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Influence of land cover changes on organic carbon and organic nitrogen concentrations in Swedish rivers

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Bachelor thesis, 15 credits, in Physical Geography and Ecosystem Analysis

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Abstract

There is increasing pressure on freshwater systems due to excessive nutrient loading by anthropogenic sources. In Sweden, freshwaters have become browner due to increasing exports of organic matter from soils into streams, rivers, and lakes. This study aimed at detecting temporal patterns in Total Organic Carbon (TOC) and Total Organic Nitrogen (TON) concentrations in 44 Swedish rivers, and to link these trends to land cover changes in the catchments. It was hypothesized that increasing TOC trends would be governed by afforestation, while TON dynamics would be determined by urbanization and/or agricultural expansion in the catchments.

Annually averaged water quality time series for TOC (1987-2012), TON (2002-2011) and the calculated TOC:TON ratio were retrieved from the database WaterBase, whereas land cover and associated changes were based on three CORINE land cover raster layers (2000, 2006 and 2012) from the European Earth observation programme Copernicus.

Net land cover changes indicated that 1.02% of Sweden changed land cover from 2000 to 2012, with directional land cover changes highlighting the role of both forest gains and losses. The analysis of water quality revealed temporal trends, with a general increase in TOC concentrations by 0.106 ± 0.082 mg C L^{-1} yr^{-1} and a simultaneous decrease in TON concentrations by 0.015 ± 0.017 mg N L^{-1} yr-^{1}.

Comparison of temporal trends in TOC, TON and TOC:TON grouped by land cover change revealed linkages between certain land cover dynamics and water chemistry trends. However, differences in TOC trends could not be connected to afforestation within the catchment. Catchments with increasing impervious surfaces showed a significantly stronger negative trend in TON (median=-0.015 mg L^{-1} yr^{-1}) compared to catchments with unchanged (median=-0.007 mg L^{-1} yr^{-1}) or decreasing (median=-0.009 mg L^{-1} yr^{-1}) urban areas, although the two latter categories were not significantly different from each other. These trends contrast the traditional view on urban and industrial areas as sources of TON and suggest considerably improved wastewater treatment. TOC dynamics significantly differed depending on agricultural land cover changes. The TOC data exhibited stronger positive trends for changing catchments, regardless of the direction of change. Both catchments with increasing (median=0.145 mg L^{-1} yr^{-1}) and decreasing (median=0.100 mg L^{-1} yr^{-1}) agricultural extent had stronger increases in TOC compared to catchments with unchanged agricultural extent (median=0.053 mg L^{-1} yr^{-1}). Potentially, these patterns are associated with changes in management that lead to more soil organic carbon (SOC) being lost in runoff. Conversion to forest leads to increases in SOC and thus more subsequent leakage. Transformation from natural land cover (pasture, grassland) to agriculture represents a disturbance that causes losses in SOC, possibly expressed in temporarily stronger TOC trends.

This study advanced the understanding of organic matter loading by establishing novel linkages between land cover change and trends in riverine TOC and TON in a country dominated by boreal vegetation. The presented findings showed a decoupling of browning trends from TON concentrations. The strong increase in TOC:TON ratio suggests a shift in organic matter origin, from dominance of (autochthonous) in-water sources toward more (allochthonous) terrestrial sources.

Keywords: Total Organic Carbon (TOC), Total Organic Nitrogen (TON), Land Cover Change, Sweden, WaterBase

Popular Abstract

For us humans, freshwater may be the most important resource on the planet. However, human activity also poses the largest threat to water quality of surface waters. This refers to eutrophication, which occurs when freshwaters receive an 'overdose' of nutrients from human sources (e.g., agricultural runoff, urban wastewater), which overly stimulates productivity and oxygen demand in the water until most/all oxygen is depleted.

In Sweden, especially organic nutrient concentrations are on the rise in surface waters, which causes darkening ('brownification'). There are multiple consequences of browning: browner surface waters emit more CO_2 to the atmosphere, lead to more expensive (and potentially less efficient) drinking water treatment, and cause more acidification in water systems.

This study uses a novel approach to link human land use to water quality and browning, as it compares changes (in land cover) with changes (in water quality parameter). Water quality data comes from the European database WaterBase, with information on two prevalent organic nutrients and their ratio, namely total organic carbon (TOC), total organic nitrogen (TON) and TOC to TON (TOC:TON). Land cover data for 2000, 2006 and 2012 was provided by the European Earth observation programme Copernicus.

These three variables were analysed for potential trends between 1987 and 2012 (TOC), or between 2002 and 2011 (TON, TOC:TON). Then, these chemistry changes were grouped by the direction of land cover change between 2000 and 2012 (Increase, Decrease, No Change).

