	35	142	4.7	4.7	0.35	0.73	14.4	4.3	3	3.2	4	9
Remmarsjön	10.2	7.6	10	17	6.3	6.0	2.7	2.9	10.9	7.3	9.2	9.4	10	13
Rotehogstjärnet	9.2	2.7	11.5	70	5.4	5.2	1.2	2.1	14	6.2	11.7	12.9	13	21
Stora Skärsjön	9.7	1.7	12	113	6.8	6.3	2.3	4	15.6	6.8	4.4	4.5	8	13
Stensjön	9.9	7.8	8	16	6.4	6.0	2.1	2.5	12.8	9.3	6.8	6.9	7	8
Stora Envättern	9.9	4.4	8	58	6.5	6.0	0.39	1.0	14.8	6.7	9.5	10.3	8	12
Älgsjön	8.8	1.6	13	26	6.8	6.3	3.0	3.7	15.5	10.6	18.1	19.2	20	29
Övre Skärsjön	9.8	8.4	16	30	5.6	5.4	1.9	2.3	13.6	5.4	8	8.3	6	8.1

Table 7. The ratio (%) between median bottom water and surface water levels of dissolved oxygen (DO), nitrogen from ammonia (NH₄-N), pH, dissolved silica (Si), water temperature (temp), total organic carbon (TOC) and total phosphorus (TP) over the period of observation (Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015).

Lake	DO	NH ₄ -N	pH	Si	Temp	TOC	TP
Abiskojaure	100	93	99	107	91	100	125
Allgjuttern	56	186	90	143	28	93	167
Brunnsjön	34	400	96	123	32	106	142
Fiolen	84	147	95	138	84	97	109
Fräcksjön	45	300	93	134	35	99	120
Härsvatten	47	406	101	209	30	107	225
Remmarsjön	74	170	95	107	67	102	130
Rotehogstjärnet	29	604	95	183	44	110	162
Stora Skärsjön	18	938	92	172	44	102	163
Stensjön	79	200	94	123	72	101	114
Stora Envättern	45	719	92	255	45	108	150
Älgsjön	18	200	93	125	68	106	145
Övre Skärsjön	86	188	96	117	40	104	135

4.1.1. Dissolved oxygen

Redox conditions are important in regulating NH₄-N and TP concentrations in bottom waters. The bottom water oxygen conditions are, thus, further elaborated in this chapter. During the summer stratification period, several lakes were anoxic or oxygen depleted, which can be observed from the DO curves depicting yearly minimum DO (Fig. 10, Appendix B). Keep in mind that there was no chemistry data from the winter stratification periods. As was seen above, the median bottom water DO concentrations ranged from 1.6 mg l⁻¹ in Älgsjön, to 11.5 mg l⁻¹ in Abiskojaure (Table 6).

In 6 study lakes, more than 40% of all bottom water samples assessed herein had DO concentrations of ≤ 4 mg l⁻¹ (Table 8). In the same lakes, 30% of the bottom water samples had DO levels of ≤ 2 mg l⁻¹. Overall, Stora Skärsjön, Älgsjön, Rotehogstjärnet and Brunnsjön were most frequently depleted in DO and had the lowest median bottom water DO concentrations (≤ 3 mg l⁻¹) (Tables 6, 8). In the clearest lake within the dataset, Abiskojaure, the DO levels were only twice below 9 mg l⁻¹. Furthermore, Stensjön, Övre Skärsjön and Remmarsjön most frequently had DO concentrations above 4 mg l⁻¹ (Table 8).

Table 8. The percentage (%) of bottom water samples in each lake with dissolved oxygen (DO) concentrations of $\leq 4 \text{ mg l}^{-1}$ or $\leq 2 \text{ mg l}^{-1}$ over the study period (Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015).

Lake	% DO $\leq 4 \text{ mg/l}$	% DO $\leq 2 \text{ mg/l}$
Stora Skärsjön	63	49
Älgsjön	63	53
Rotehogstjärnet	54	45
Brunnsjön	51	37
Fräcksjön	47	35
Stora Envättern	42	31
Härsvatten	38	21
Allgjuttern	29	5.1
Fiolen	25	15
Remmarsjön	17	5.7
Övre Skärsjön	15	8.1
Stensjön	11	0.95
Abiskojaure	0.76	0

4.2. Time trends in lake water chemistry

Multiple water chemical parameters have significantly (Mann-Kendall, $p < 0.001$ to $p < 0.05$) changed over the period of observation in several assessed lakes. The statistically significant trends were generally pointing in the same direction within the respective water layer (i.e. surface or bottom waters). For some parameters, the general trends or lack of trends differed between surface and bottom waters (Tables 9, 10).

In the surface waters, conductivity levels have significantly decreased in all lakes except for Abiskojaure. This is consistent with observed time trends in SO_4^{2-} , since SO_4^{2-} levels have decreased in 11 lakes and increased in Abiskojaure (Table 9). Signs of recovery from acidification in terms of increasing pH and alkalinity were observed in more than half of the studied lakes. Moreover, surface water TOC levels have increased in 8 lakes, as is consistent with previous studies (Futter *et al.*, 2014; Garmo *et al.*, 2014). The filtered absorbance (420 nm/5 cm) has accordingly increased in 9 lakes, which means that these lakes are becoming less transparent (brownification). Furthermore, the surface water TP concentrations have significantly declined over time in 7 of the studied lakes (Table 9), which is in agreement with the previous Swedish study (Huser *et al.*, 2018).

Table 9. Statistically significant time trends (Mann-Kendall) in surface water chemistry and the direction of trends. Time period: Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015. Two signs indicate $p < 0.001$ and one sign indicates $p < 0.05$. Abs F = absorbance (filtered, 420 nm/5 cm), alk = alkalinity, chl α = chlorophyll α , cond = conductivity, NH₄-N = nitrogen from ammonia, Si = dissolved silica, temp = water temperature, TOC = total organic carbon and TP = total phosphorus.

Lake	Abs F	Alk	Chl α	Cond	NH ₄ -N	pH	Si	SO ₄	Temp	TOC	TP
Abiskojaure		++		++		+		++			-
Allgjuttern	+	++		--	-		+	--			--
Brunnsjön	+			--	+	+		--		+	
Fiolen	+	++	+	--		++		--		+	
Fräcksjön	++	++		--	-	+		--	+	++	-
Härsvatten	++		+	--		++	+	--		++	-
Remmarsjön				-				--			
Rotehogstjärnet	++			--				--		++	
Stora Skärsjön		++		--		+		--	+		
Stensjön	+	+		-		+	+	--		+	-
Stora Envättern	++		+	--			+	--		++	-
Älgsjön				-							
Övre Skärsjön	++	++	-	--		++		--		++	-

In all studied lakes except for Abiskojaure, the bottom water TOC concentrations have significantly increased over time (Table 10). Significant TOC trends were, thus, more prevalent in the bottom waters compared to surface waters. Declines in overall bottom water DO concentrations were not prevalent, however, DO levels have significantly decreased in 4 out of 13 lakes. Furthermore, trend analysis showed that the bottom water pH levels have increased in 6 lakes. The bottom water NH₄-N concentrations have increased in 7 lakes and in 4 of these lakes, bottom water TP levels have also increased. Otherwise, the bottom water time series data generally lacked significant TP trends. On the contrary, significant trends in bottom water Si concentrations were widespread (Table 10). Visual inspection of the bottom water Si plots revealed that in more than half of the studied lakes, Si measurements followed a similar temporal pattern with a local decline during the mid-2000s, followed by an increase towards the end of the monitoring period (Appendix B). In 7 lakes, the lowest reported Si concentration coincided in October 2005. The last measurement of the year generally occurs in October.

Table 10. Statistically significant time trends (Mann-Kendall) in bottom water chemistry and the direction of trends. Time period: Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015. Two signs indicate $p < 0.001$ and one sign indicates $p < 0.05$. Cond = conductivity, DO = dissolved oxygen, $\text{NH}_4\text{-N}$ = nitrogen from ammonia, Si = dissolved silica, temp = water temperature, TOC = total organic carbon and TP = total phosphorus.

Lake	Cond	DO	$\text{NH}_4\text{-N}$	pH	Si	Temp	TOC	TP
Abiskojaure	++			+	+			
Allgjuttern	--				+	-	+	
Brunnsjön	-		+	+	+		+	+
Fiolen	--		+	++	+		++	
Fräcksjön	-						+	
Härsvatten	-		+	++	+		++	+
Remmarsjön	-						+	
Rotehogstjärnet	--	-	+		+	+	++	
Stora Skärsjön		-	+		+		+	+
Stensjön	--			+	+		+	-
Stora Envättern		--	++	-	++	-	++	+
Älgsjön							+	
Övre Skärsjön	--	-	+	+	+		++	

The seasonal (by month) Mann-Kendall trend test indicated that the surface water temperatures have increased over time in 10 lakes ($p < 0.05$, Table 11). However, this is merely indicative since no correction for multiple comparisons was performed. Rising surface water temperatures were generally restricted to September, as 8 lakes showed positive trends in September. In Fräcksjön, indications of increasing surface water temperatures were observed for multiple months, which is consistent with the previously presented overall warming of the surface water in Fräcksjön (Tables 9, 11). Seasonal trends (by month) in bottom water temperatures were less prevalent (Table 12). However, in the bottom water of Stora Envättern, the temperature has become cooler in 6 out of 8 sampling months, which is consistent with the observed overall cooling of the bottom water in Stora Envättern (Table 10, 12). Furthermore, in the deepest lake within this study (Allgjuttern), the bottom water has become cooler in April, September and October, which also corresponds to the overall bottom water trends (Tables 10, 12). Moreover, Härsvatten and Stora Envättern have significant but opposite trends in surface (warming) and bottom (cooling) waters. On the contrary, in Rotehogstjärnet and Remmarsjön both surface and bottom waters have become warmer over the period of observation (Tables 11, 12).

Table 11. Significant monthly trends (Seasonal Mann-Kendall, $p < 0.05$) in surface water temperatures over the study period (Fräcksjön 1988-2011, all other lakes 1988-2015) and the direction of trends. Empty cells = non-significant, grey cells = not tested due to a sampling frequency of <60%.

Lake	1	2	3	4	5	6	7	8	9	10	11	12
Abiskojaure						+						
Allgjuttern		-										
Fiolen									+			
Fräcksjön				+				+	+	+		
Härsvatten							+					
Remmarsjön								+	+			
Rotehogstjärnet									+			
Stora Skärsjön									+	+		
Stensjön									+			
Stora Envättern		-							+			
Övre Skärsjön									+			

Table 12. Significant monthly trends (Seasonal Mann-Kendall, $p < 0.05$) in bottom water temperatures over the study period (1988-2015) and the direction of trends. Empty cells = non-significant, grey cells = not tested due to a sampling frequency of <60%.

Lake	1	2	3	4	5	6	7	8	9	10	11	12
Allgjuttern				-					-	-		
Härsvatten						-						
Remmarsjön										+		
Rotehogstjärnet		+						+		+		
Stora Envättern				-	-	-	-		-	-		

Several study lakes have significant declining trends in yearly minimum, median or maximum bottom water DO concentrations or temperatures (Mann-Kendall trend test, Tables 13, 14). Regarding bottom water DO trends, 9 out of 13 lakes have significant declining trends in either yearly minimum, median or maximum DO concentrations, or for two of the tested variables (Table 13). Trends in bottom water temperatures were not as prevalent, however, the results show that the deeper water layers in 4 lakes have become cooler over the period of observation (Table 14).

Table 13. Statistically significant time trends (Mann-Kendall) in yearly minimum, median and maximum bottom water DO concentrations and the direction of trends. Time periods: Härsvatten 1988-2012, Stora Skärsjön 1989-2015, Älgsjön 1997-2011, all other lakes 1988-2015. Two signs indicate $p < 0.001$ and one sign indicates $p < 0.05$.

Lake	Min DO	Median DO	Max DO
Brunnsjön		–	
Fiolen	–	–	
Härsvatten		–	–
Remmarsjön	–		
Rotehogstjärnet		--	–
Stora Skärsjön		–	
Stora Envättern		–	–
Älgsjön	–		
Övre Skärsjön	–	–	

Table 14. Statistically significant time trends (Mann-Kendall) in yearly minimum, median and maximum bottom water temperatures and the direction of trends. Time periods: Fräcksjön 1988-2011, Härsvatten 1988-2012, all other lakes 1988-2015. Two signs indicate $p < 0.001$ and one sign indicates $p < 0.05$.

Lake	Min Temp	Median Temp	Max Temp
Allgjuttern	–	–	
Fräcksjön	+		
Härsvatten		–	
Stensjön	--		
Stora Envättern		–	–

4.2.1. Theil-Sen slopes estimates of the significant trends

Theil-Sen slopes were calculated for the water chemical parameters with statistically significant trends (Mann-Kendall trend test, $p < 0.05$). The steepest trends in surface water chemistry were observed for alkalinity ($+3.8\% \text{ yr}^{-1}$), SO_4^{2-} ($-3.5\% \text{ yr}^{-1}$) and absorbance ($+3.4\% \text{ yr}^{-1}$) (Table 15). Considering individual trends, the steepest change rate was observed in Övre Skärsjön, where alkalinity has increased by $14\% \text{ yr}^{-1}$. Härsvatten has the steepest significant time trends in most other assessed surface water parameters, including absorbance ($+10\% \text{ yr}^{-1}$) and TOC ($+5.1\% \text{ yr}^{-1}$). The highest rate of decline in surface water TP was observed in Abiskojaure, where TP concentrations have declined $4.9\% \text{ yr}^{-1}$ (Table 15).

Table 15. Theil-Sen slopes in percent of median values for surface water chemical parameters with statistically significant time trends (Mann Kendall, $p < 0.05$) over the study period (Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015). The calculated Theil-Sen slopes are estimates of the median yearly rate of change for each parameter. Abs = absorbance (filtered, 420 nm/5 cm), alk = alkalinity, chl a = chlorophyll a , cond = conductivity, $\text{NH}_4\text{-N}$ = nitrogen from ammonia, Si = dissolved silica, TOC = total organic carbon and TP = total phosphorus. Grey = maximum rates of change.

Lake	ΔAbsF	ΔAlk	$\Delta\text{Chl } a$	ΔCond	$\Delta\text{NH}_4\text{-N}$	ΔpH	ΔSi	ΔSO_4	ΔTOC	ΔTP
Abiskojaure		1.6		1.6		0.079		3.1		-4.9
Allgjuttern	1.3	0.74		-1.5	-3.9		1.0	-2.6		-3.4
Brunnsjön	2.5			-1.3	2.7	0.15		-3.5	1.8	
Fiolen	2.8	4.4	2.1	-1.6		0.28		-4.7	1.7	
Fräcksjön	3.6	2.4		-2.1	-4.9	0.22		-6.4	1.9	-2.1
Härsvatten	10		6.1	-2.5		0.68	2.9	-5.7	5.1	-2.3
Remmarsjön				-0.46				-3.2		
Rotehogstjärnet	3.7			-1.8				-5.3	2.7	
Stora Skärsjön		1.9		-0.89		0.15		-2.5		
Stensjön	1.2	1.3		-0.52		0.12	1.5	-3.1	0.87	-2.7
Stora Envättern	2.5		2.9	-1.4			1.9	-3.2	1.7	-1.2
Älgsjön				-1.0						
Övre Skärsjön	2.9	14	-1.8	-2.2		0.32		-4.5	2.2	-1.8
Mean	3.4	3.8	2.3	-1.2	-2.0	0.25	1.8	-3.5	2.3	-2.6

The mean yearly rate of change in bottom water chemistry was highest for $\text{NH}_4\text{-N}$ (+11.3% yr^{-1}), followed by TP (+3.8% yr^{-1}) and DO (-3.7% yr^{-1}) (Table 16). In 4 lakes, most of the analysed bottom water chemical parameters have significantly changed over time (Mann-Kendall trend test, < 0.05) and often at a comparatively steep rate. This includes Brunnsjön, Härsvatten, Stora Skärsjön and Stora Envättern. The trends in $\text{NH}_4\text{-N}$ concentrations in the bottom waters of Stora Envättern (+29% yr^{-1}), Stora Skärsjön (+23% yr^{-1}) and Brunnsjön (+11% yr^{-1}) were most noteworthy. Härsvatten has several of the highest change rates determined for individual parameters in bottom waters (as in surface waters), including TP (9.7% yr^{-1}), TOC (7.9% yr^{-1}) and pH (1.0% yr^{-1}). The most substantial change in Si was observed in Stora Envättern (+6.0% yr^{-1}), which also had the steepest decrease in DO (-6.0% yr^{-1}) (Table 16).

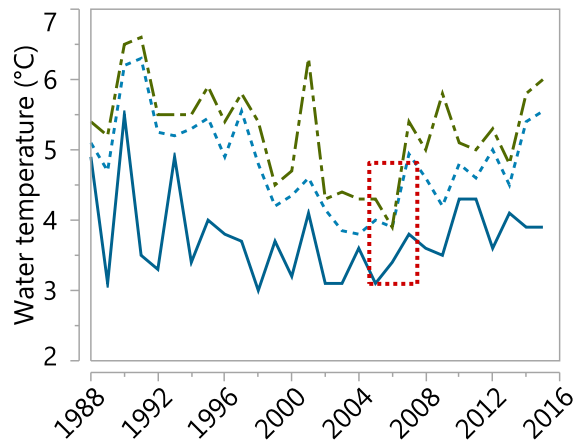
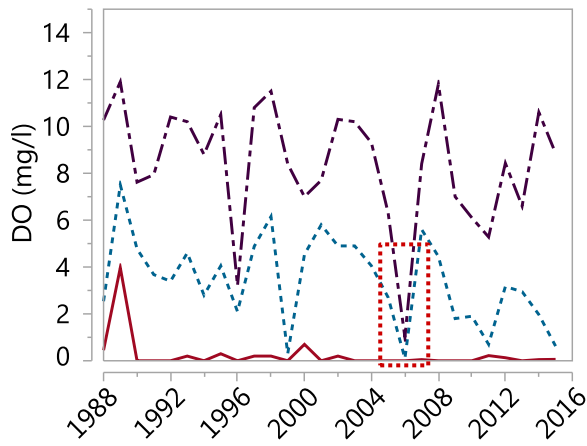
Table 16. Theil-Sen slopes in percent of median values for bottom water chemical parameters with statistically significant time trends (Mann Kendall, $p < 0.05$) over the study period (Fräcksjön 1988-2011, Älgsjön 1997-2011, all other lakes 1988-2015). The calculated Theil-Sen slopes are estimates of the median yearly rate of change for each parameter. Cond = conductivity, DO = dissolved oxygen, $\text{NH}_4\text{-N}$ = nitrogen from ammonia, Si = dissolved silica, temp = water temperature, TOC = total organic carbon and TP = total phosphorus. Grey = maximum rates of change.