The 44 study sites showed clear temporal trends in all three chemical parameters. TOC has predominantly increased between 1987 and 2012. This aligns with previously observed browning trends, where stable TOC cannot be degraded and remains unprocessed in the water. With more TOC entering surface waters, water colour becomes browner. On the other hand, most measurement sites recorded a decrease in TON since 2002, which suggests that the browning trend in Sweden is not related to TON in the water. The ratio between carbon and nitrogen generally increased between 2002 and 2011 in the catchments, which implies that organic matter entering the water is more stable and less degradable. This organic matter causes less eutrophication, as nutrients cannot be freed and taken up by aquatic organisms.

Changes in agricultural and urban areas influenced water chemistry trends in the 44 rivers and surrounding areas. Urbanization led to a stronger decrease in TON than unchanged or decreasing urban areas. This can be explained by stricter filtering regulations for new wastewater treatment plants, causing expanding urban areas to release less TON.

Catchments with changing agricultural coverage had a stronger increase in TOC than unchanged areas. The possible reasons depend on the direction of land cover change. When agriculture decreases by transforming into forest, the soils generate more organic matter, which could potentially leach into freshwaters. The increase of agriculture at the expense of pasture and grassland releases large quantities of soil organic carbon into freshwater systems, which cease when a new steady state is reached.

This study advanced the understanding of organic matter by successfully linking trends in TOC and TON to changes in land cover in Sweden. As TON concentrations decreased while browning increased, it could be assumed that browning was not caused by TON developments. The strong increase in TOC:TON ratio implied a change in organic matter source. The surrounding land seemingly contributed a lot more organic matter than could be generated by microorganisms in the water.

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1 Introduction

Water can be considered the most important resource on the planet. Despite its prevalence on the surface, only 3% is available for consumption in the form of freshwater (Svenskt Vatten 2019). There is increasing pressure on water resources globally, both by direct anthropogenic interference (e.g., land use change, sectoral and individual water demand) and human-induced climate warming that changes temperature and precipitation patterns (Jiménez Cisneros et al. 2014). Regional differences in magnitude and relative contribution of these pressures lead to large spatial variability in freshwater status (Jiménez Cisneros et al. 2014).

Globally, water quality is mainly impaired by excessive nutrient export to surface waters enhancing primary productivity (of e.g., phytoplankton, algae) to an unsustainable degree, with sedimenting dead organic matter depleting the bottom water of oxygen, causing hypoxia (Carpenter 2008; Rabalais et al. 2009). Hypoxia decreases aquatic biodiversity, as species either migrate toward less oxygen-poor water or are lost (Rabalais et al. 2009). This increased nutrient loading to freshwaters and coastal regions is mainly attributed to human activity (Rabalais et al. 2009; Jiménez Cisneros et al. 2014).

In the European Union, there have been large-scale efforts to improve water quality by mitigating nutrient and organic pollution, which affect around 28% and 18% of European water bodies respectively (European Environment Agency 2018). While this eutrophication continues to be a problem, nutrient loading has declined since the 1990s, which can be attributed to stricter regulations for anthropogenic nutrient addition from i.e., the agricultural sector and urban and industrial wastewater (European Environment Agency 2018).

Sweden has the largest areal extent of freshwater systems (lakes, river, streams) in the EU (European Environment Agency 2018). Despite a longer-term decrease in nitrogen (N) and phosphorus (P) export (1997-2017), eutrophication is still a major problem in Swedish inland and coastal waters (Naturvårdsverket 2020). According to the Swedish Environmental Agency (Naturvårdsverket 2020), 20% of the investigated lakes and 30% of running waters were classed as eutrophic in 2019, based on the measured P concentrations. Especially waters in southern Sweden are affected by eutrophication, due to enhanced agricultural activity and higher population density compared to the North (Naturvårdsverket 2020). Eutrophication mitigation measures led to an overall reduction of inorganic nutrient concentrations in Swedish surface waters (European Environment Agency 2018).

This stands in contrast to organic nutrient loading in Sweden (Naturvårdsverket 2020). In the last 50 years, a ‘browning’ trend has been observed in boreal freshwaters, expressed in changes in water colour (Kritzberg and Ekström 2012; Kritzberg et al. 2020; Skerlep et al. 2020) and biogeochemical properties of the water (Solomon et al. 2015). This trend is associated with increasing exports of dissolved organic carbon (DOC) leaching from soils of the surrounding catchments into streams, rivers, and lakes (Kritzberg and Ekström 2012; Meyer-Jacob et al. 2015; Kritzberg et al. 2020). Understanding the underlying mechanisms of DOC export and fluxes is important, as organic carbon directly influences the global Carbon cycle (Monteith et al. 2007; Kellerman et al. 2014; Kritzberg et al. 2020) and (drinking) water quality (Laudon et al. 2012; Weyhenmeyer et al. 2014; Kritzberg et al. 2020). Despite extensive research, knowledge gaps exist in the field of DOC (Laudon et al. 2012; Solomon et al. 2015; Kritzberg 2017). The various drivers of browning and their relative strengths are debated (Kritzberg 2017; Kritzberg et al. 2020). Especially the relationships and feedback systems between rising organic matter inputs and ecosystem processes are not well understood (Laudon et al. 2012; Solomon et al. 2015).

Dissolved organic nitrogen (DON) plays a large role in eutrophication (Carpenter 2008). Yet, there is limited research on the connection of organic N and browning trends (Corman et al. 2018). Aquatic ecosystems are polluted by dissolved organic matter with high DON content

from terrestrial sources, such as urban and agricultural runoff (Berman and Bronk 2003). This anthropogenic nitrogen addition is linked to increases in eutrophication and subsequent hypoxia in Swedish freshwaters (Naturvårdsverket 2020). DON compounds are available to bacteria and phytoplankton in two ways: a small fraction of DON can be utilized directly while the majority of DON needs to be converted into inorganic N forms by microorganisms before further uptake (Berman and Bronk 2003; Zhou et al. 2010). Properties of DON are more or less synonymous to those of Total organic nitrogen (TON), as TON mainly comprises of DON in boreal freshwaters (Berman and Bronk 2003; Rosenqvist et al. 2010).

The ratio between carbon and nitrogen (TOC:TON) in the water is a measurement of organic matter quality, which informs about source (Berggren and Al-Kharusi 2020) and degradation potential/reactivity (Balakrishna and Probst 2005; Ågren et al. 2008; Berggren et al. 2015). There is a lack of knowledge about the connection between C:N properties and increased organic matter loading (Berggren and Al-Kharusi 2020). In the context of browning, potential shifts in organic matter quality and degradability are not well known (Berggren and Al-Kharusi 2020). Higher degradation, and thus, better quality, is attributed to organic matter with a higher N content relative to C (Sobek et al. 2007; Rowe et al. 2014; Solomon et al. 2015).

There is a discourse about the controls on organic matter export into rivers (Kritzberg et al. 2020; Skerlep et al. 2020). In literature, climate-related factors influencing temperature (Andersson et al. 2000; Oni et al. 2013; Deininger et al. 2020) and/or hydrology (Sobek et al. 2007; Laudon et al. 2012; Kritzberg et al. 2020), as well as anthropogenic deposition of sulphur (Monteith et al. 2007; Skerlep et al. 2020) or nitrogen (European Environment Agency 2018; Naturvårdsverket 2020) are considered as drivers of organic nutrient transport into Swedish freshwaters. Recent findings highlight the influence of anthropogenic land use (Chen et al. 2016; Giri and Qiu 2016) and especially land cover changes (e.g., agriculture-forest dynamics) (Kritzberg 2017; Kritzberg et al. 2020; Skerlep et al. 2020) on TOC and TON concentrations. However, trends in water chemistry have rarely been linked to land cover changes in literature.

1.1 Aim and hypotheses

The overall aim of this study is to find out how water quality in the form of TOC and TON data and the related ratio TOC:TON changed over the period 1987-2012 (TOC) respectively 2002-2011 (TON, TOC:TON) at landscape scale. Further, it is investigated whether water quality changes can be linked to land cover changes between 2000-2012. A novel approach to investigate TOC and TON was used, as the study focuses on comparing change in land cover with change in water quality parameter. Additionally, new knowledge about the role of TON in surface browning is contributed, contrasting the more prominent focus of eutrophication. Based on this, the following hypotheses are investigated.

1. Since 1987, there has been an increase in TOC concentrations in Swedish rivers (Kritzberg and Ekström 2012; Kritzberg et al. 2020).
2. Urbanization leads to stronger trends in TON.
3. The trend in TOC concentrations increases in areas with afforestation.
4. The rise in TON concentrations increases in catchments with increasing wetland areas.
5. Catchments with increasing agricultural areas have stronger positive trends in TON.

2 Background

2.1 Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)

2.1.1 What is DOC?

Dissolved organic matter (DOM) describes a range of soluble compounds comprised of many different elements of which carbon is the most abundant, i.e., dissolved organic carbon (DOC) (Rosenqvist et al. 2010; Ahlgren 2018). DOC consists of partly decomposed particulate organic matter (Laudon et al. 2012). In contrast to (unfiltered) total organic carbon (TOC) (Ahlgren 2018), DOC in the water is derived by filtering the sample through a 0.45 micrometre filter (Oni et al. 2013) and thus, excludes the particulate fraction (Attermeyer et al. 2018; Berggren and Al-Kharusi 2020). The dominance of DOC in the TOC fraction (~90%) allows inference from TOC concentration onto DOC (Sobek et al. 2007; Berggren and Al-Kharusi 2020). However, exclusion of the (suspended) fraction of particulate organic carbon might underestimate the true bioreactivity and degrading potential of organic carbon in the water (Attermeyer et al. 2018), which influences oxygen consumption (Berggren and Al-Kharusi 2020) and determines conversion to and outgassing of CO_2 (Lapierre et al. 2013).