Lake	ΔCond	ΔDO	$\Delta\text{NH}_4\text{-N}$	ΔpH	ΔSi	ΔTemp	ΔTOC	ΔTP
Abiskojaure	1.6			0.12	1.4			
Allgjuttern	-1.1				1.4	-1.2	1.0	
Brunnsjön	-1.2		11	0.25	1.2		2.4	5.6
Fiolen	-1.5		1.5	0.28	1.8		1.8	
Fräcksjön	-1.9						1.5	
Härsvatten	-1.5		7.5	1.0	3.0		7.9	9.7
Remmarsjön	-0.6						1.9	
Rotehogstjärnet	-1.7	-4.4	2.1		2.1	1.2	2.4	
Stora Skärsjön		-2.4	23		3.5		4.4	2.0
Stensjön	-0.5			0.11	1.3		1.1	-1.3
Stora Envättern		-6.0	29	-0.2	6.0	-1.4	3.3	3.2
Älgsjön							2.3	
Övre Skärsjön	-1.8	-2.0	5.2	0.22	1.6		2.6	
Mean	-1.0	-3.7	11.3	0.25	2.3	-0.46	2.7	3.8

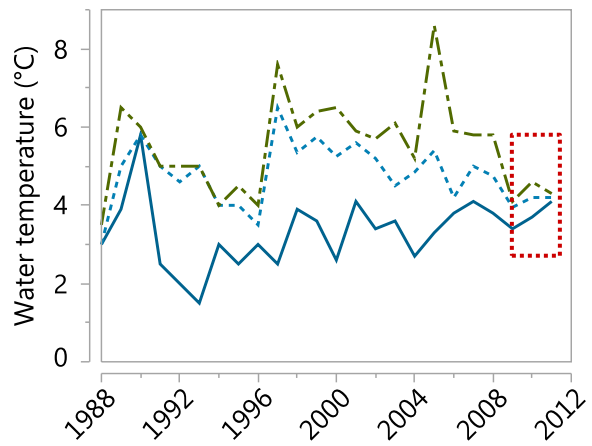
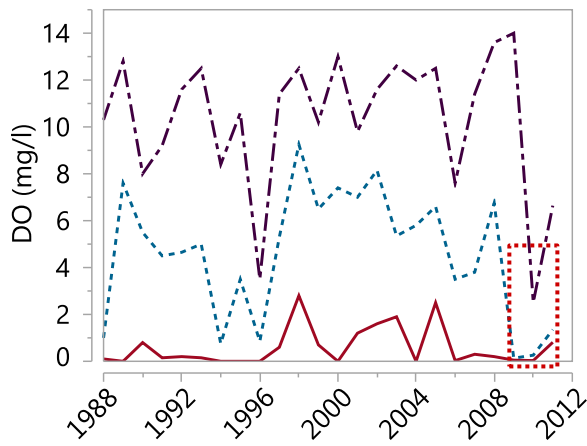
4.3. Synchronous patterns of bottom water DO and temperatures

In some study lakes, sustained periods (\geq one year) of anoxia or low oxygen levels were observed, and these periods are displayed below as points in time when yearly minimum, median and maximum DO concentrations merge (Fig. 10). Visual observation of plots displaying minimum, median and maximum bottom water temperatures show that the anoxic events seem to correspond with a decreased variation in yearly bottom water temperatures during the same time period (Fig. 10). For the remaining study lakes, equivalent time series plots are available in Appendix B.

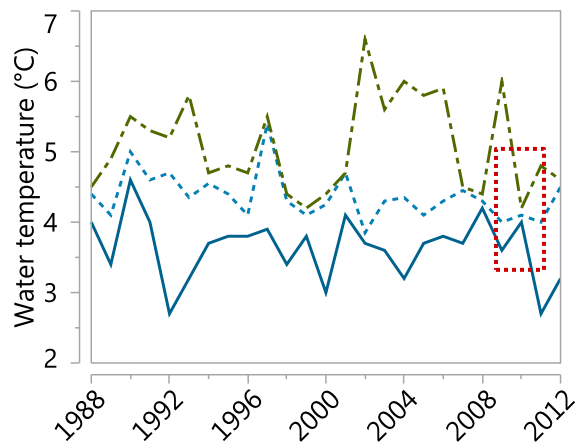
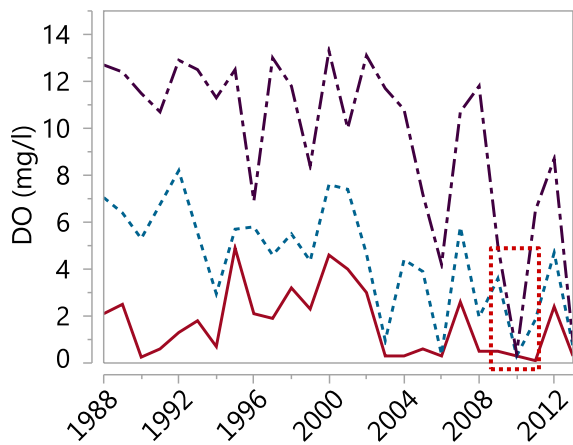
a) Brunnsjön



b) Fräcksjön



c) Härsvatten



— Min DO - - - Median DO - - - Max DO

— Min temp - - - Median Temp - - - Max temp

f) Stora Envättern

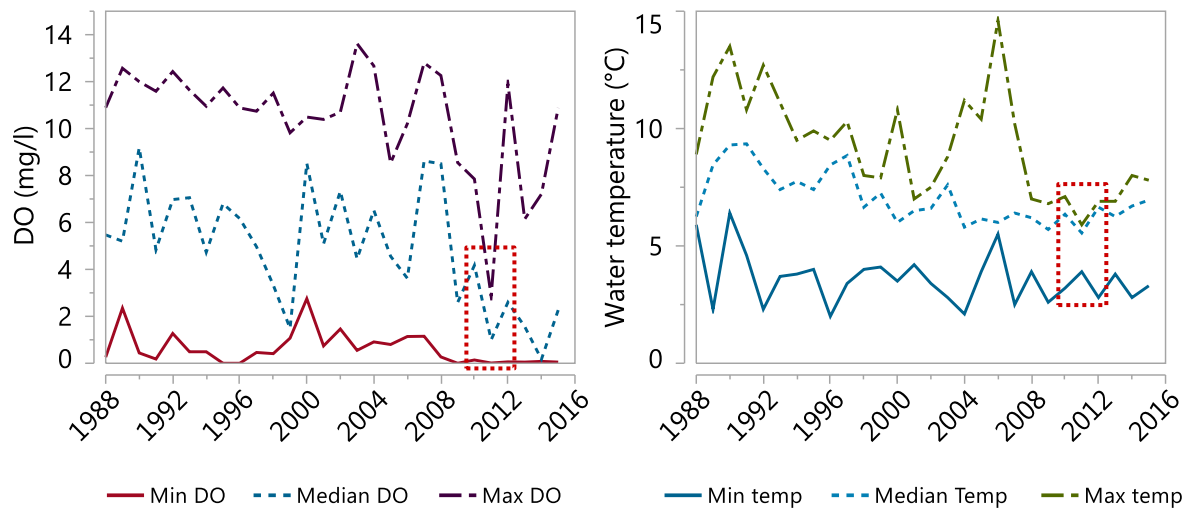


Figure 10. Minimum, median and maximum bottom water dissolved oxygen (DO) concentrations (left) as well as minimum, median and maximum bottom water temperatures (right) in selected study lakes. The red rectangles exemplify a period of anoxia or low and converging minimum, median and maximum DO concentrations, as well as concurrent low variation in yearly bottom water temperatures.

4.4. Comparisons of surface and bottom water TOC, TP, NH₄-N and Si concentrations in relation to bottom water DO

In this chapter, temporal dynamics of surface and bottom water concentrations of TOC, TP, NH₄-N and Si are presented and compared for a selection of lakes. A collection of time series plots for all studied lakes showing the surface and bottom water concentrations of the selected parameters are compiled in Appendix B. The temporal dynamics of bottom water chemical parameters were elaborated in further detail, as bottom water chemistry was the focus of this study. Moreover, in order to investigate the seasonality of maximum bottom water concentrations of the selected parameters, the monthly incidence of the yearly maximum bottom water concentrations were also assessed.

4.4.1. Occurrence of maximum TOC, TP, NH₄-N and Si and sampling frequency

The yearly maximum concentrations of bottom water NH₄-N usually occurred in August, whereas the yearly maximum bottom water TP concentrations generally occurred in September (Fig. 11). In the case of TOC, the yearly maximum levels usually occurred in October. The results show a succession of maximum concentrations, starting out with NH₄-N peaking in August, followed by TP in September and TOC in October. In the case of Si, the maximum concentrations predominantly occurred in February, although February was not sampled as frequently as April-October. A smaller share of the maximum Si peaks occurred during late summer and early autumn (Fig. 11).

It was not possible to evaluate the lake water chemistry during winter stratification or late autumn within this study, as these months were either not sampled at all or generally not sampled (Fig. 11, right). Furthermore, samples from February were underrepresented in the dataset. Therefore, the occurrence of maximum concentrations in February may be underrepresented. For the selected lakes

that were further elaborated (below in this chapter), the overall monthly sampling frequency showed similar patterns (Fig. 12).

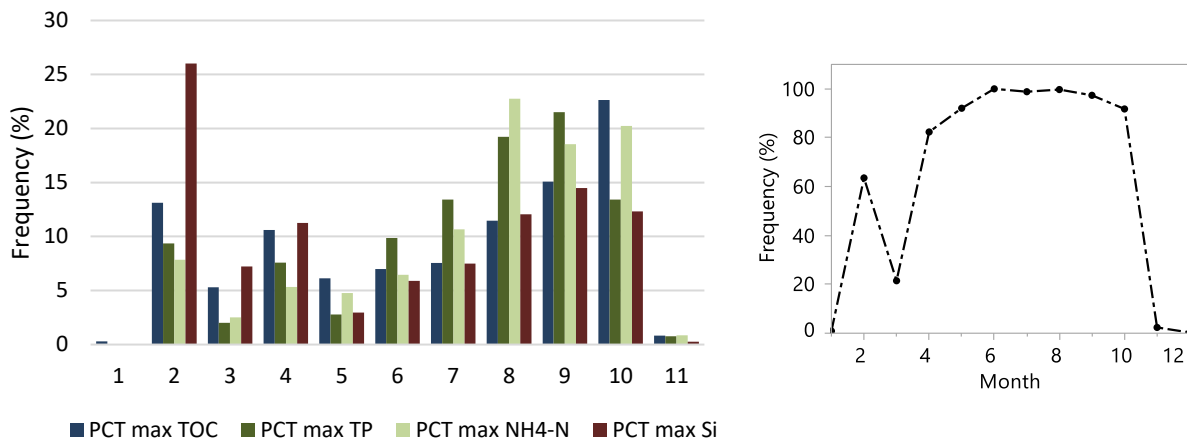


Figure 11. The monthly frequency (%) of the yearly maximum bottom water concentrations of total organic carbon (TOC), total phosphorus (TP), nitrogen from ammonia (NH₄-N) and dissolved silica (Si). It was first calculated for each lake and then summed up (left). Monthly sampling frequency (%) relative to June, which had the highest total number of samples (right).

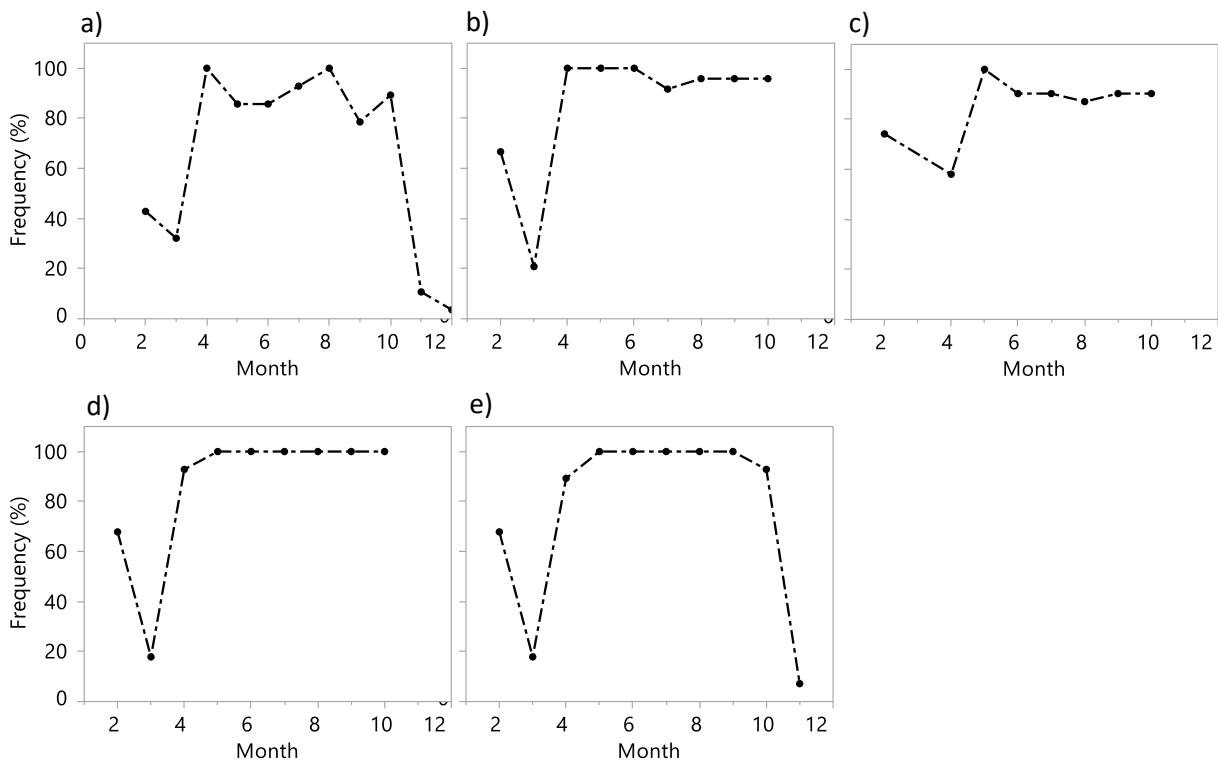


Figure 12. The overall monthly sampling frequency (%) relative to the month(s) with the highest number of samples in the respective lake, plotted for a) Härsvatten, b) Fräcksjön, c) Övre Skärsjön, d) Stora Envättern and e) Brunnsjön.

4.4.2. TOC dynamics

In several lakes, there was a substantial seasonal difference between the surface and bottom water TOC concentrations. This was the case for Brunnsjön, Härsvatten, Stora Skärsjön, Stora Envättern and Älgsjön (Figs. 13, 14, Appendix B). The seasonal variation in TOC was most pronounced in the bottom waters. In the remaining study lakes, surface and bottom water concentrations were generally following similar patterns, with some periodical exceptions (Appendix B). The timing of the yearly maximum TOC concentrations varied (Fig. 11). In Stora Envättern and Övre Skärsjön, the predominant share of the yearly maximum TOC concentrations occurred in February, followed by October. In 4 lakes (Brunnsjön, Remmarsjön, Rotehogstjärnet and Stora Skärsjön) a substantial share of the maximum TOC concentrations occurred in October. Both February and October are at the end of either the winter or summer stratification period.

In Härsvatten (south-western Sweden, $z = 26.2\text{m}$) TOC concentrations markedly peaked and remained elevated during two periods of sustained anoxia (August 2005 – November 2006, July 2009 – October 2010) (Fig. 13). The latter period is displayed below and the plot shows that TOC and DO levels followed synchronous opposite patterns, i.e. when TOC peaked, DO levels dropped (Fig. 13c). TP and $\text{NH}_4\text{-N}$ concentrations also distinctly peaked during the episodes of sustained anoxia (Fig. 15, Appendix B).

Härsvatten

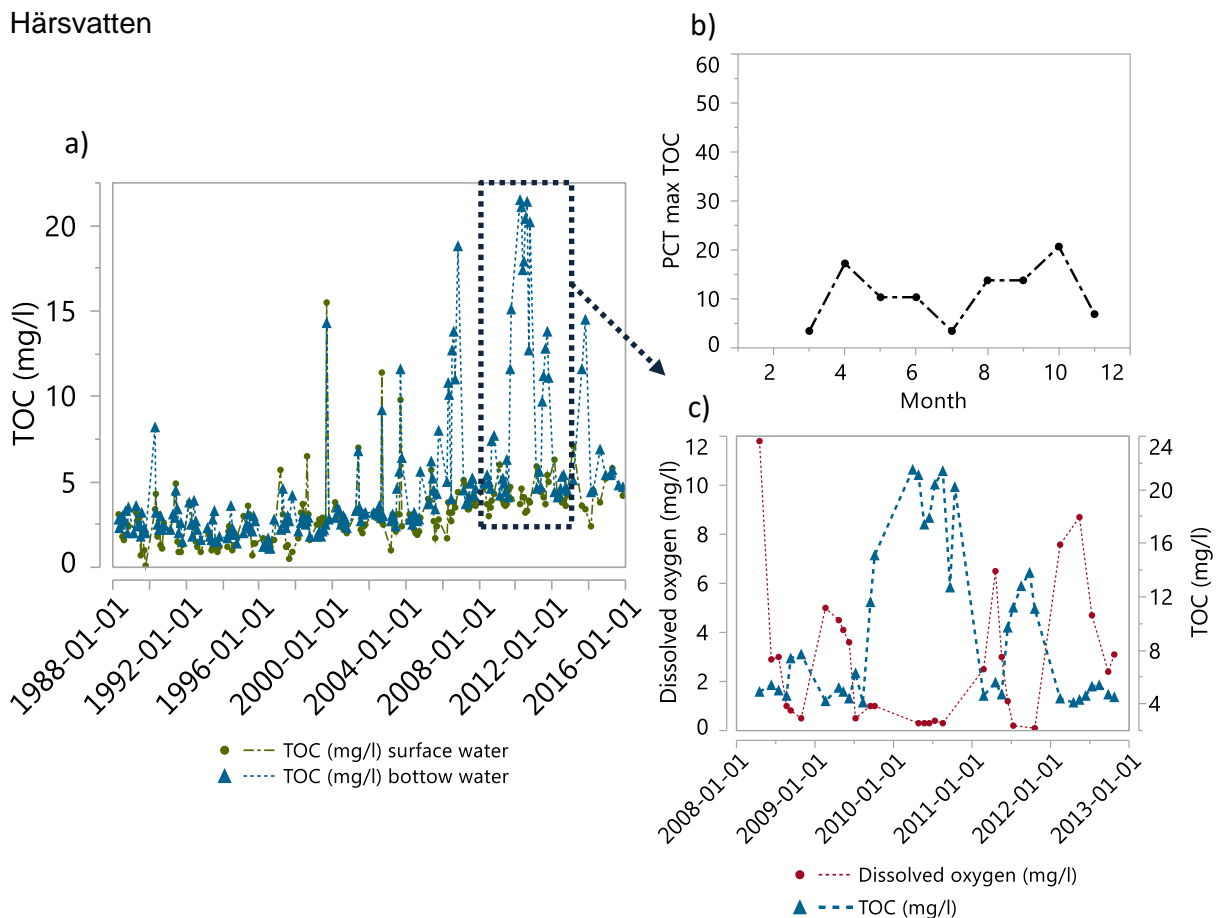


Figure 13. Total organic carbon (TOC) in Härsvatten. a) TOC concentrations in surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water TOC concentrations, and c) close-up on the highest observed peaks in bottom water TOC concentrations during a period of sustained anoxia.

In Fräcksjön (south-west, $z = 14.5\text{m}$), both surface and bottom water TOC significantly increased over the study period (Fig. 14, Tables 9, 10). There were however no other significant trends in the bottom waters, except for decreasing conductivity (Table 9). Observation of time series plots revealed that there was a period of steep seasonal peaks in TOC, TP and $\text{NH}_4\text{-N}$ that started approximately 1989 and ended around early to mid-90s (Figs. 14, B5). Then, at the end of the study period, from approximately 2009, several simultaneous changes in the bottom water chemistry occurred. As displayed below, TOC levels increased when DO levels dropped (Fig. 14c). Moreover, TP and $\text{NH}_4\text{-N}$ levels substantially peaked (Fig. B5), whereas the seasonal variation in water temperature decreased to the lowest variation observed during the study period (Fig. 10).

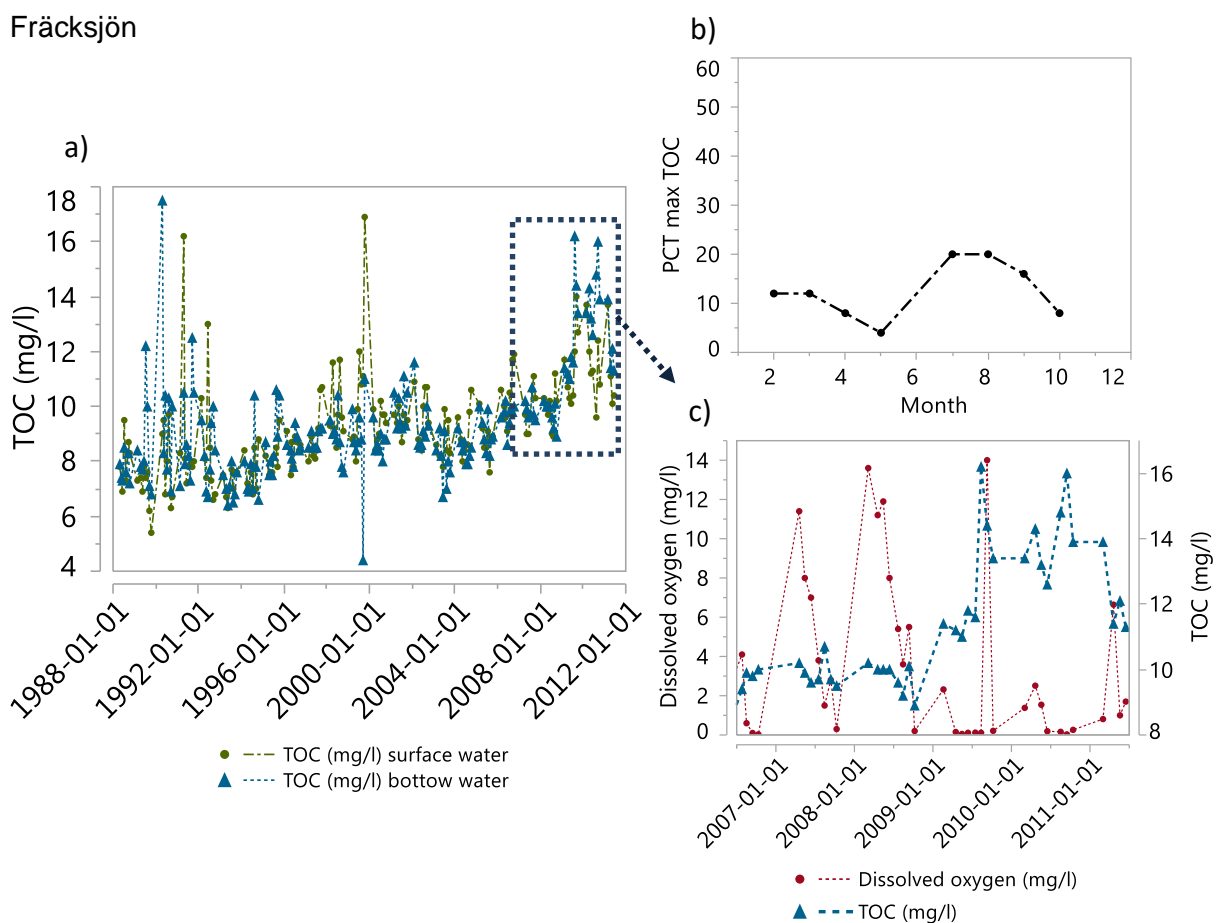


Figure 14. Total organic carbon (TOC) in Fräcksjön. a) TOC concentrations in surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water TOC concentrations, and c) the latest sampling period showing a steep increase in bottom water TOC and a simultaneous drop in dissolved oxygen.

4.4.3. TP dynamics

The difference between surface and bottom water chemistry was even more apparent when comparing TP concentrations (Figs. 15, 16, Appendix B). The surface water TP concentrations have significantly declined over time in 7 lakes (Table 9). On the contrary, bottom water TP levels have significantly increased in 4 lakes (Brunnsjön, Härsvatten, Stora Skärsjön and Stora Envättern) (Table 10). The variation in bottom water TP was seasonal (Appendix B) and the yearly maximum bottom water TP concentrations generally occurred during late summer or early autumn (Fig. 11).

In Härsvatten (south-west, $z = 26.2\text{m}$) the surface and bottom water levels of TP were generally following a similar temporal pattern in the beginning of the monitoring period (Fig. 15). From approximately 1997, the seasonal variation in bottom water TP started to increase. Härsvatten was in fact one of the 4 lakes with significant increasing trends in bottom water TP levels, and at the steepest rate ($+9.7\% \text{ yr}^{-1}$, Table 15). During the two sustained anoxic periods in the lake described above (August 2005 to November 2006 and July 2009 to October 2010), bottom water TP concentrations were particularly and continuously high. The earlier anoxic period is displayed in Fig. 15c, which shows that the TP levels peaked when DO dropped, and that TP remained elevated until the bottom water was re-oxygenated.

Härsvatten

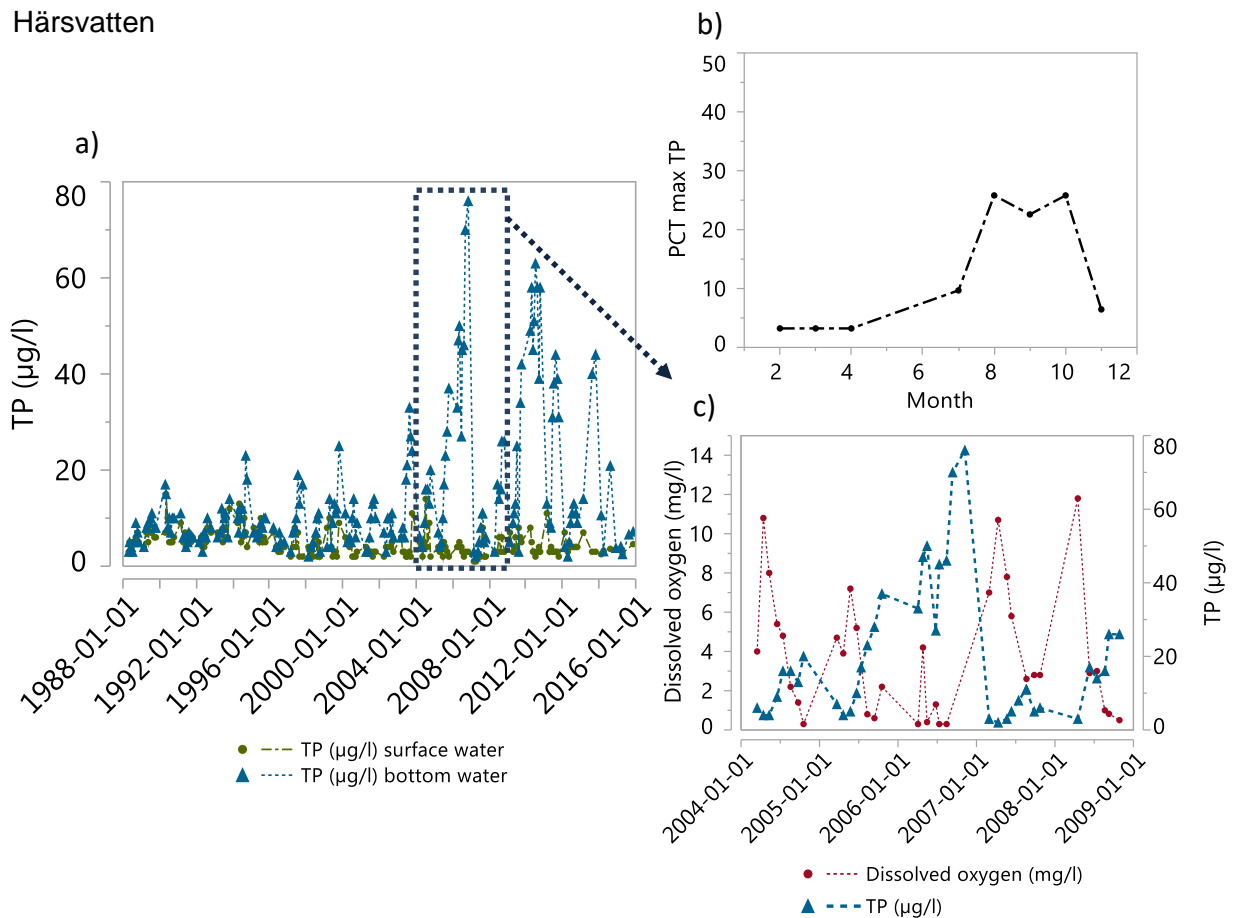


Figure 15. Total phosphorus (TP) in Härsvatten. a) TP concentrations in surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water TP concentrations, and c) close-up on a period with sustained anoxia and elevated TP concentrations in the bottom water.

The temporal dynamics of TP concentrations in Övre Skärsjön (mid to south, $z = 32\text{m}$) showed periods of high seasonal variation in bottom water TP, as well as periods when the surface and bottom water TP co-varied. The periods with large seasonal variation in TP coincided with episodes of oxygen depletion during thermal stratification. However, during periods when the bottom waters of Övre Skärsjön were not depleted in oxygen (1988-1994 and 2006-2009), TP levels did not peak noticeably

(Figs. B13, 16). Fig. 16c displays a shift from a period with low TP levels and sufficient DO levels, to a period with seasonal depletion of oxygen and synchronised peaks in TP.

Övre Skärsjön

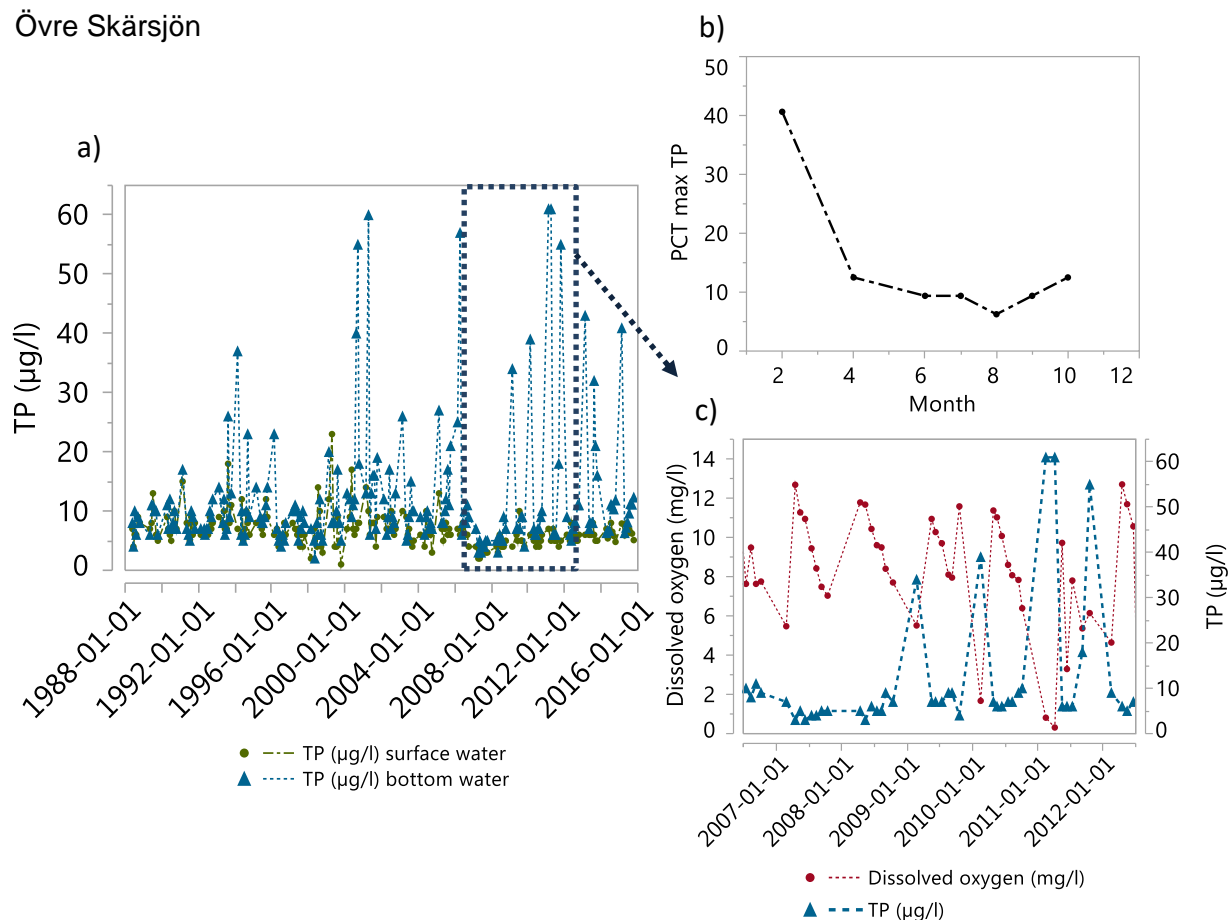


Figure 16. Total phosphorus (TP) in Övre Skärsjön. a) TP concentrations in the surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water TP concentrations, and c) close-up on a period with comparatively low bottom water TP, with parallel limited seasonal depletion of dissolved oxygen, followed by a period with more profound seasonal depletion of dissolved oxygen and simultaneous TP peaks.

4.4.4. $\text{NH}_4\text{-N}$ dynamics

The temporal dynamics of surface and bottom water $\text{NH}_4\text{-N}$ levels substantially differed in most studied lakes (Figs. 17, 18, Appendix B). Bottom water $\text{NH}_4\text{-N}$ levels have significantly increased in 7 lakes, whereas $\text{NH}_4\text{-N}$ concentrations in surface waters have increased in two lakes and decreased in two lakes. $\text{NH}_4\text{-N}$ time series plots showed that the seasonal peaks in bottom water $\text{NH}_4\text{-N}$ concentrations were often substantially elevated compared to baseline levels (Figs. 17, 18, Appendix B). Furthermore, the yearly maximum $\text{NH}_4\text{-N}$ concentrations generally occurred between August and October (Fig. 11).

Most of the analysed parameters have significantly changed over time in the bottom water of Stora Envättern (south-east, $z = 14.5\text{m}$). $\text{NH}_4\text{-N}$, Si, TOC and TP concentrations have increased over time, whereas DO, pH and water temperature have declined (Table 9). The seasonal variation in $\text{NH}_4\text{-N}$ was particularly pronounced, with high peaks compared to baseline levels (Fig. 17a). Most of the yearly

maximum concentrations occurred during October, followed by September (Fig. 17b), which generally is at the end of the summer stratification period. A close-up plot showing a period with low seasonal TP peaks, followed by the highest peaks observed over the whole study period, clearly shows how TP and DO concentrations fluctuate synchronously in opposite directions. The 3 highest TP peaks occurred in October (Fig. 17c).