While relatively low quantities of DOC can be produced within aquatic systems by autotrophs (referred to as autochthonous DOC) (Kritzberg et al. 2004; Oni et al. 2013), most riverine DOC originates from soil organic matter in the catchment (called allochthonous DOC) (Guo and Gifford 2002; Schelker et al. 2012; Skerlep et al. 2020). Nevertheless, DOC produced in-water appears to be preferentially consumed by bacteria (Kritzberg et al. 2004). The overall quantity of DOC export from the soils is controlled by C stored in the organic horizon (Fröberg et al. 2011; Kritzberg 2017), or humus layer (Laudon et al. 2012). Moreover, organic-rich soils with high DOC export, such as riparian area and valley bottoms, (Ågren et al. 2008; Laudon et al. 2012), are characterized by comparably high soil moisture. Hence, fast interactions with groundwater (Oni et al. 2013) enable rapid release of DOC.

Export rates of organic carbon are governed by the solubility of DOC in the soils (Fröberg et al. 2011; Solomon et al. 2015; Kritzberg et al. 2020), which in turn is determined by acidity of the soils, and molecular properties (molecular size, aromaticity and charge density) (Andersson et al. 2000; Monteith et al. 2007). Aromaticity refers to the ring-like structure of the C and H atoms in the molecule, which enhance stability (Cazorla 2020) and directly reduce bioavailability and reactivity (Ågren et al. 2008). The term aliphatic describes molecules with straight carbon chains, low aromaticity and higher bioavailability (Ågren et al. 2008). Generally, the solubility of DOC in the soil increases with higher soil pH (Andersson et al. 2000; Monteith et al. 2007; Fröberg et al. 2011).

Similarly, the chemical composition of DOC is determined by organic matter content in the soils, which is a function of tree litter composition (Oni et al. 2013; Rowe et al. 2014; Solomon et al. 2015) depending on tree species (Cronan and Aiken 1985; Fröberg et al. 2011), stand height and age (Rosenqvist et al. 2010). This governs the bioavailability and degradability of the DOC compounds (Kellerman et al. 2014). The chemically diverse DOC structures (Dunn et al. 2015; Björnerås et al. 2017) consist to a large degree of humic substances (describing both humic and fulvic acids) (Solomon et al. 2015). The molecular weight of the compound indicates the presence of complex hydrocarbons (aromaticity) (Ågren et al. 2008). High molecular weight (HMW) DOC is aromatic, which translates into a lower degradation potential and enhanced export of unprocessed DOC into freshwaters (Ågren et al. 2008; Solomon et al. 2015). Low molecular weight (LMW) DOC is more aliphatic, which implies higher bioavailability and more utilization and decomposition by microorganisms (Ågren et al. 2008).

2.1.2 Why is research on DOC important?

In freshwater systems, rising DOC concentrations cause browning, with water colour (Weyhenmeyer et al. 2014) changing towards a more "tea-stained colour" (Solomon et al. 2015), varying "from yellow to brown or black" (Ahlgren 2018). This has a direct influence on light and heat absorption, with more absorption in the UV and short-wave visible spectrum (Oni et al. 2013) and associated impacts on heat capacity in the water (Solomon et al. 2015).

In Swedish freshwater systems, most DOC originates from boreal soils (Kritzberg and Ekström 2012), which contain vast amounts of organic C (Laudon et al. 2012; Schelker et al. 2012; Attermeyer et al. 2018). Kritzberg et al. (2020) highlight the impacts of climate change on further degradation of carbon-rich peat soils, thus making more terrestrial C available for export into rivers. Overall, inputs into the rivers are low, which was seen in Swedish rivers, with low levels of eutrophication between 1972 and 2010 (Kritzberg and Ekström 2012).

DOC concentrations in boreal freshwater systems influence the global C cycle (Kellerman et al. 2014; Kritzberg 2017; Kritzberg et al. 2020). Processing of terrestrially derived DOC in the water contributes to C emissions from inland waters (Ågren et al. 2008; Fröberg et al. 2011; Kritzberg et al. 2020). This includes the mineralization of DOC, with successive outgassing of gaseous CO_2 from the freshwater system (Lapierre et al. 2013); sedimentation and burial of DOC in rivers and lakes (Kritzberg et al. 2020) and the subsequent transport of DOC into coastal areas and oceans (Monteith et al. 2007; Nebbioso and Piccolo 2013).

On a more regional scale, drinking water quality is negatively impacted by rising DOC concentrations (Laudon et al. 2012; Weyhenmeyer et al. 2014; Kritzberg et al. 2020), as treatment will become more expensive and potentially less efficient (Meyer-Jacob et al. 2015). In Sweden, the cost for drinking water will increase by up to 5% to stay below the recommendation of 4 mg L^{-1} for DOC (Kritzberg 2017; Kritzberg et al. 2020). However, there is a risk that filtering might become less efficient, potentially causing higher concentrations of harmful substances (Kritzberg 2017; Kritzberg et al. 2020) in the water. Currently, 50% of drinking water comes from surface waters, which are directly affected by DOC (Kritzberg et al. 2020). Additionally, climate warming and human interference will lead to lowered groundwater levels and thus, more reliance on surface waters (Kritzberg et al. 2020). This might impact parts of the 25% of drinking water that is presently sourced from groundwater in Sweden (Svenskt Vatten 2019; Kritzberg et al. 2020).

Moreover, increasing DOC concentrations cause changes in the aquatic ecosystem (Kritzberg and Ekström 2012; Kritzberg 2017). Especially the impact of DOC on biogeochemistry in freshwater systems is highlighted (Schelker et al. 2012), with further implications for other water quality parameters (Oni et al. 2013). In freshwater systems, DOC concentrations directly control water acidity (Rosenqvist et al. 2010; Schelker et al. 2012). While the magnitude of acidification depends on the acid strength of the various compounds (Andersson et al. 2000), the pH was mainly observed to decrease with increasing DOC concentration in 66 long-term monitored lakes in Sweden (Kritzberg and Ekström 2012; Kritzberg 2017).

Further, the increase in DOC concentrations is linked to higher oxygen demands and depletion in the water (Guo et al. 2017). The degradation and utilization of more DOC by microorganisms requires more oxygen, accelerating the oxygen consumption in boreal freshwaters (Ågren et al. 2008; Carpenter 2008; Kellerman et al. 2014). As boreal soil organic matter has higher C:N ratios (Rowe et al. 2014), microbial consumption/degradation can only occur during longer water residence times (Solomon et al. 2015). Less microbial consumption translates into higher DOC concentrations leaching into the waters, as less carbon can be released in the form of gaseous CO_2 through soil respiration (Sobek et al. 2007).

The terrestrial addition of DOC to the water systems facilitates changes in aquatic biodiversity (Weyhenmeyer et al. 2014). In Toolik Lake and adjacent streams in Alaska, shifts

in community composition toward more DOC-consuming bacteria could be induced by increased DOC inputs, regardless of previous community characteristics (Judd et al. 2006). An increase in DOC resulted in a loss of biodiversity in the freshwaters (Judd et al. 2006; Weyhenmeyer et al. 2014).

In addition to the effects of increased DOC concentrations, other elements, such as metals and pollutants (Laudon et al. 2012), are transported by organic carbon particles into the water (Schelker et al. 2012; Oni et al. 2013; Kritzberg et al. 2020). This, in turn, affects the nutrient regimes of inland waters (Schelker et al. 2012; Weyhenmeyer et al. 2014), supplying more nutrients for aquatic organisms (Laudon et al. 2012; Kritzberg et al. 2020), thus causing algal bloom with subsequent oxygen depletion in the water (Carpenter 2008) and/or promoting both processing and production of organic matter in the freshwater (Kellerman et al. 2014).

While this input of nutrients might enhance primary production in the water at low DOC levels, higher DOC concentrations inhibit light penetration, therefore limiting productivity (Schindler and Scheuerell 2002; Kritzberg et al. 2020). This further causes loss of benthic (bottom) vegetation due to light-limited photosynthesis (Schindler and Scheuerell 2002; Cremona et al. 2016).

2.2 Total Organic Nitrogen (TON) and Dissolved Organic Nitrogen (DON)

Compared to DOC, there is less focus on dissolved organic nitrogen (DON) connected to increased DOM loading (Ahlgren 2018; Deininger et al. 2020). In contrast to more directly bioavailable inorganic nitrogen compounds (Carpenter 2008; Ahlgren 2018), such as ammonium (Stepanauskas et al. 2000), nitrate (Carpenter 2008; Solomon et al. 2015) and nitrite, not all DON components can be taken up by organisms (Berman and Bronk 2003; Berggren et al. 2015; Ahlgren 2018). While most consumption and utilization by microorganisms can occur directly, DON particles need to be degraded and subsequently mineralized into inorganic nitrogen compounds for consumption by bacteria and phytoplankton (Berman and Bronk 2003; Zhou et al. 2010; Berggren et al. 2015). DON has often been observed to be the dominant nitrogen fraction in freshwaters (>50%) (Berman and Bronk 2003; Rosenqvist et al. 2010). The related particulate fraction of nitrogen accounts for 5-10% of the total N pool (Berman and Bronk 2003; Rosenqvist et al. 2010). Therefore, properties of DON are assumed to apply to unfiltered Total Organic Nitrogen (TON) considered in this study. This is further justified, as DON constitutes the majority of both the total dissolved nitrogen (58-77%) and the total nitrogen (71%) pool (Stanley and Maxted 2008; Cazorla 2020).