Stora Envättern

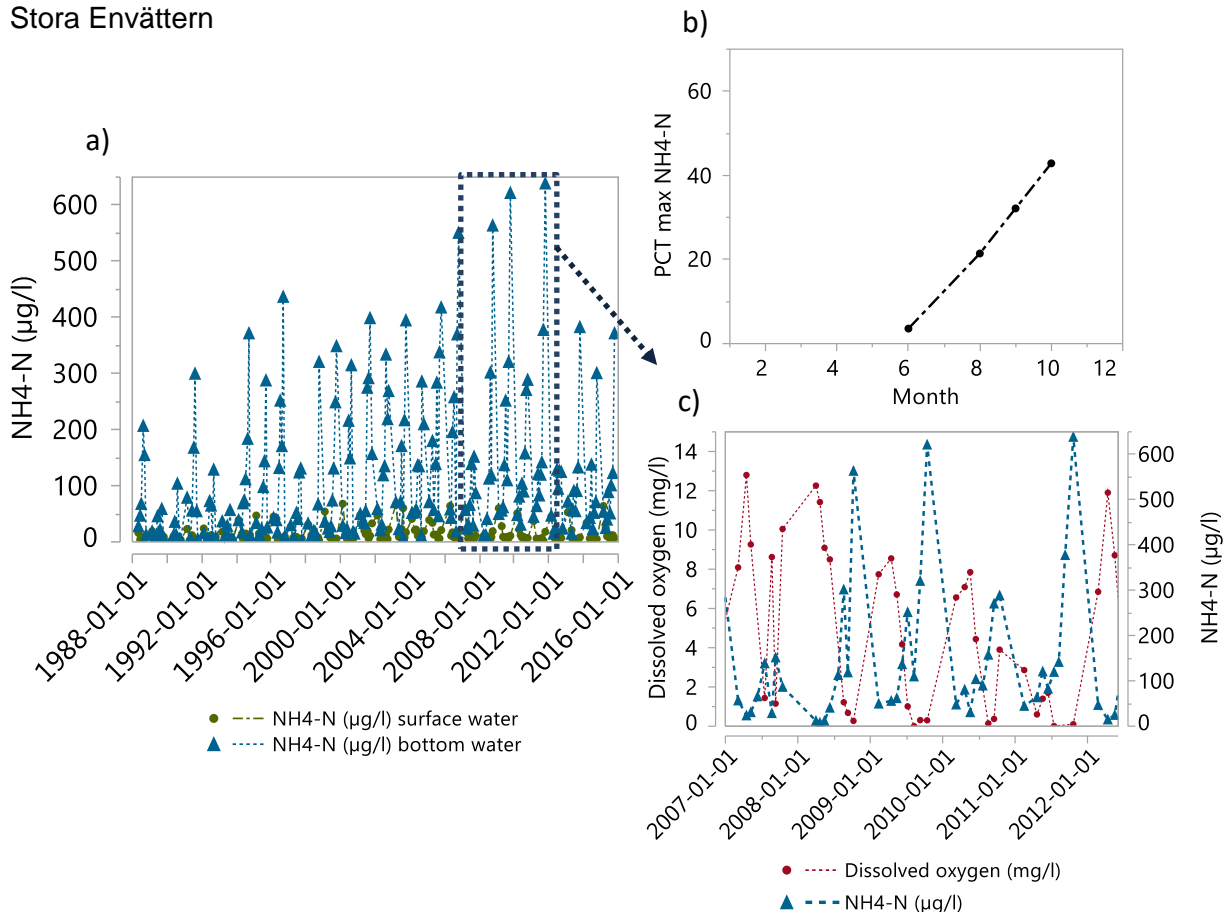


Figure 17. Nitrogen from ammonia (NH₄-N) in Stora Envättern. a) NH₄-N concentrations in the surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water NH₄-N concentrations, and c) close-up on a period with low seasonal bottom water NH₄-N peaks followed by the highest peaks observed, with a concurrent decline in dissolved oxygen.

In Brunnsjön, the predominant share of the yearly maximum NH₄-N levels were sampled in October, at the end of the summer stratification period (Fig. 18b). Brunnsjön is the southernmost lake in the dataset and very humic (mean absorbance (filtered, 420 nm/5 cm) for 2013-2015 was 0.477). Throughout a period that lasted slightly over one year, from August 2005 to October 2006 (last sample that year), Brunnsjön had anoxic bottom water (Fig. 10). During this episode, bottom water NH₄-N levels sharply increased (Figs. 18a, c). TOC and TP levels also peaked and followed a similar pattern (Fig. B3). Additionally, the overall maximum bottom water NH₄-N and TP levels in Brunnsjön occurred during this episode. In the section below the temporal dynamics of Si concentrations during this episode are also described (Fig. 20).

Brunnsjön

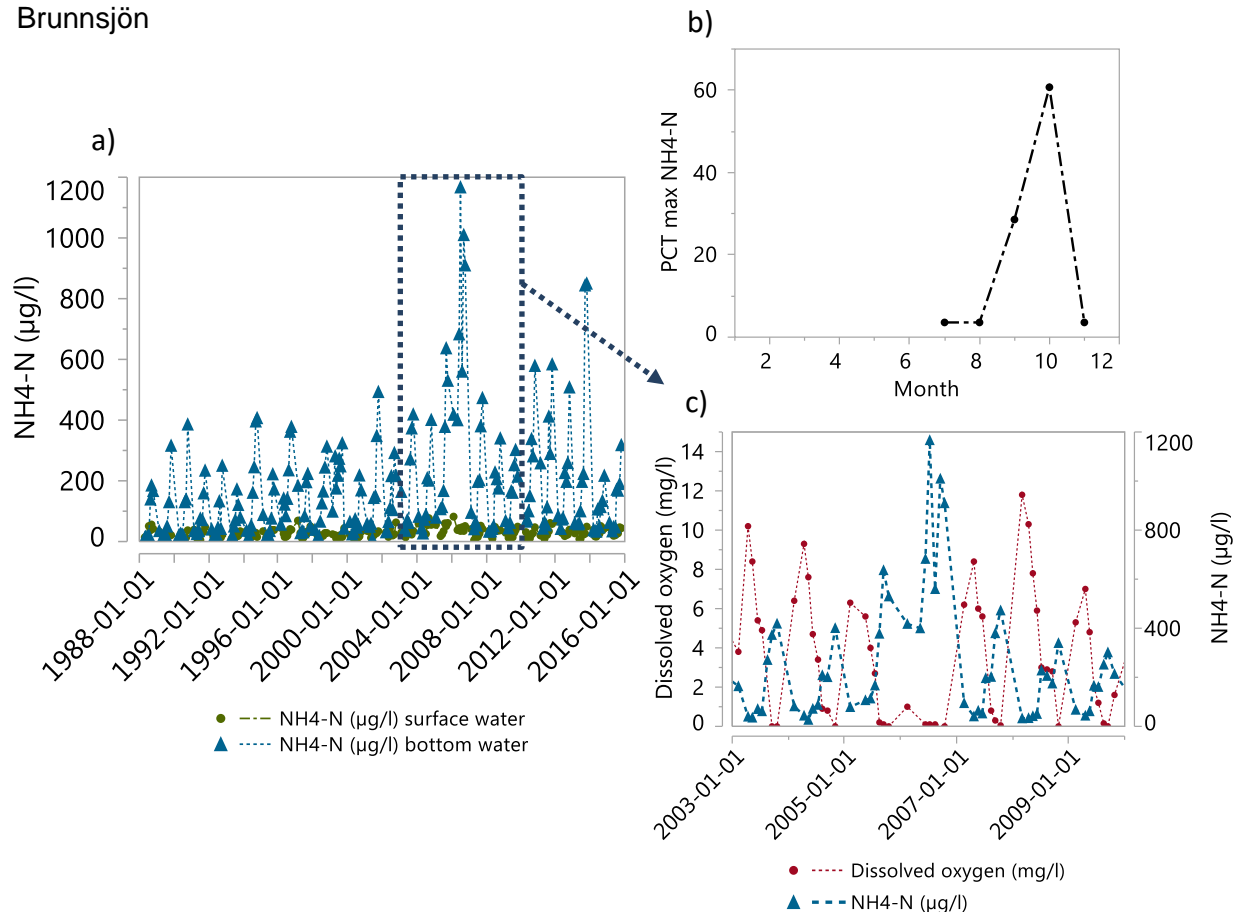


Figure 18. Nitrogen from ammonia (NH₄-N) in Brunnsjön. a) NH₄-N concentrations in the surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water NH₄-N concentrations, and c) close-up on the highest peaks in bottom water NH₄-N, which occurred during a sustained anoxic period.

4.4.5. Si dynamics

Over the period of observation, the Si concentrations in the studied lakes followed a similar temporal pattern with a distinct drop during the mid-2000s and subsequent rising concentrations (Appendix B). The overall minimum bottom water Si concentrations coincided in 7 lakes during October 2005. In two additional lakes, minimum Si concentrations occurred in September 2004. Despite this local drop, the bottom water Si concentrations have significantly increased (Mann-Kendall, $p < 0.05$) in 10 out of 13 studied lakes, whereas surface water concentrations have increased in 4 lakes. Time series plots of Si concentrations showed that in around half of the assessed lakes, the bottom water Si concentrations were generally higher than in the surface water of the respective lake (Fig. 20, Appendix B).² Moreover, surface and bottom water Si levels did not follow the same seasonal pattern in general. On the contrary, when surface water Si concentrations decreased during the summer period, the bottom water levels generally increased (Fig. 20e, Appendix B). The yearly minimum Si concentrations therefore occurred at different times in surface and bottom waters (Fig. 19).

² See Allgjuttern, Brunnsjön, Fräcksjön, Härsvatten, Rotehogstjärnet, Stora Skärsjön and Stora Envättern in Appendix B.

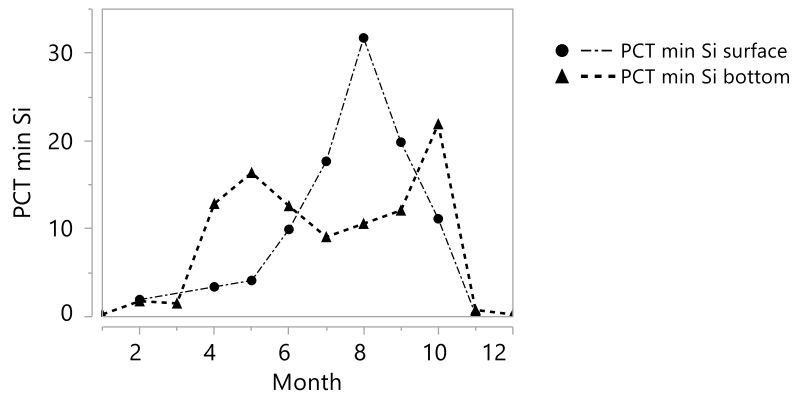


Figure 19. The overall monthly frequency (%) of yearly minimum Si concentrations in surface (circles) and bottom (triangles) waters. It was first calculated for each lake individually and then summed up.

In the case of Brunnsjön, bottom water Si concentrations generally peaked in October followed by February (Fig. 20c). The temporal pattern described above, that overall minimum bottom water Si concentrations occurred around the mid-2000s, is also evident in Brunnsjön (although the actual minimum was sampled in the 90s) (Fig. 20a). Furthermore, the time series plot shows a step change in bottom water Si concentration that occurred in February 2006. This was followed by a stabilisation of the Si concentrations around a higher average value. The average Si concentration before the step change was 4.73 mg l^{-1} ($\pm 0.99 \text{ mg l}^{-1}$, $n=78$, between 1996-04-29 and 2005-10-17), whereas the average Si concentration following the episode was 6.24 mg l^{-1} ($\pm 0.41 \text{ mg l}^{-1}$, $n=78$, until 2015-10-20). This marked increase occurred at the start of the anoxic period described above (August 2005 to October 2006), when TOC, $\text{NH}_4\text{-N}$ and TP levels peaked in Brunnsjön (Figs. 18, 20, B3). Another observation regarding Si dynamics in Brunnsjön was that a couple of years prior to the anoxic period, Si concentrations in surface and bottom waters followed a similar pattern (Fig. 20d). However, several years after the step change (from approximately 2010), surface and bottom water Si concentrations followed opposite but synchronous seasonal patterns (Fig. 20e).

Brunnsjön

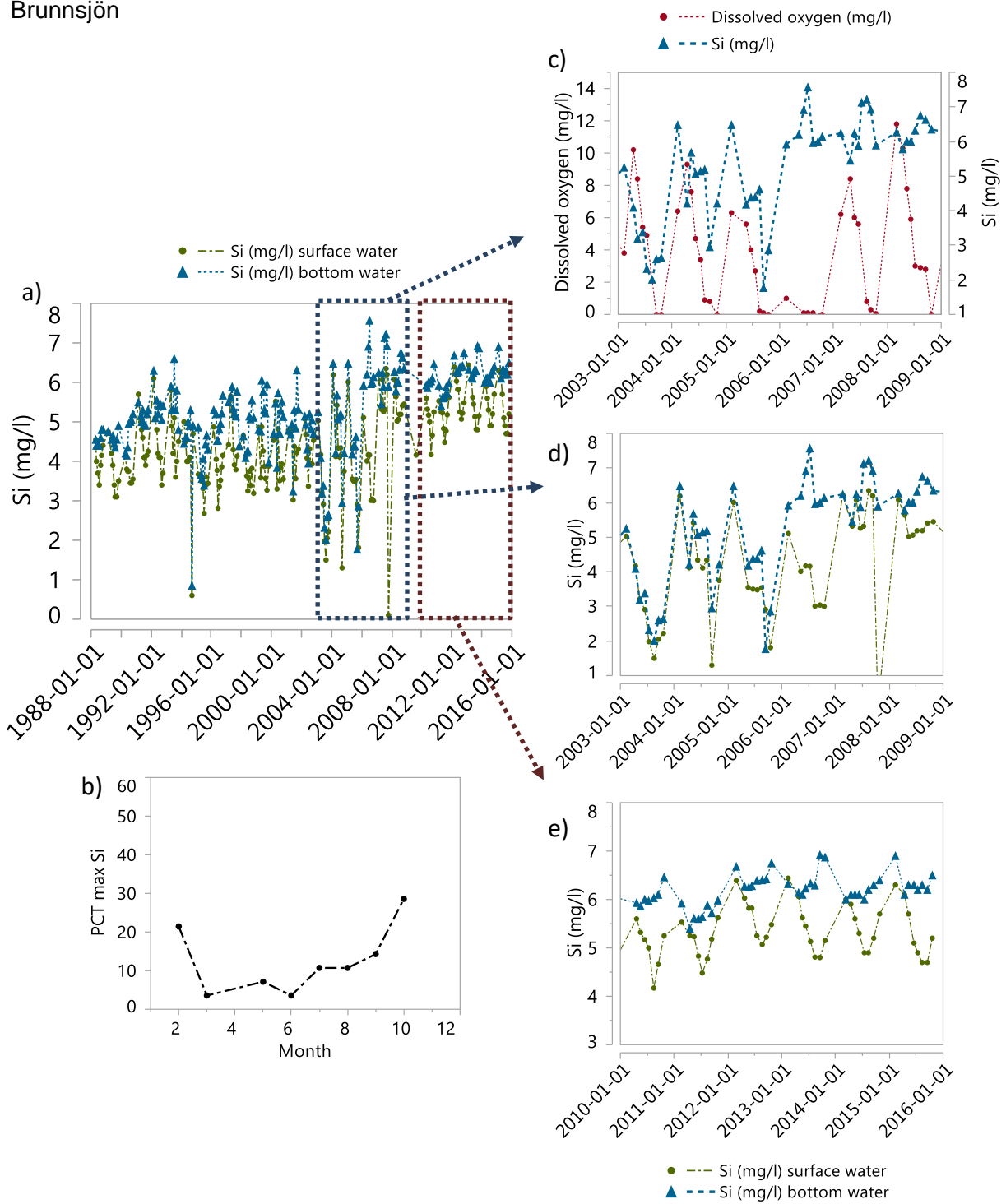


Figure 20. Dissolved silica (Si) in Brunnsjön. a) Si concentrations in the surface and bottom waters, b) the monthly frequency (%) of yearly maximum bottom water Si concentrations, c) close-up on a step change in bottom water Si, which coincided with a drop in dissolved oxygen followed by a sustained anoxic period, d) additional close-up on the step change in bottom water Si, showing changing Si dynamics in surface and bottom waters, and e) close-up on the period after the step change, showing comparatively stable but opposite seasonal patterns of surface and bottom water Si concentrations.

In several lakes the seasonal Si dynamics with opposite but synchronous patterns in surface and bottom water Si concentrations were obscured during the mid to late 2000s, around the occurrence of the overall minimum Si concentrations. The seasonal pattern was later on stabilised, as is shown in Fig. 20e in the case of Brunnsjön.

5. Discussion

The aim of this study was to evaluate long-term trends and dynamics in bottom water chemistry, mainly in relation to variations in TOC and DO. The overall hypothesis was that the widely occurring increases in DOC concentrations in temperate lakes (Monteith *et al.*, 2007; Garmo *et al.*, 2014) may have increased the depletion of DO in hypolimnia of affected Swedish lakes. The underlying mechanism of the hypothesised DOC induced depletion of bottom water DO is related to effects on thermal structure. DOM can absorb sunlight and re-emit the energy as heat. Increasing DOC concentrations over time might, thus, decrease the energy input to bottom waters in lakes, as more energy would be absorbed in the top layers. This may result in warmer surface waters and cooler bottom waters over time, which consequently might prolong the duration of summer stratification (reviewed in Solomon *et al.*, 2015). Less mixing of the water column translates into decreased oxygen input to bottom waters and may exaggerate the depletion of oxygen, as DO is continuously consumed via decomposition processes. As a result of the hypothesised longer duration or increased occurrence of anoxia in hypolimnion, the bottom water composition of dissolved substances was expected to have changed over time. In particular, increasing temporal trends in bottom water TP and NH₄ levels were anticipated. The underlying mechanisms related to the expected changes in bottom water chemistry are associated with decomposition of organic material in anoxic environments, as described in the background section.

5.1. TOC and DO dynamics and trends

As is consistent with previous studies (Futter *et al.*, 2014; Garmo *et al.*, 2014), the surface water TOC concentrations have increased in 8 out of 13 study lakes. In 6 of these lakes (and one additional), median bottom water DO concentrations have declined over time. Interestingly, bottom water TOC levels have increased in all lakes except for Abiskojaure. Visual observation of time series plots revealed that the seasonal peaks in bottom water TOC were periodically substantially higher than peaks in surface water TOC (Figs. 13, 14, Appendix B). Seasonal variation in lake water chemistry is related to the annual temperature cycle described in the background section (chapter 2.2.1). A closer inspection of particularly pronounced bottom water TOC peaks showed that TOC concentrations increased markedly during periods of sustained anoxia in several lakes, such as in Härsvatten and Fräcksjön (Figs. 13, 14). In some lakes, the seasonal variation in surface and bottom water TOC was generally synchronous and had a similar range (see for instance Remmarsjön and Rotehogstjärnet in Figs. B7, B8).

The herein observed positive TOC trends in both surface and bottom waters were expected, as rising surface water TOC concentrations are a widespread phenomenon in the northern hemisphere (Evans *et al.*, 2006; Monteith *et al.*, 2007). However, the observed pronounced seasonal variation in bottom water TOC and the extreme TOC peaks during periods of anoxia were not foreseen (see for instance Härsvatten in Fig. 13). The driver of the bottom water TOC peaks is very likely a hypolimnetic process,

since the peaks were not discernible in surface waters. Moreover, the relationship between TOC and bottom water DO levels is likely bidirectional, since the extreme TOC peaks only occurred during anoxic conditions. In other words, an increase in surface and bottom water TOC may lead to oxygen depletion in the bottom waters and, reciprocally, anoxic conditions may result in pronounced peaks in bottom water TOC concentrations. In a previous mesocosm experimental study, simultaneous fluxes of Fe, POC and DOC from anoxic surface sediments into the overlying water were observed (Skoog & Arias-Esquivel, 2009). When oxygen was introduced into the system, Fe, POC and DOC concentrations dropped. The authors suggested that reductive dissolution of iron oxyhydroxides, with release of associated organic carbon, was a likely underlying cause of the simultaneous increase in Fe and organic carbon concentrations in the water column. Furthermore, co-precipitation of organic carbon compounds with iron-containing minerals was a suggested underlying mechanism of the simultaneous drop in Fe and organic carbon concentrations (Skoog & Arias-Esquivel, 2009). This explanation certainly fits the observations made within this study, as TOC peaked at the onset of anoxia in several cases and dropped when oxygen levels increased (Figs. 13, 14). A conclusion made from the observations herein and the mechanistic relationship previously observed by Skoog & Arias-Esquivel (2009), was that bottom water TOC levels are likely controlled by reductive dissolution of Fe(III) hydrous oxides in lakes with seasonal anoxia.

The subsequent research question to be addressed is if bottom water DO concentrations have changed over time, possibly as a result of increasing TOC concentrations. Trend analysis revealed that bottom water DO levels have significantly declined in 4 study lakes (Mann-Kendall, $p < 0.05$, Table 10). However, analysis of yearly minimum, median and maximum bottom water DO concentrations indicate that 9 lakes are affected by long-term reductions in DO levels (Mann-Kendall, $p < 0.05$, Table 13). Moreover, visual inspection of DO plots showed that the bottom waters in several lakes were often seasonally anoxic or severely oxygen depleted, and generally became re-oxygenated during mixing events (see Brunnsjön, Fräcksjön, Rotehogstjärnet, Stora Skärsjön, Stora Envättern, Älgsjön, Fig. 10 or Appendix B). In most of the seasonally anoxic lakes, the yearly median or maximum DO concentrations have decreased over time, which indicates a less efficient mixing of the water layer. Some study lakes that initially in general did not have seasonally anoxic bottom waters, became oxygen depleted more frequently during later years, including Fiolen, Härsvatten and Övre Skärsjön (Fig. 10, Appendix B). Evidence from this study indicate that bottom water DO concentrations have declined in most of the Swedish study lakes. As the assessed lakes may be viewed as a representative sample of Swedish southern lakes unaffected by local pressures other than forestry, the downward trends in DO concentration may be widespread and should be further investigated.

Considering that the declining trend in DO is not a local phenomenon, the driver of change should also not be of local character. Increasing TOC concentrations is a probable driver, since the trend is widespread (Garmo *et al.*, 2014), and, as there are several known mechanistic connections between rising TOC levels and subsequent effects on DO (Tanentzap *et al.*, 2008; Solomon *et al.*, 2015). One additional connection between TOC and DO is related to decomposition of organic matter. The observed increase in bottom water TOC concentrations infers that substrate availability for microbial decomposers of organic matter has increased. This may translate into an increased rate of oxygen consumption in the hypolimnion. Since bottom waters are disconnected from epilimnetic input of DO during thermal stratification, a higher oxygen demand leads to faster depletion of oxygen in the hypolimnion, which may exacerbate the already oxygen limited conditions in stratified lakes. The multiple mechanistic

connections between TOC and DO presented herein, accompanied by the confirmed widely occurring rise in lake water TOC, strongly indicates that TOC increase is a probable driver of the observed decline in DO.

5.2. Potential effects on water temperature

Rising TOC levels and subsequent hypothesised effects on DO is associated with lake thermal structure (Solomon *et al.*, 2015), which can be assessed by observing temporal patterns in water temperatures. If the observed increase in TOC has affected the thermal structure of some study lakes, there may be evidence in terms of temporal changes in surface and bottom water temperatures. Overall, the water temperature time series data generally lacked significant trend results. However, surface water temperatures have significantly increased (Mann-Kendall, $p < 0.05$) in two lakes, whereas bottom water temperatures have declined in two lakes and increased in one lake. Furthermore, decreasing trends in either one or two of the minimum, median or maximum bottom water temperatures were observed in 4 study lakes. The lack of significant trends in other lakes might have been a result of high seasonal variation. Monthly trend tests (Seasonal Mann-Kendall, $p < 0.05$) were thus performed. The results indicated that the surface water temperatures measured in September have increased over time in 8 study lakes. As September is at the end of the summer stratification period, annual surface water temperatures are expected to be warmest at this time period. An increase in surface water temperatures at the end of the stratification period might translate into a longer duration of the thermal stratification due to increased resistance to mixing, resulting from higher temperature gradients between surface and bottom waters (Boehrer & Schultze, 2008). Moreover, the significant decrease in median bottom water temperatures in Allgjuttern, Härsvatten and Stora Envättern indicates a longer period of cooler bottom water, possibly due to prolonged stratification. In order to assess temporal trends in lake thermal structure, depth temperature profiles are highly useful. A temperature profile would for instance show if the thermocline depth has changed over time and resulted in a larger hypolimnetic, and potentially anoxic, volume of water which may result in a cooling of whole-lake temperatures (Tanentzap *et al.*, 2008). In this study, some lakes did exhibit the hypothesised changes in surface (warming) and bottom (cooling) water temperatures, possibly induced by rising TOC levels, climate warming, or both combined.

Additional interesting temporal patterns were apparent from visual observation of plots showing yearly minimum, median and maximum bottom water temperatures. For instance, in several lakes the yearly bottom water minimum, median and maximum temperatures coincided or were more similar during sustained periods of anoxia. This was observed in Brunnsjön, Härsvatten and Stora Envättern (Fig. 10). Similar bottom water temperatures throughout the year indicates that hypolimnion was isolated from epilimnion for a sustained period and possibly that the lakes were not homogenised during autumn turnover. During the periods of sustained anoxia, several other observations were made that will be further discussed in the following section.

5.3. Potential common driver of observed trends in bottom water chemistry

The subsequent research question to be evaluated is if the observed changes in bottom water DO levels lead to the hypothesised rising trends in bottom water TP and NH_4^+ . The flux of NH_4^+ and TP from sediments to the overlying waters is regulated by the redox conditions at the sediment-water interface. When lakes are stratified, DO is depleted via decomposition of organic matter. The next electron acceptor used in decomposition processes is NO_3^- , which yields NH_4^+ . Fe(III) (in iron hydrous oxides) is one of the subsequent electron acceptors used in anaerobic conditions (as dictated by redox potentials), and Fe(III) is reduced to the water soluble Fe^{2+} (Stumm & Morgan, 1981; Wetzel, 2001). Dissimilatory reduction of Fe(III) can release associated organic carbon (Skoog & Arias-Esquivel, 2009), phosphate (Nürnberg, 2009) and Si (Kato, 1969; Tallberg *et al.*, 2008) into bottom waters.

Overall, significant trends in bottom water $\text{NH}_4\text{-N}$ were more prevalent than trends in TP. Bottom water $\text{NH}_4\text{-N}$ levels have increased over time in 7 study lakes, whereas bottom water TP concentrations have increased in 4 of these lakes (Table 10). Rising trends in bottom water TP were observed in Brunnsjön, Härsvatten, Stora Skärsjön and Stora Envättern, lakes which were frequently DO depleted (Table 8). Interestingly, yearly median bottom water DO concentrations have significantly decreased in all lakes with significant rising trends in $\text{NH}_4\text{-N}$ and TP. Additionally, in three of these lakes, yearly maximum bottom water DO concentrations have also declined. The observed rising concentrations in bottom water $\text{NH}_4\text{-N}$, and to some extent TP, in connection with concurrent DO trends, strongly indicates that the bottom waters of the affected study lakes are experiencing long-term changes in internal loading of nutrients as a result of declines in DO. Furthermore, the declining trends in surface water TP concentrations observed in 7 study lakes and in a previous Swedish study (Huser *et al.*, 2018), might have overshadowed increased internal loading of P in some lakes. Moreover, if P is the limiting nutrient, increased internal loading of P and bottom water TP concentrations might not translate into rising surface water TP levels, since P would be rapidly consumed by phytoplankton following turnover events.

As was presented in chapter 4.4, surface and bottom water concentrations of $\text{NH}_4\text{-N}$, TP and Si generally differed, at least seasonally, with often exceptionally high seasonal peaks in bottom water levels. The monthly timing of the yearly maximum bottom water TP, $\text{NH}_4\text{-N}$, Si and TOC concentrations showed a similar pattern, although with a slight temporal shift (Fig. 11). Yearly maximum $\text{NH}_4\text{-N}$ concentrations most commonly occurred in August, whereas TP peaks were more prevalent in September, and maximum TOC generally occurred in October. Since the period between August and October is at the culmination or end of summer stratification, the depletion of oxygen in the hypolimnion has likely resulted in suboxic or anoxic conditions during this period. The highest flux rates of reduced species (e.g. NH_4^+ , Fe^{2+}) and associated compounds (e.g. DOC, phosphate, Si) from the sediment to overlying waters should therefore occur during this period. The yearly maximum Si concentration predominantly occurred in February, which is at the end of winter stratification and, thus, also a period with depleted bottom water DO levels. The observed sequence of peaks might be a result of ecological succession of microbes that mediate oxidation of organic matter and use different electron acceptors. According to the redox sequence, NO_3^- is the most energetically favoured electron acceptor following depletion of DO. This should theoretically translate into NH_4^+ peaking first, as was observed. Since P release is governed by dissimilatory reduction of Fe(III) oxyhydroxides (Nürnberg, 2009), the later peak in TP corresponds with that Fe(III) is a less energetically favoured electron acceptor. This temporal pattern in bottom water chemistry further exemplifies the importance of

processes at the sediment-water interface in regulating the composition of dissolved substances in lake water. In order to obtain a complete representation of long-term trends in lakes and their possible drivers (i.e. internal or external processes), monitoring of bottom water chemistry is vital.

An additional and unexpected time trend was observed in the case of bottom water Si concentrations. In 10 out of 13 study lakes, bottom water Si concentrations have increased over time, whereas the surface water Si concentrations have significantly increased in 4 lakes. The higher prevalence of significant trends in surface waters indicates that the observed increasing trends in Si concentrations are a result of hypolimnetic processes. Evidence of a potential underlying driver was obtained from visual inspection of plots showing bottom water Si concentrations and DO. As has previously been mentioned, some assessed lakes were anoxic or had exceptionally low oxygen levels for periods (\geq one year) that lasted longer than the summer stratification months. The sustained anoxia coincided with particularly pronounced peaks in bottom water $\text{NH}_4\text{-N}$, TP and TOC levels, as shown for Härsvatten, Fräcksjön and Brunnsjön (Figs. 13, 14, 15, 18). A similar observation was made regarding bottom water Si concentrations in Brunnsjön. During the anoxic period, Si concentrations peaked to the overall maximum concentration and subsequently fluctuated around a 32% higher average concentration (Fig. 20). Prior to the observed step change, the average bottom water Si concentration was 4.73 mg l^{-1} ($\pm 0.99 \text{ mg l}^{-1}$, $n=78$, between 1996-04-29 and 2005-10-17), whereas the subsequent average Si concentration was 6.24 mg l^{-1} ($\pm 0.41 \text{ mg l}^{-1}$, $n=78$, until 2015-10-20). Considering that the observed step change in Si concentrations coincided with the sustained anoxic period and with the maximum observed concentrations in TP, a similar underlying cause is probable.

It has previously been suggested that the concentrations of dissolved Si in hypolimnion is controlled by redox related dynamics of Fe and Mn hydrous oxides (Kato, 1969). In a mesocosm study, Kato (1969) observed that Si concentrations increased upon dissolution of Fe and Mn hydrous oxides under anoxic conditions. As oxygen was introduced into the system, Si concentrations decreased simultaneously with Fe and Mn concentrations (Kato, 1969). In the present study, long-term monitoring of bottom water Fe and Mn was discontinued in 2003 and subsequently started in 2013 in most lakes (with current sampling of bottom waters). Fe and Mn dynamics were thus not further investigated.

In a much more recent study, the effects of anoxia on Si dynamics in sediments were investigated by sequential extraction under oxic and anoxic conditions as well as release dynamics experiments (Siipola *et al.*, 2016). The study aimed at addressing the theory that processes that affect P and its release from sediments might also affect Si, as both compounds produce anionic ligands that may compete for adsorption sites on mineral surfaces. The authors hypothesised that increased dissimilatory reduction of Fe(III) under anoxic conditions should increase the release of adsorbed Si, and that Fe-Si colloids are formed under anoxic conditions. Their results were however ambiguous, showing that Si dynamics differed from the behaviour of P under anoxic conditions. In the loosely sorbed and redox-sensitive fractions, the release of Si generally decreased under anoxic conditions. Moreover, the 28 days release dynamics experiment showed that the release of Si was time-dependant and slower in anoxic conditions. From additional results, Siipola *et al.*, (2016) argued that the observed behaviour of Si might be explained by resorption to Al oxides and formation of colloidal Fe-Si oxides. Considering the results obtained in the study of Siipola *et al.*, (2016), short-term anoxic events may not lead to increased release rates of Si, as the authors noted. However, in the present study, the sustained anoxic conditions in, for instance, Brunnsjön lasted more than a year. In the absence of sufficient adsorption sites, or if the adsorption sites are filled by other ligands, such as organic acids, the herein observed increase in

Si might have been caused by release of redox-sensitive Fe-bound Si. Clearly, the behaviour of Si is a topic that is in need of further research. Especially as Si is an important nutrient for phytoplankton (mainly diatoms), and since increased concentrations of Si may favour some species at the cost of others.

Any sustained changes in bottom water DO may strongly affect the flux of constituents at the sediment-water interface as well as the benthic species dependent on DO for survival. Clearly, lake ecosystems are adapted to seasonal fluctuations and temporary anoxia during thermal stratification. However, rising TOC concentrations (or climate change) may result in longer duration of thermal stratification, resulting in increased oxygen depletion, potentially destabilising the ecosystem. Ecosystems have the ability to recover to *baseline conditions* after a perturbation (e.g. sustained anoxia, acidification). However, if the pressure is severe, the departure from baseline conditions might result in a breakdown of internal feedback mechanisms. Following a turbulent time, this may eventually lead to a stabilisation of the ecosystem at an altered state, i.e. *regime shift* (Spears *et al.*, 2017). In this study, the observed step change in bottom water Si concentration in Brunnsjön, followed by a stabilisation of Si concentrations at a 32% higher level (Fig. 20), is an indicator of a possible regime shift that should be further evaluated.

5.4. Outlook: recommendations for future monitoring of lakes in Sweden

The general perspective of anoxia during summer stratification is often related to eutrophic lakes. Highly productive lakes have a large input of nutrients and settling organisms to the bottom waters, which results in high decomposition rates at the sediment-water interface, rapidly depleting the available DO from the onset of stratification (Wetzel, 2001). In this study it was however observed that meso- and oligotrophic lakes are also subject to substantial oxygen depletion during summer stratification.

Observation made within this study demonstrate the importance of monitoring bottom water chemistry as a complement to assessment of surface waters. Since the sediment-water interface is important in regulating the composition of lakes, it is highly relevant to assess the seasonal and long-term patterns in bottom water chemistry, especially during thermal stratification. Moreover, to evaluate potential effects of TOC on lake thermal structure and DO dynamics, bottom waters should not be neglected. Firstly, I recommend that the existing monitoring of bottom waters should be maintained and that the sampling frequency should not be decreased. In the case of Härsvatten, the sampling frequency was cut from 8 samples per year to 4. Visual inspection of Härsvatten time series data showed that the decrease in sampling frequency obscured trends in DO and likely resulted in that true peaks in pH, TOC, TP and NH₄-N (occurring during anoxic conditions) were not detected (Fig. B6). Therefore, I recommend that the sampling frequency of bottom waters should be re-instated to the previous level in Härsvatten, as well as in other lakes in which it was cut. Furthermore, in lakes for which monitoring of bottom waters were ceased altogether (for instance in Fräcksjön), I highly recommend that it should be re-instated. The long time series of Swedish lake water chemistry data are highly valuable and essential for tracking human impacts on freshwater resources; predicting future challenges to freshwater resource management and informing sound policy measures.

6. Conclusions

The herein observed increasing trends in bottom water TOC, NH₄-N, and to some extent TP levels, coupled with known mechanistic relationships between these substances and bottom water DO, indicate that prolonged periods of oxygen depleted hypolimnia is a probable underlying driver. This was confirmed by visual inspection of temporal dynamics in bottom water chemistry (chapter 4.4). Considering the prevalence of rising trends in bottom water TOC, NH₄-N and Si, there are very likely more lakes in Sweden that are experiencing similar changes. Rising bottom water TP concentrations were not as prevalent, although the short-term temporal dynamics showed peaks in bottom water TP when DO dropped. Potential increased internal loading of P in DO depleted bottom waters may have been masked in some cases, due to decreasing surface water TP concentrations observed herein and in a recent Swedish study (Huser *et al.*, 2018). Future research within this topic should aim at evaluating the drivers of changes in lake thermal structure and duration of stratification, such as the relative importance of rising DOC concentrations and climate warming.