DON can either be generated in-water (autochthonously), i.e., by submerged macrophytes and benthic algae in shallow streams, or DON can originate terrestrially (allochthonously) from both natural and anthropogenic sources (Berman and Bronk 2003; Cazorla 2020). Natural sources in the form of terrestrial leaching and runoff add mostly humic substances originating from plant detritus and soils into rivers and lakes, with comparably low N content (Berman and Bronk 2003; Cazorla 2020). Notably, DON from natural sources such as forests was found to contribute roughly 2% to the total dissolved nitrogen pool in rivers in the north-eastern US (Berman and Bronk 2003). Nitrogen from anthropogenic sources comprises a large part of the N-dynamics in freshwater systems and resulted in doubling nitrogen inputs to the terrestrial N cycle in the last 100 years, as compiled by a global literature study conducted by Berman and Bronk (2003). Through N-enrichment, soil chemical properties and fluxes from the soil can be significantly altered, with impacts on food web, litter composition and microbial community composition (Solomon et al. 2015; Hellsten et al. 2017). Especially the agricultural sector, with large-scale N_2-fixation in the soils (Carpenter 2008) and N-rich fertilizer (Solomon et al. 2015; Hellsten et al. 2017), contributes to the human-induced nitrogen input. It was found that DON increases linearly with ‘human-dominated cover’ (agriculture and urban areas) in 84 streams sampled across Wisconsin, US (Stanley and Maxted 2008). In industrial areas, smog containing

reactive N originating from fossil fuel combustion could add to the total aquatic N pool through precipitation (Berman and Bronk 2003; Carpenter 2008). While quantity and timescale of atmospheric N deposition are variable (Berman and Bronk 2003), an increase in N from atmospheric sources, as well as strong retention potential of volatile N, was observed in catchments across freshwater bodies in the boreal zone in the US, Canada and Europe between 1990 and 2004 (Monteith et al. 2007)

DON is further processed and utilized in freshwater environments (Berman and Bronk 2003). DON can be broken down or potentially modified by photochemical decomposition, which in turn provides more biologically available N compounds to riverine systems (Berman and Bronk 2003). Through abiotic adsorption, DON molecules are bound to the surface of other particles or colloids, thus being removed from further degradation (Berman and Bronk 2003). Direct uptake of certain (intermediate) DON parts, as well as a mixture of uptake and utilization, might occur rapidly by phytoplankton and bacterial communities, with bacterial uptake possibly having the largest impact on DON concentrations in the water (Berman and Bronk 2003). Yet, the magnitude and rates of utilization depend on the rather heterogeneous community compositions of phytoplankton and bacteria in the aquatic ecosystem (Berman and Bronk 2003). As certain DON components are taken up by algae, DON are commonly linked to eutrophication, expressed in algal bloom that further causes oxygen depletion in water systems (Berman and Bronk 2003; Carpenter 2008).

Both hydrosphere and atmosphere are affected by DON components (Berman and Bronk 2003; Carpenter 2008). An excess of N has acidifying effects on freshwater ecosystem (Berman and Bronk 2003), polluting waters and air and thus affecting health (Carpenter 2008). The increase in primary productivity through N fertilization might result in decreased biodiversity, both on land and in the water (Berman and Bronk 2003; Carpenter 2008). Water pollution and decreased aquatic biodiversity have far-reaching impacts, from headwaters and streams to coastal and marine ecosystems (Berman and Bronk 2003).

2.3 Carbon to Nitrogen ratio

The ratio of carbon to nitrogen (TOC:TON, also referred to as C:N in literature) shows the quality of organic matter in the freshwater (Berggren and Al-Kharusi 2020). While indicative of organic matter quality, there is a difference between TOC:TON ratio of total organic matter and the TOC:TON ratio of the bioavailable organic carbon and nitrogen (Berggren et al. 2015). The bioavailability of C and N is governed by microbial processing prior to organic matter export (Ågren et al. 2008; Laudon et al. 2011).