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Appendix A

Table A1. Current laboratory analysis methods for the assessed water chemical parameters. Previous methods are available at <https://www.slu.se/vatten-miljo/vattenanalyser>. Abs F = absorbance measured on filtered sample, DO = dissolved oxygen, NH₄-N = nitrogen from ammonia, Si = silica, TN = total nitrogen, TOC = total organic carbon and TP = total phosphorus.

Variable	Method	Principle	Measurement range	Uncertainty	Range
Abs F, 420 nm, cuvette 5 cm	SS-EN ISO 7887-2012, part B	Photometry	0.01-1 abs units	17% 5%	< 0,100 a.u ≥ 0.100 a.u
Acidity ¹	St Methods 16th Ed. 402, p. 265-269	Titration	0-0.100 mekv/l	24%	
Alkalinity	SS-EN ISO 9963-2, 1 st edition, mod	Titration	0-4.0 mekv/l	0.009 mekv/l 5%	< 0,1 mekv/l ≥ 0,1 mekv/l
Chlorophyll <i>a</i>	SS 02 81 46, 1 st edition	Photometry	>0.5 µg/l	16%	
Conductivity, electrical	SS-EN 27888, 1 st edition		0.1-150 mS/m	10% 5%	< 0.10 mS/l ≥ 0.10 mS/l
DO	SS-EN 25813, 1 st edition, mod	Titration	0-20 mg/l	5%	
DO	ISO 17289:2014	Optical sensor	0.1-20 mg/l	5%	
NH ₄ -N	ISO 15923-1:2013	Discrete analysis, photometry	3-1000 µg/l	4µg/l 11%	< 60 µg/l ≥ 60 µg/l
pH	SS-EN ISO 10523:2012, mod		3-10 pH-units	0.28 pH-units	
Si ²	SS-EN ISO 17294-2:2005	ICP-MS	0.01-10 mg/l	14%	
TN	SS EN 12260:2004	Combustion	50-10000 µg/l	15%	
TOC	SS-EN 1484, 1 st edition Shimadzu Instrument manual	Combustion	0.5-100 mg/l	10% 11%	< 0,20 mg/l ≥ 0,20mg/l
TP	SS-EN ISO 6878:2005, mod Bran Luebbe, Method No G-175-96 for AAIII	Flow analysis, photometry	1-200 µg/l	1 µg/l 10%	< 5µg/l ≥ 5µg/l

¹ At the time of this study, acidity was listed as negative alkalinity in the database and the data was kept in this format.

² Prior to 2014, the method used measured molybdate reactive silica, which corresponds to dissolved silica. A quality assurance comparison of previous and current methods showed similar measurement results (http://www.slu.se/globalassets/ew/org/inst/vom/_vatten-och-miljo_dok/laboratorier/kemlab/kisel---byte-av-metod.pdf).

Appendix B

Abiskojaure

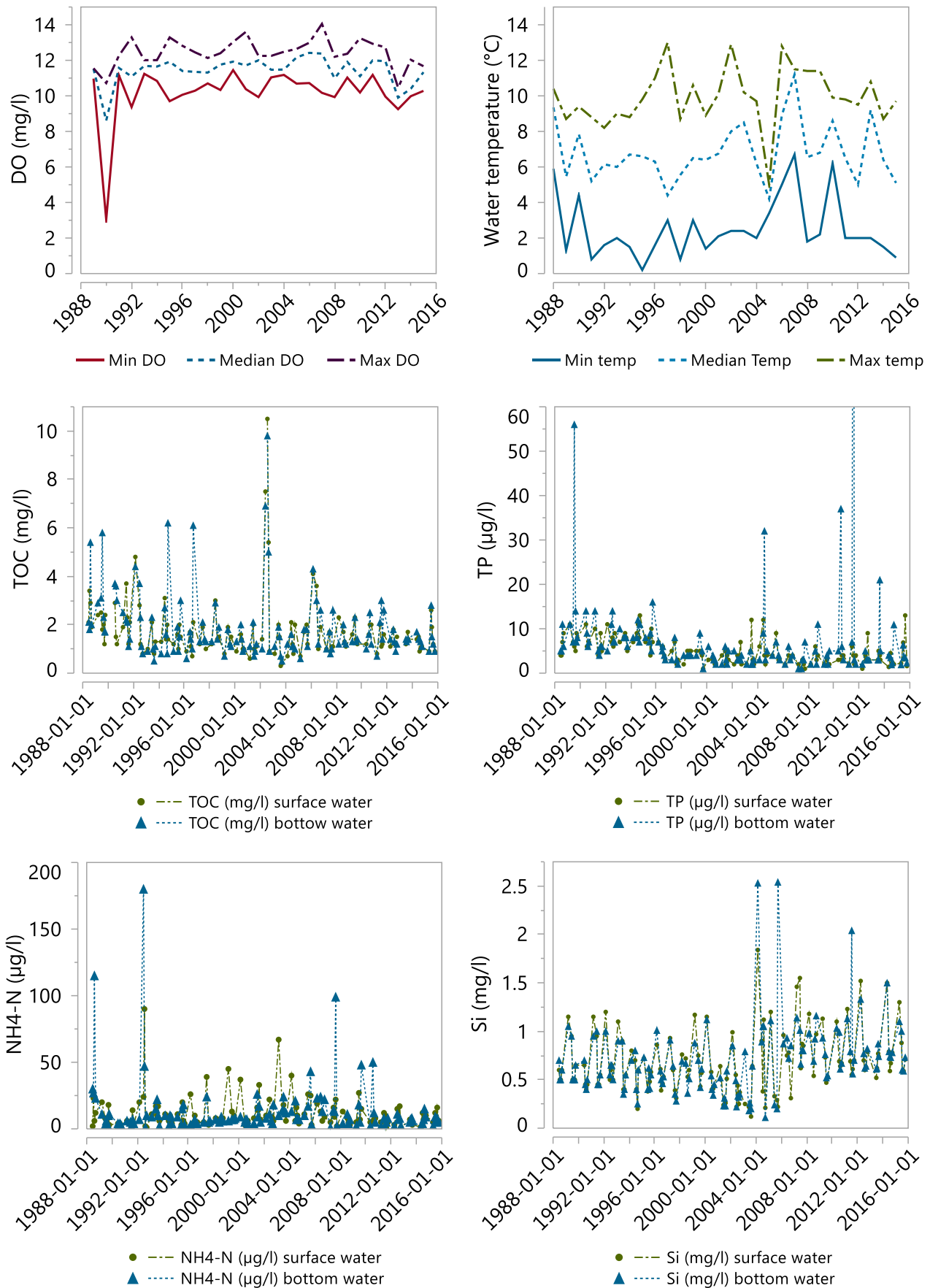


Figure B1. Lake water chemistry in Abiskojaure: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off TP peak was 175 µg l⁻¹.

Allgjuttern

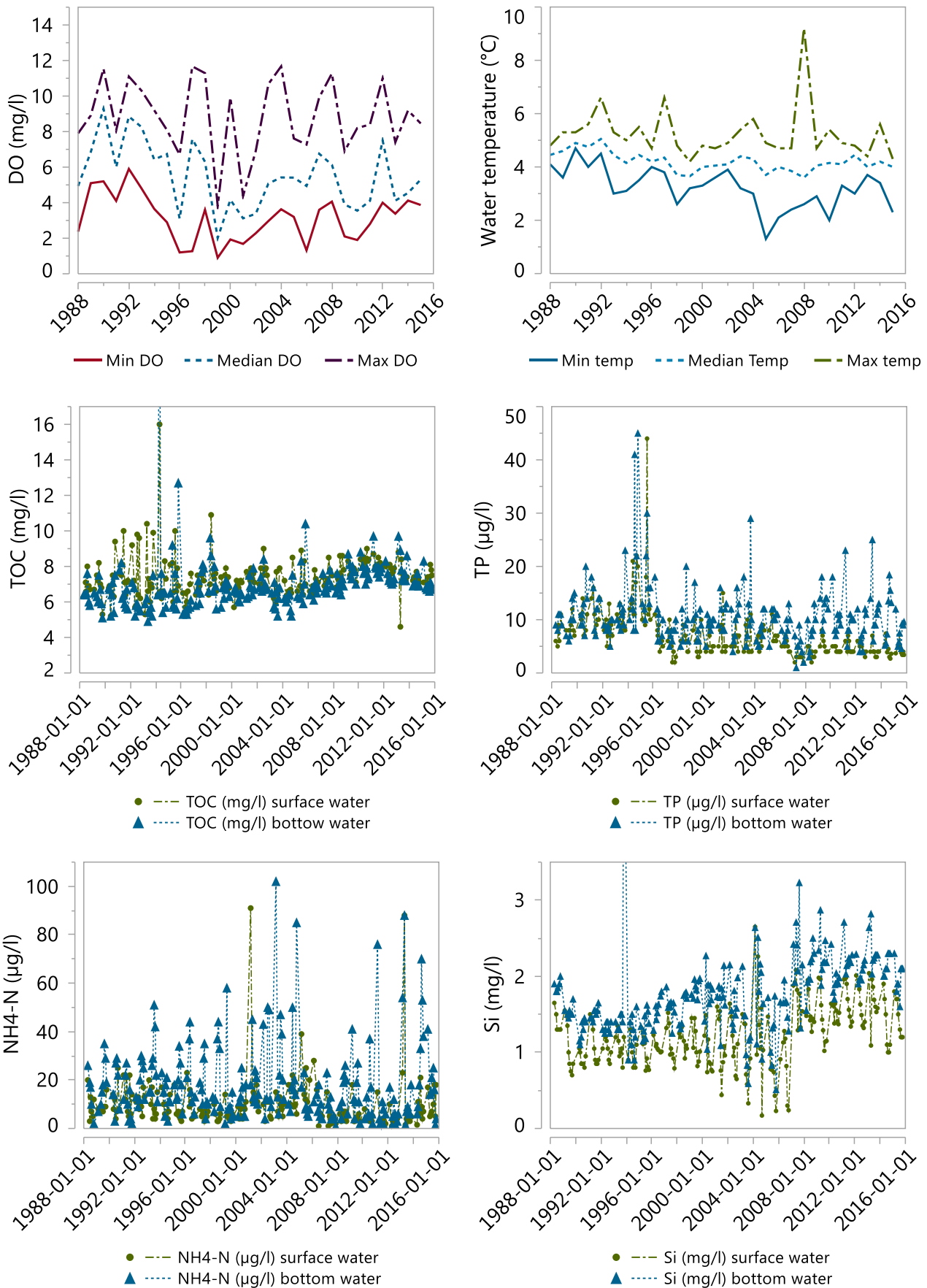


Figure B2. Lake water chemistry in Allgjuttern: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off TOC peak was 25.5 mg l⁻¹, and the Si peak was 5.9 mg l⁻¹.

Brunnsjön

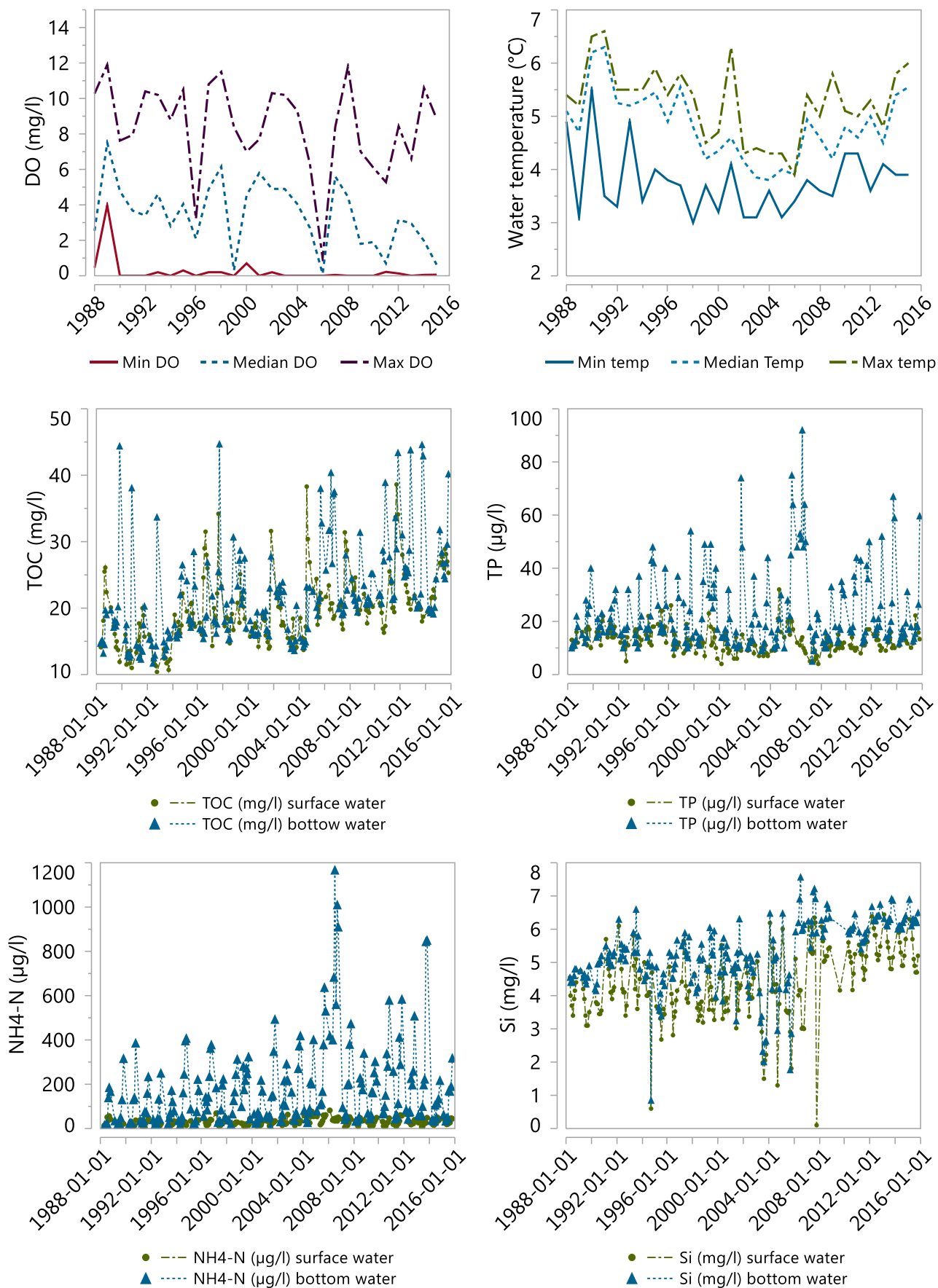


Figure B3. Lake water chemistry in Brunnsjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations.

Fiolen

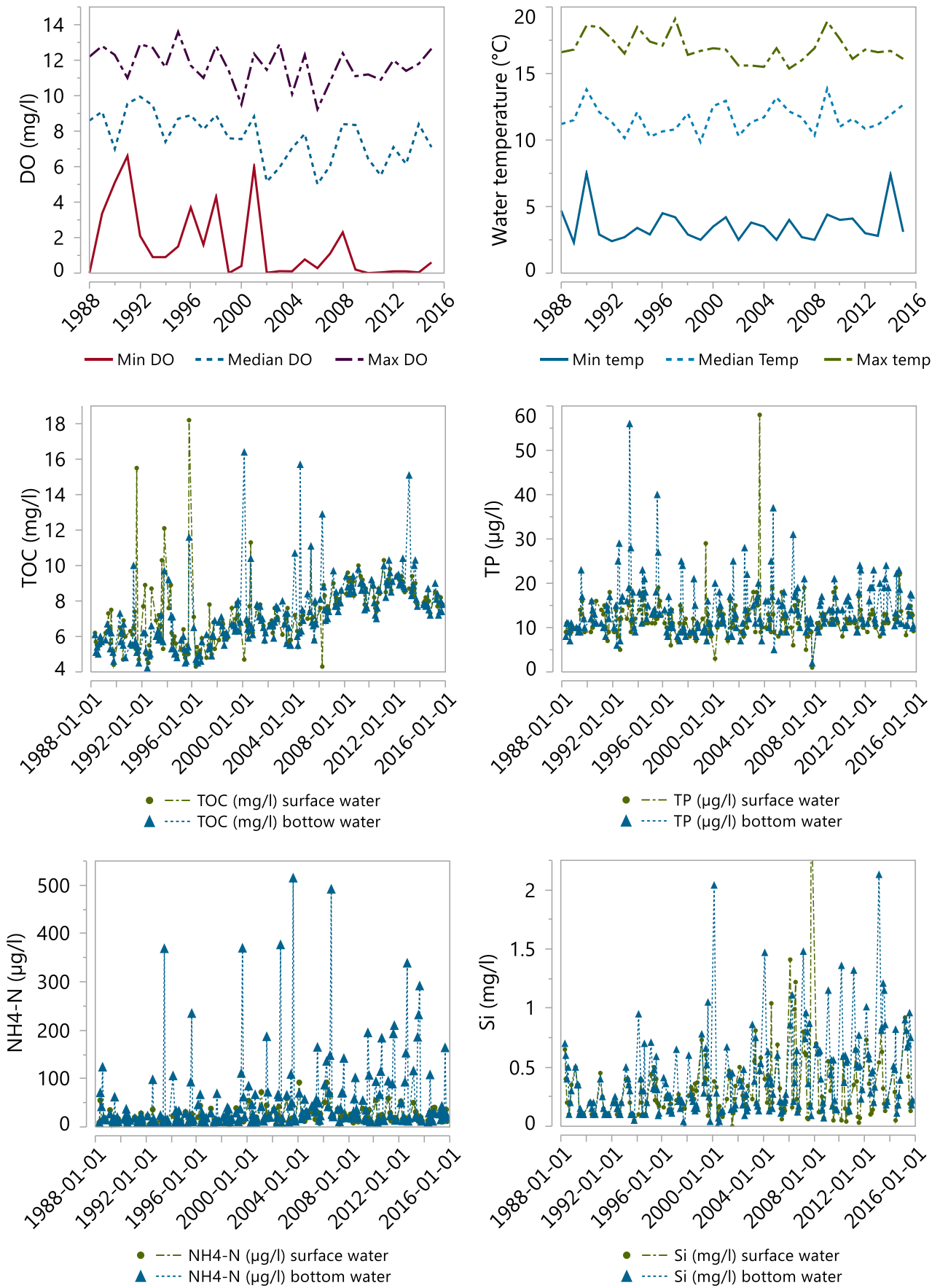


Figure B4. Lake water chemistry in Fiolen: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations.

Fräcksjön

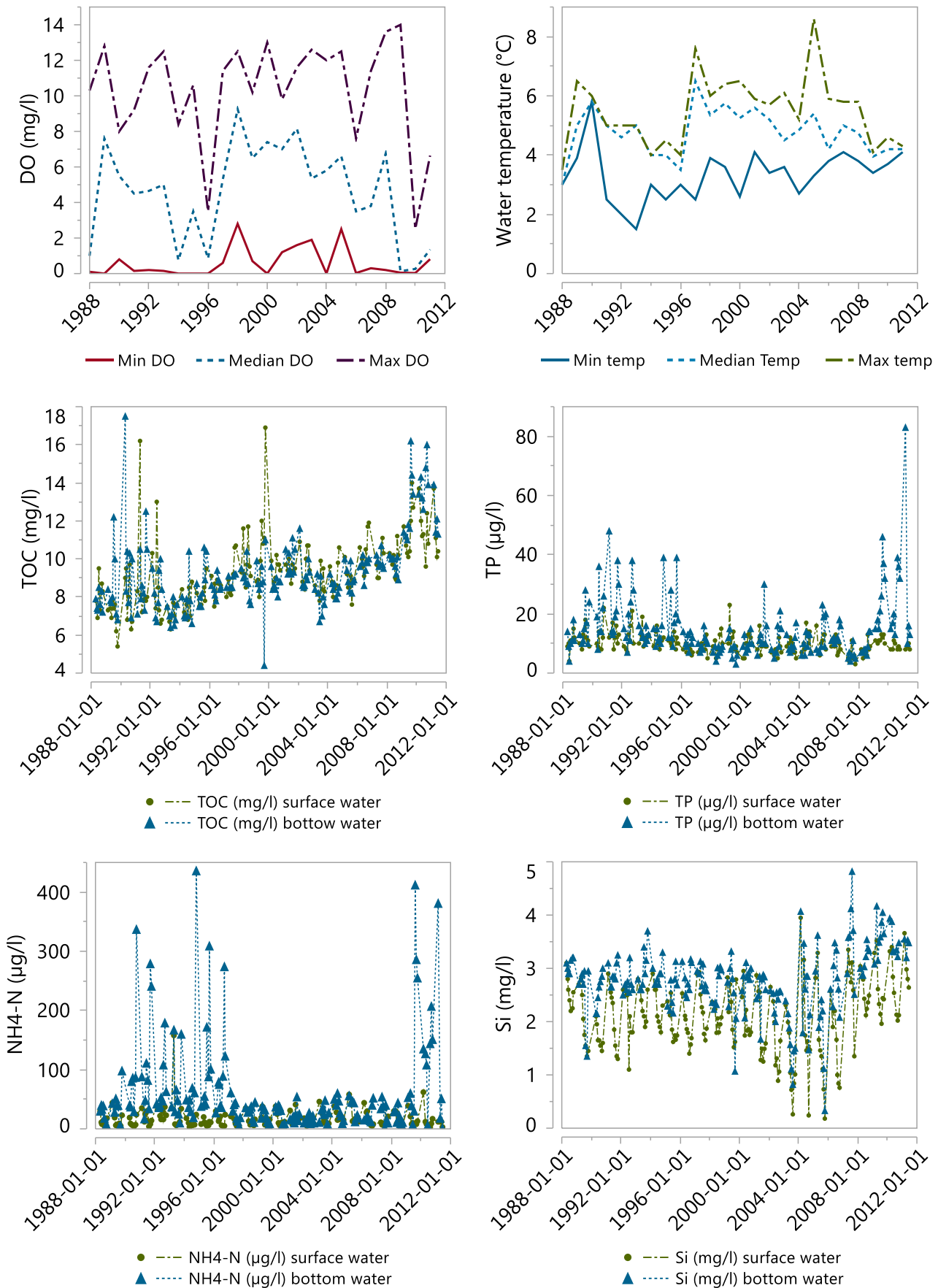


Figure B5. Lake water chemistry in Fräcksjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations.

Härsvatten

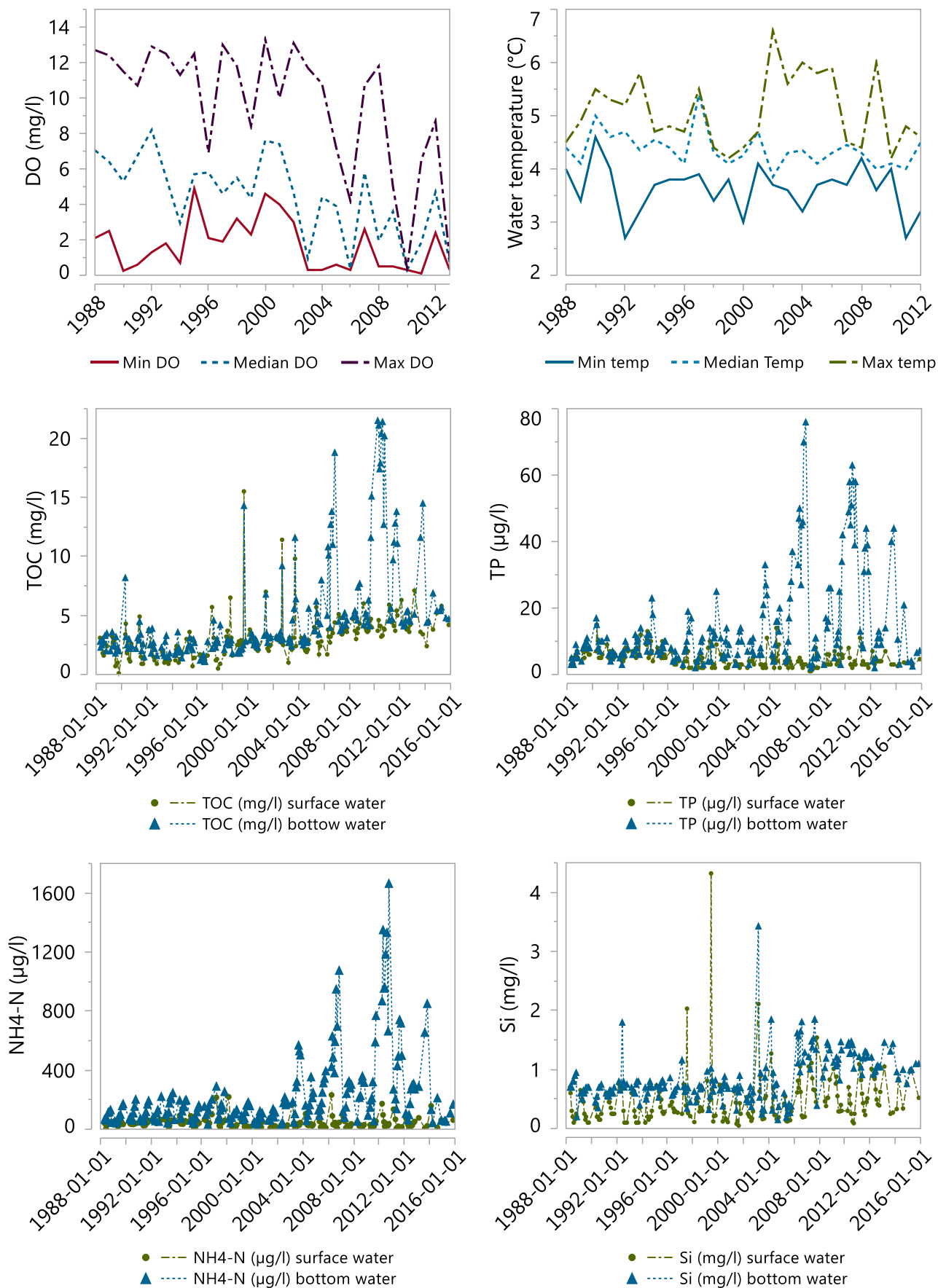


Figure B6. Lake water chemistry in Härsvatten: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations.

Remmarsjön

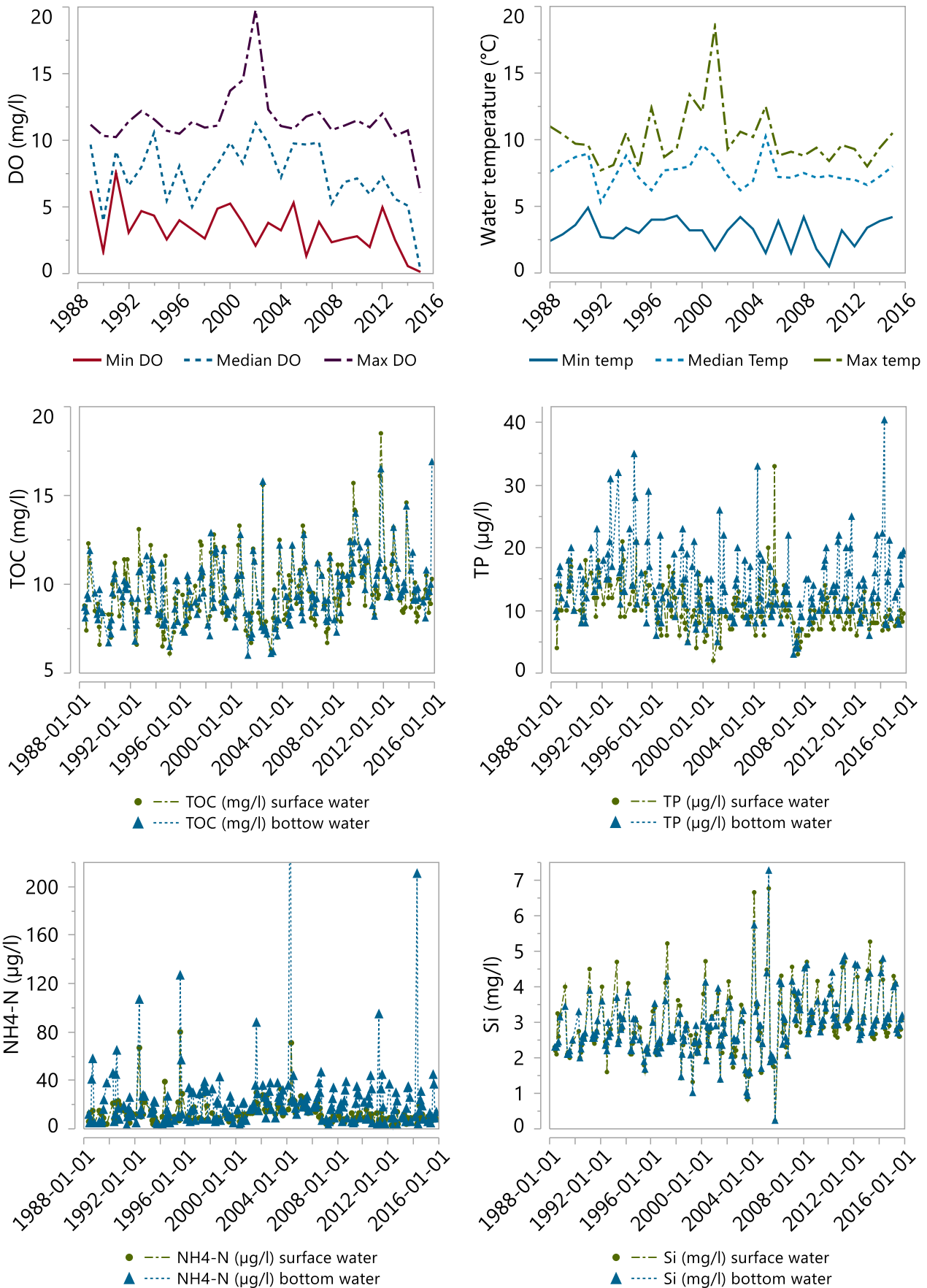


Figure B7. Lake water chemistry in Remmarsjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off NH₄-N peak was 357 µg l⁻¹.

Rotehogstjärnet

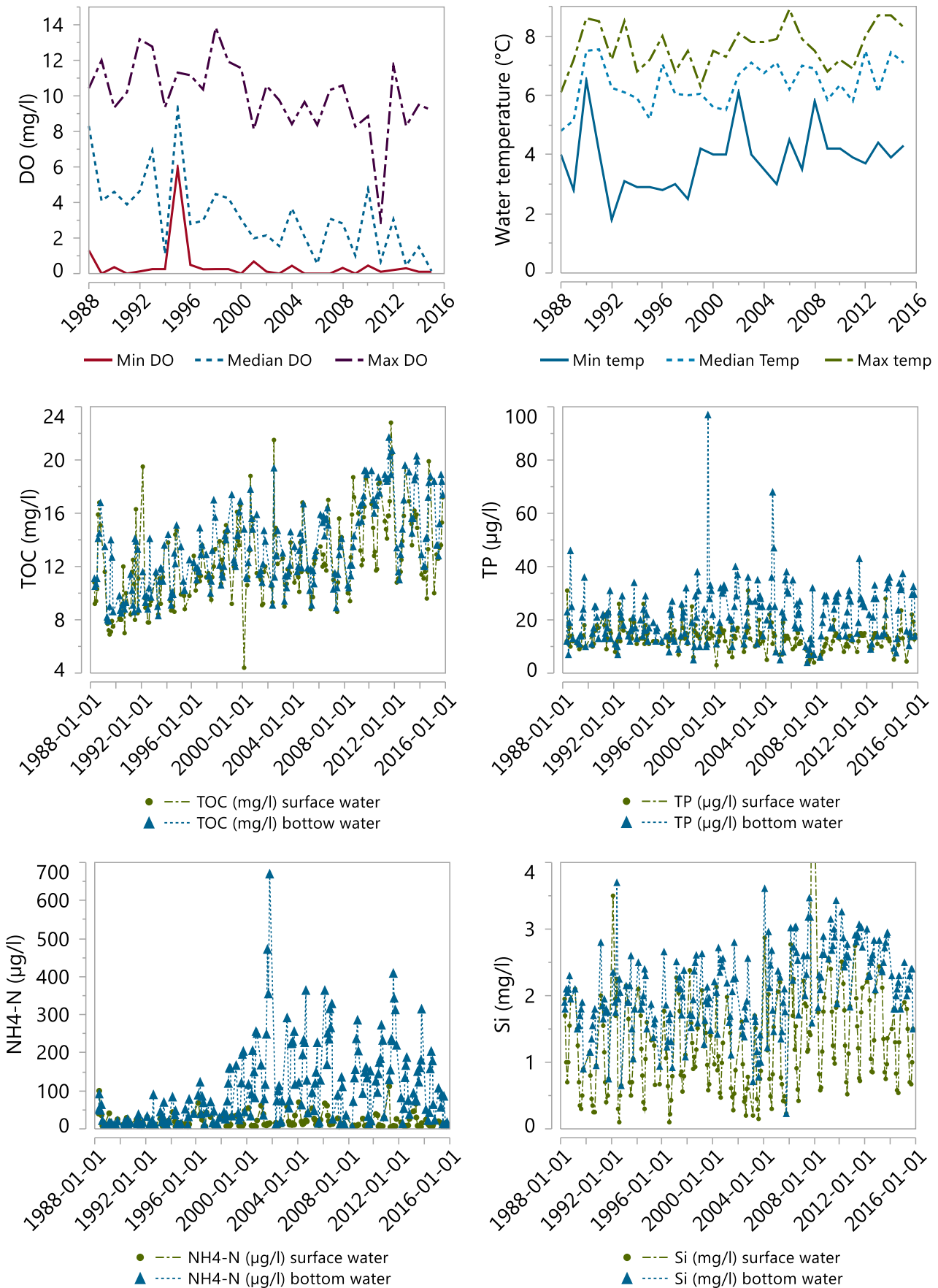


Figure B8. Lake water chemistry in Rotehogstjärnet: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off Si peak was 7.15 mg l⁻¹.