This ratio informs about the source of the organic matter, with low N contents, and thus higher TOC:TON values, indicating natural sources (TOC:TON > 15) (Kim et al. 2014; Berggren and Al-Kharusi 2020). Moreover, TOC:TON was linked to both aromaticity of the organic matter and its specific light absorption, with a larger ratio implying more stable, less degradable compounds resulting in darker water colour (Berggren and Al-Kharusi 2020). Terrestrially derived organic matter has less degradation and utilization potential (Sobek et al. 2007; Rowe et al. 2014; Solomon et al. 2015). Consequentially, more aromatic DOM compounds are transported from rivers into coastal and marine environments without further processing (Monteith et al. 2007; Nebbioso and Piccolo 2013), with detrimental consequences for e.g. the Baltic Sea (Naturvårdsverket 2020). The quality of organic matter has implications for CO_2 and oxygen dynamics in the water (Ågren et al. 2008; Lapierre et al. 2013). Due to lower bioavailability of DOC and subsequent degradation/utilization, the oxygen demand of microbes is lower, reflected in less oxygen depletion in the freshwater systems (Guo and Gifford 2002; Ågren et al. 2008; Berggren and Al-Kharusi 2020). Lower quality organic matter from plant sources inhibits degradation, which in turn reduces the release of CO_2 via outgassing (Lapierre et al. 2013; Berggren and Al-Kharusi 2020).

Conversely, organic matter with higher N values, and thus a lower TOC:TON ratio, is considered of better quality, referring to its higher biodegradability by microbial organisms (Berggren and Al-Kharusi 2020). This suggests enhanced degradation rates with higher CO_2 emissions through outgassing and faster oxygen depletion (Guo and Gifford 2002; Ågren et al. 2008; Berggren and Al-Kharusi 2020). Thus, lower quantities of aromatic compounds might coincide with clearer water (Lapierre et al. 2013). However, organic carbon concentrations and oxygen demand in the water showed an inverted relationship in central Europe, as shown by Berggren and Al-Kharusi (2020). This indicates lower relative reactivity of TOC, associated with less severe oxygen depletion and outgassing than expected from the measured TOC concentrations (Lapierre et al. 2013; Berggren and Al-Kharusi 2020).

TOC:TON might also reflect whether anthropogenic inputs are present in the catchment (Deininger et al. 2020), with agricultural areas releasing more N into the water (Berggren and Al-Kharusi 2020).

2.4 Controls on water quality

The export rates and magnitudes of both DOC and DON are controlled by a multitude of factors, with varying relative contributions and interactions (Skerlep et al. 2020).

2.4.1 Environmental factors

The enhancing effects of climate change (Oni et al. 2013; Dunn et al. 2015; Deininger et al. 2020) on primary productivity (Laudon et al. 2012; Kritzberg et al. 2020) are identified as key drivers of organic matter dynamics in boreal regions, as this directly affects soil organic matter properties (Rowe et al. 2014; Solomon et al. 2015) and the intricate linkage between decomposition rates (Kritzberg and Ekström 2012; Meyer-Jacob et al. 2015; Skerlep et al. 2020) and DOC (Andersson et al. 2000; Pregitzer et al. 2004) and DON production (Kellerman et al. 2014). This is expressed in temperature-related variables (Laudon et al. 2012; Rowe et al. 2014), such as growing degree days (number of days with temperature above 5°C) (Oni et al. 2013; Kritzberg 2017; Skerlep et al. 2020). Some studies further relate CO_2 fertilization to primary productivity in Scandinavia (Erlandsson et al. 2008; Kritzberg 2017), with related effects on water chemistry.

Additionally, hydrology directly controls transport (Laudon et al. 2012; Solomon et al. 2015) and production of organic matter (Kritzberg and Ekström 2012; Kritzberg 2017; Kritzberg et al. 2020). To detect this, relationships between water chemistry and hydrological parameters, such as precipitation (Kellerman et al. 2014), runoff patterns (Sobek et al. 2007; Solomon et al. 2015), discharge (Oni et al. 2013; Deininger et al. 2020) and groundwater flow variables (Laudon et al. 2012; Schelker et al. 2012; Meyer-Jacob et al. 2015) were established. Following modelled paths of global warming, these variables will change towards a more extreme hydrological cycle, with tremendous impacts on pollutant transport (Erlandsson et al. 2008; Rowe et al. 2014; Dunn et al. 2015).

Furthermore, significant inputs of sulphur to the atmosphere and subsequent emission reduction and recovery from soil acidification contributed to rising DOC levels in boreal freshwaters (Monteith et al. 2007; Kritzberg and Ekström 2012; Solomon et al. 2015). However, soils will eventually stabilize at pre-deposition acidity levels, and therefore no longer be influenced by acidification (Erlandsson et al. 2008; Solomon et al. 2015; Kritzberg et al. 2020).