Stora Skärsjön

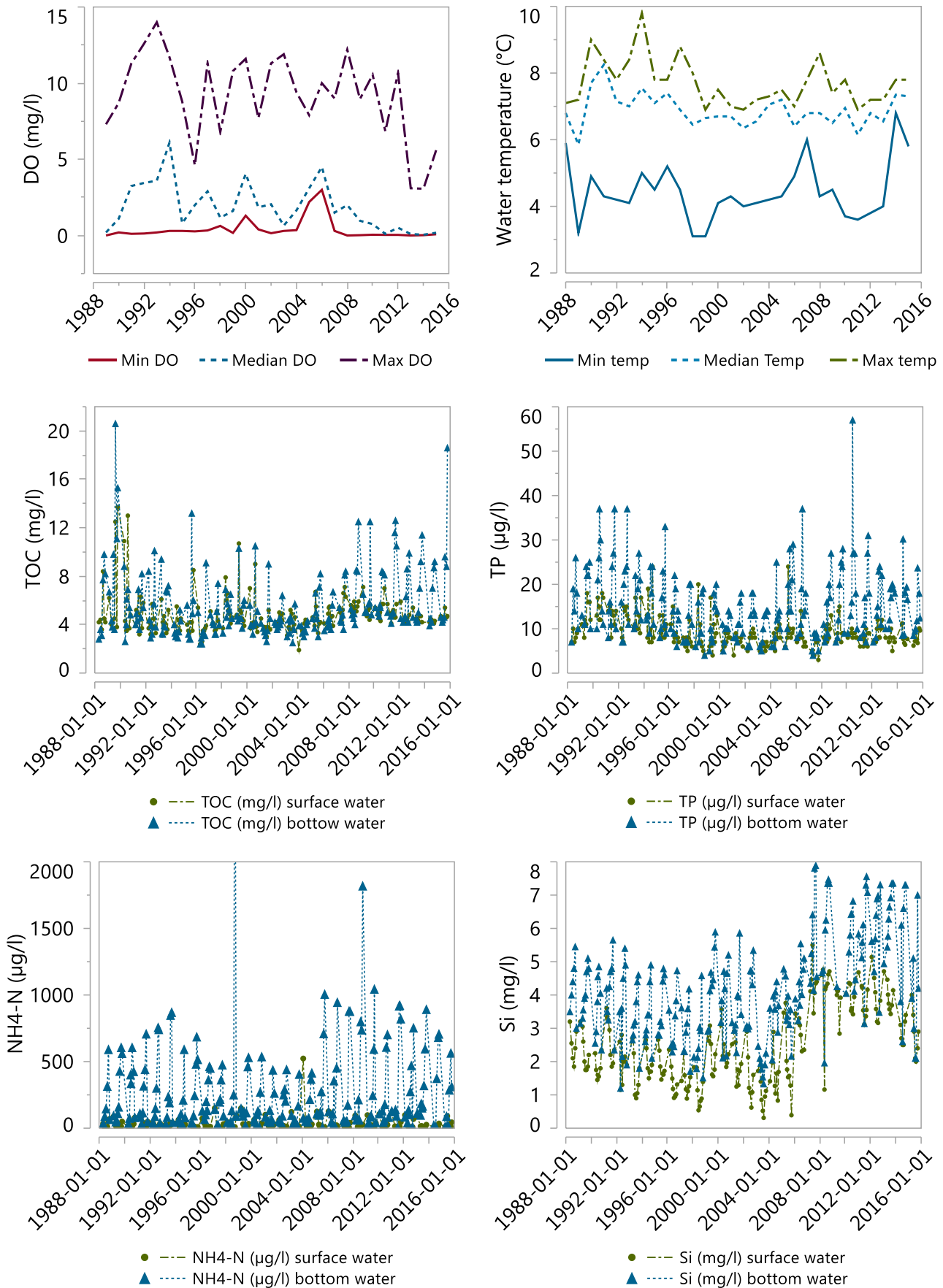


Figure B9. Lake water chemistry in Stora Skärsjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off NH₄-N peak was 3885 µg l⁻¹.

Stensjön

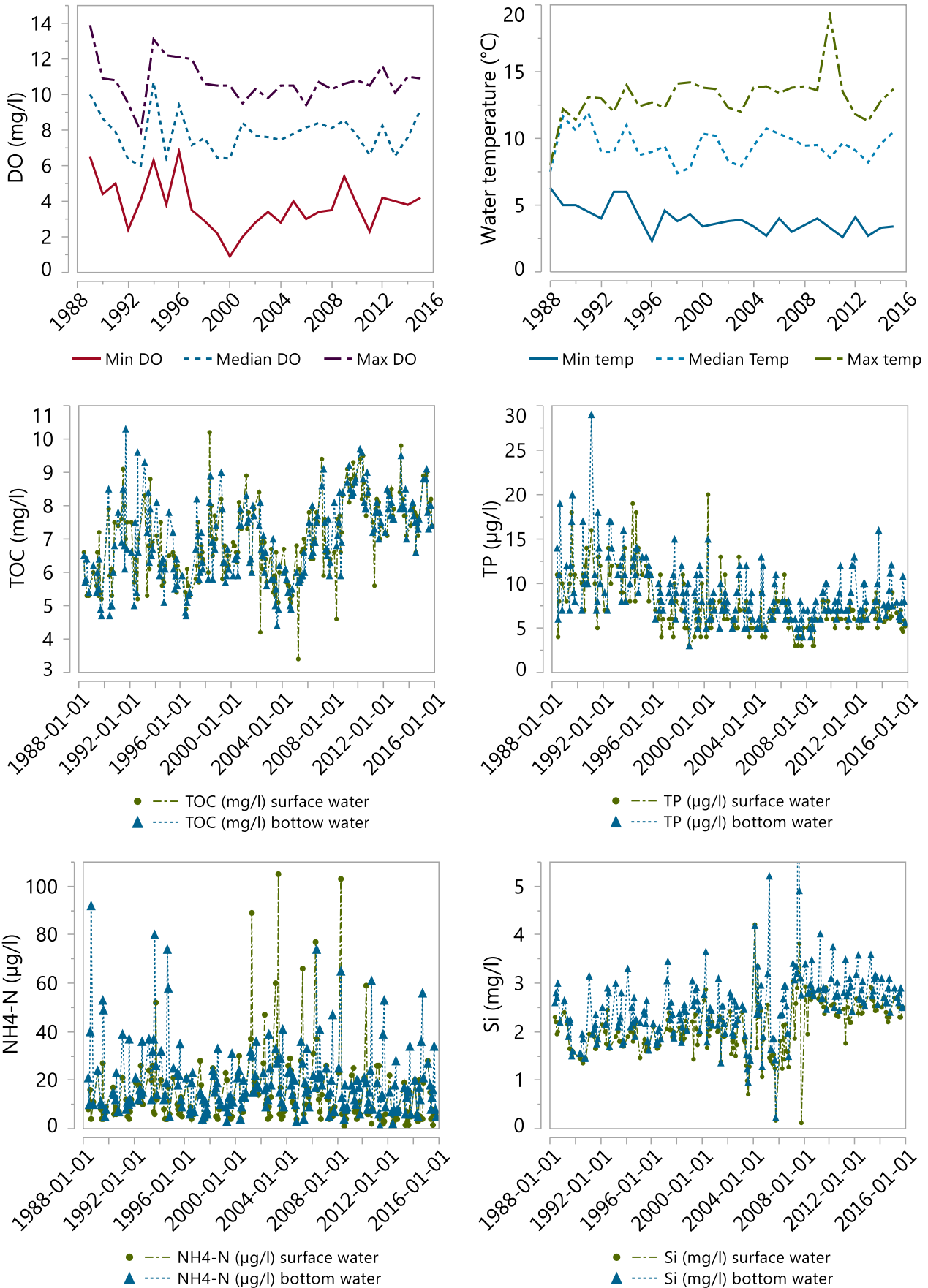


Figure B10. Lake water chemistry in Stensjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off Si peak was 8.51 mg l⁻¹.

Stora Envättern

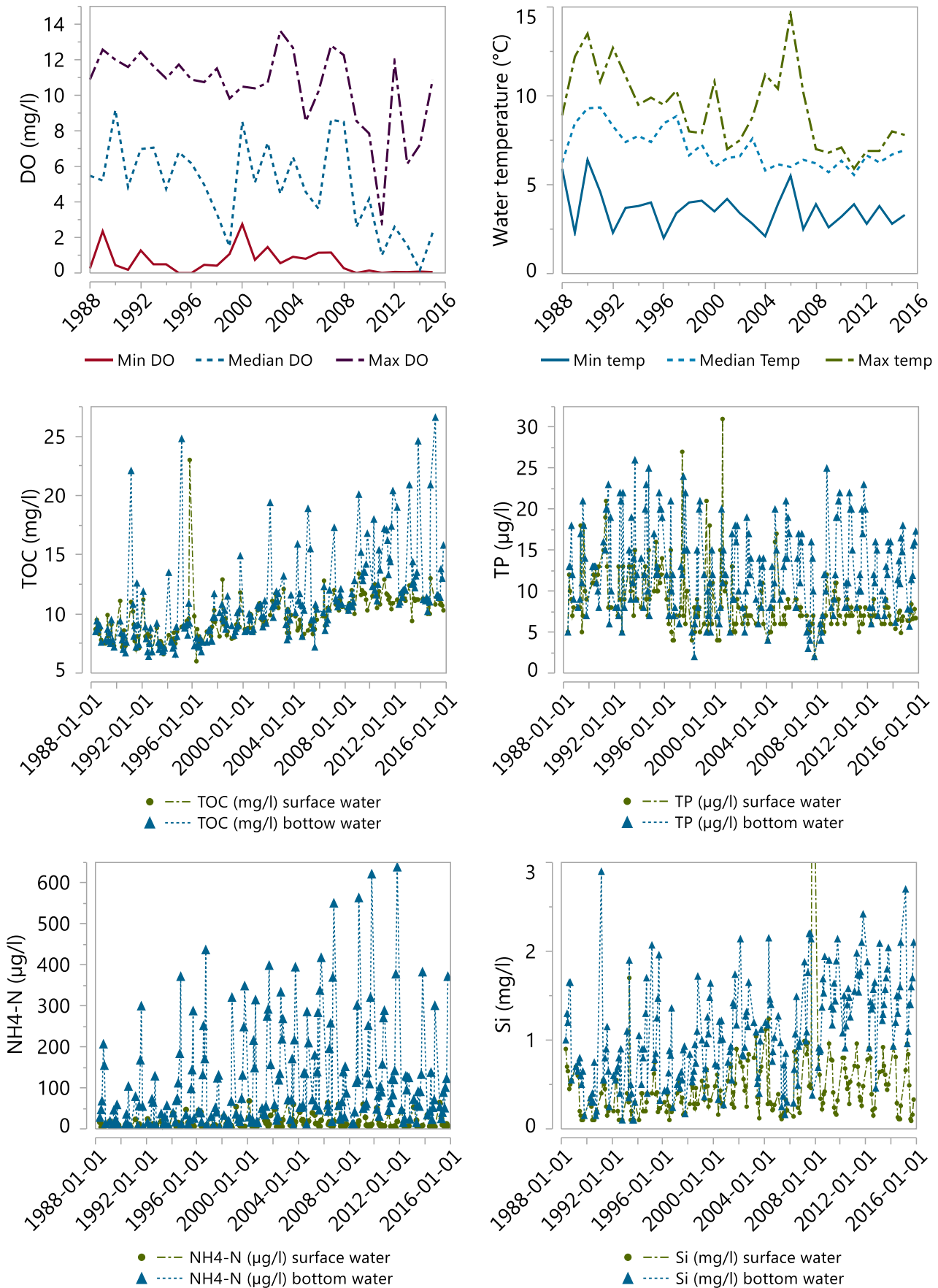


Figure B11. Lake water chemistry in Stora Envättern: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off Si peak was 5.68 mg l⁻¹.

Älgsjön

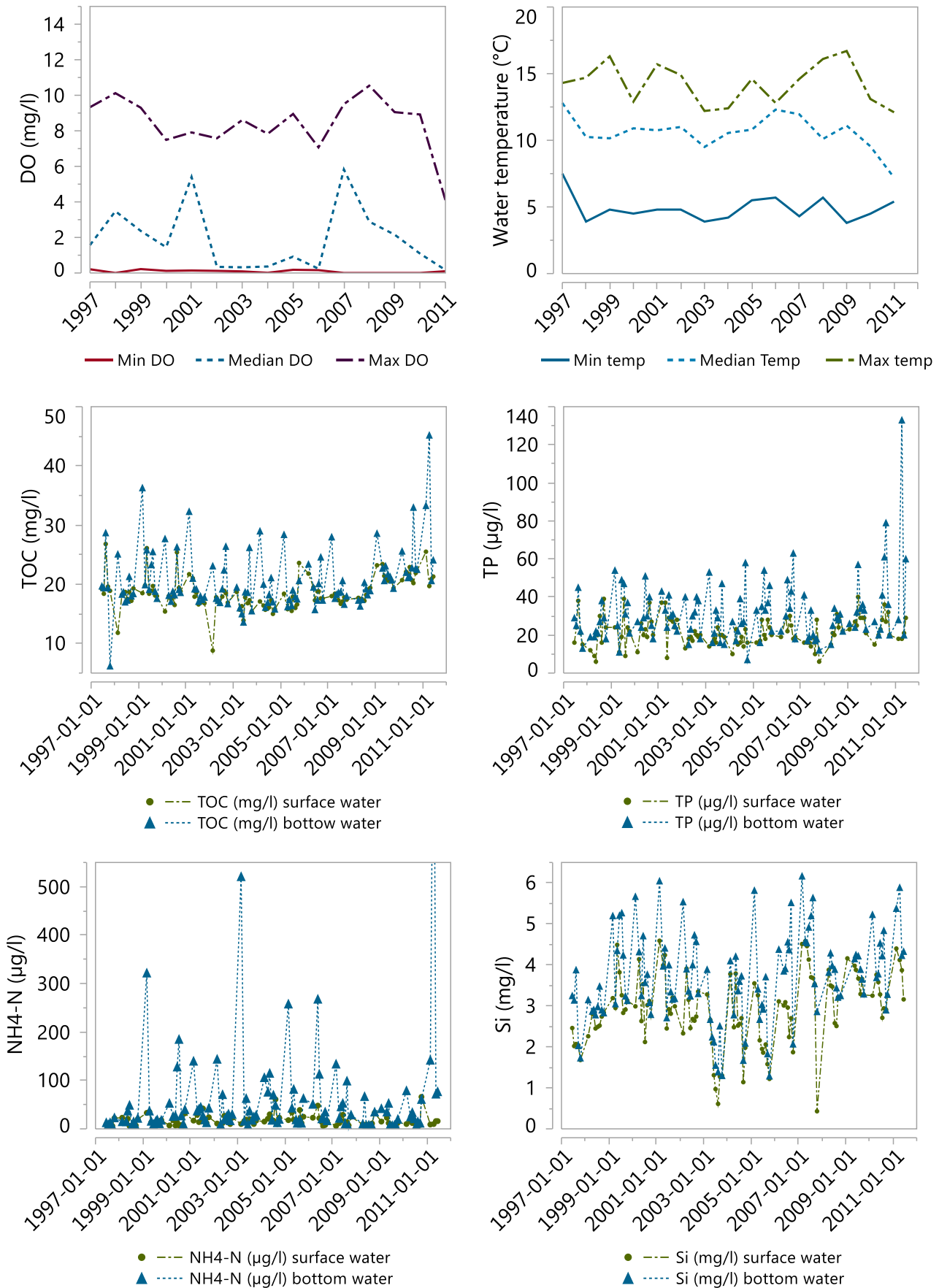


Figure B12. Lake water chemistry in Älgsjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations. The cut off NH₄-N peak was 1031 µg l⁻¹.

Övre Skärsjön

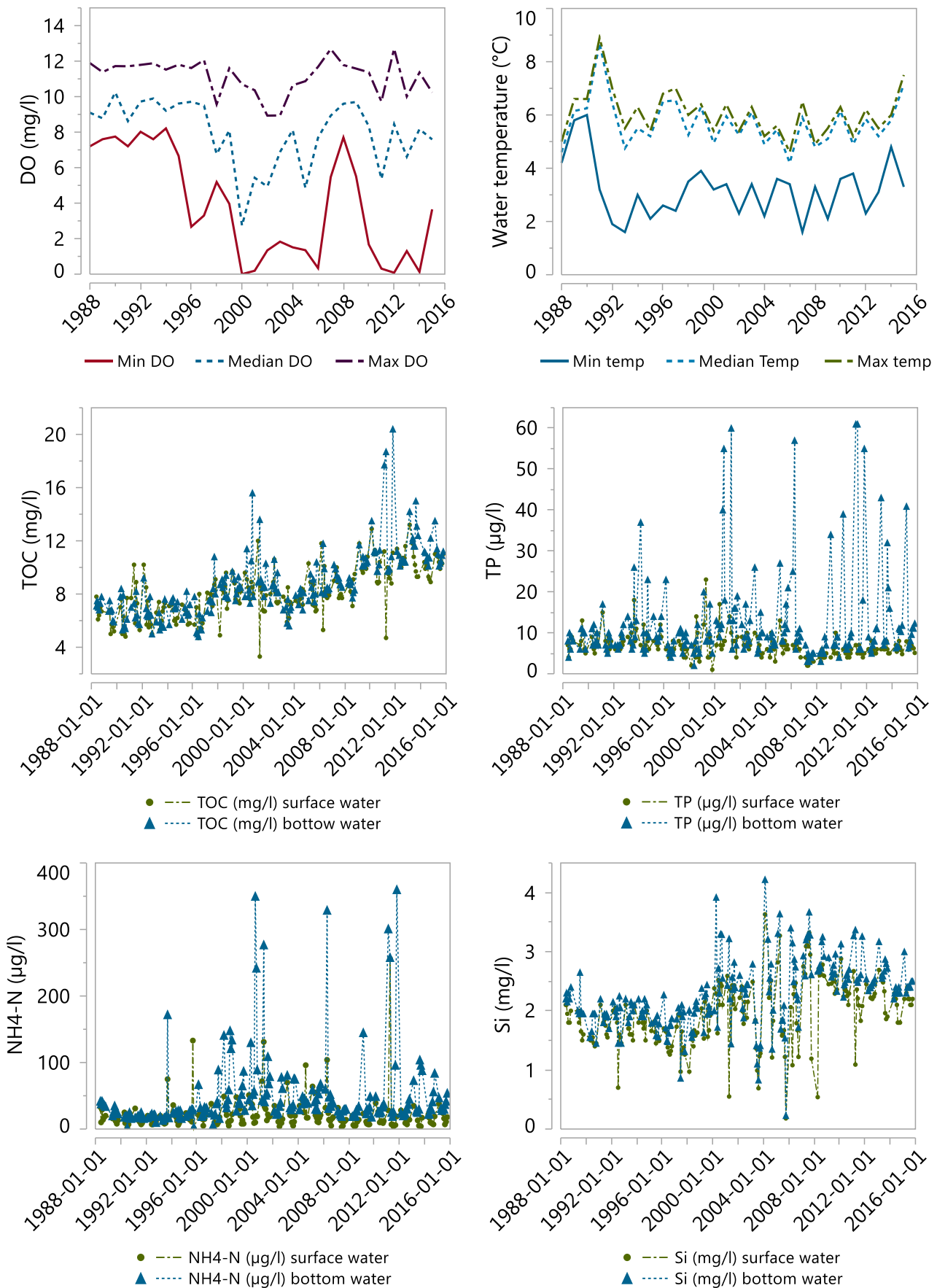


Figure B13. Lake water chemistry in Övre Skärsjön: Yearly minimum, median and maximum bottom water DO and temperatures (top). Time series of surface and bottom water TOC, TP, NH₄-N and Si concentrations.