2.4.2 Land cover change and water quality

Recent literature acknowledged the role of land cover and land cover changes on browning (Kritzberg 2017; Kritzberg et al. 2020; Skerlep et al. 2020). Despite mostly stable land coverage in later years (Kritzberg 2017), the browning trend in boreal freshwaters could be

partly attributed to anthropogenic land cover changes (Dunn et al. 2015; Skerlep et al. 2020), with changing land (Meyer-Jacob et al. 2015) and vegetation cover (Kritzberg et al. 2020) governing the export rates (Solomon et al. 2015) and magnitudes (Erlandsson et al. 2008) of organic matter from the soil into rivers.

In Sweden, the largest change in land cover forest is an increase in forests (afforestation) (Fuchs et al. 2015), with focus on heavy industrial forestry (Schelker et al. 2012) and losses in terms of agricultural areas (Skerlep et al. 2020). Since afforestation dynamics lead to an increase in organic matter in the soil (Guo and Gifford 2002), DOC properties and thus, browning of freshwaters, is influenced (Kritzberg 2017; Skerlep et al. 2020). Generally, wetlands export more recalcitrant DOC from shallow soil organic matter layers (Stepanauskas et al. 2000; Guo and Gifford 2002; Laudon et al. 2012). Due to a lower degradation potential (Ågren et al. 2008; Laudon et al. 2011; Oni et al. 2013), more unprocessed TOC is transported from wetlands into coastal areas (Nebbioso and Piccolo 2013).

The impact of agriculture on water chemistry is mainly associated with surface runoff, often containing high N concentrations (Cazorla 2020), further nutrients, such as P (Chen et al. 2016; Berggren and Al-Kharusi 2020) and other pollutants (Carpenter 2008). Exporting these components to freshwater systems presents a large nutrient input, causing eutrophication with detrimental consequences on biodiversity in freshwaters and coastal regions (Carpenter 2008; Cazorla 2020). However, the attribution of pollution to non-point sources, namely agriculture and urban areas, is complicated by the complexity of land cover feedback systems (Liegel et al. 1991; Giri and Qiu 2016; Ahlgren 2018). Especially in boreal catchments, anthropogenic influences are assumed to be comparably small (Berggren and Al-Kharusi 2020).

3 Methods

Spatial analysis was conducted in ArcMap 10.5.1 (ESRI, Redlands, California). Numerical analysis and statistical testing were carried out in Excel. The Real Statistics Resource Pack software (Release 7.2) (Zaiontz 2020) was used for more extensive statistical tests.

3.1 Study Site Description

This study was conducted on water monitoring sites located in Sweden, spanning between latitude 55.4° to 66.0° and longitude 13.6° to 22.0° (Fig. 1). The study locations were chosen in accordance with the available dataset retrieved from WaterBase by Cazorla (2020). Looking at multiple European countries with water monitoring data, Sweden had the largest spread of sites measuring both TOC and TON concentrations (Cazorla 2020). Additionally, initial analysis of the CORINE land cover information revealed that large areas changed land cover in Sweden, compared to the European average.

Three different climatic zones following primarily a latitudinal gradient cover the country of Sweden (Kritzberg and Ekström 2012). In the northern parts of Sweden, polar Tundra climate with little humidity is prevalent (Kritzberg and Ekström 2012). Mean annual temperature (MAT; reference period: 1961-1990) in these regions ranges between -3°C and 0°C, with colder temperatures towards the mountain range in the northwest (SMHI 2009a). While high mean annual precipitation values (MAP; reference period: 1961-1990) are measured along the mountains, less precipitation occurs in central northern and northeastern Sweden (between 500-700mm) (SMHI 2009b). Most of Sweden has a boreal climate corresponding to Dfc in the Köppen-Geiger climate classification (Kritzberg and Ekström 2012), with relatively mild MAT ranging from 0°C to 5°C (SMHI 2009a) and MAP between 600mm to 900mm (SMHI 2009b). Southern Sweden, on the other hand, has a warm temperate, humid climate more consistent with Dfb (Kritzberg and Ekström 2012), expressed in warmer temperatures (MAT between 5°C and 8°C) (SMHI 2009a). Precipitation patterns in the South are governed by westerly winds,

leading to MAP between 600mm along the east coast and up to 1200mm on the west coast (SMHI 2009b).

3.2 Analysis of land cover and land cover changes

Information about land cover and land cover changes in Sweden was deduced from the CORINE Land Cover (CLC) inventory datasets (Copernicus Programme 2020a, b, c, d, e). These raster layers were chosen for initial analysis of land cover in Europe (Table A1). After focusing on Sweden, the CLC images with land cover information for Sweden were retrieved for analysis, namely 2000 (Copernicus Programme 2020a), 2006 (Copernicus Programme 2020b) and 2012 (Copernicus Programme 2020c). The earlier CLC inventory (1990) had to be discarded due to a lack of data for Sweden. The CLC inventory provides detailed information about land cover in Europe, with 44 land cover classes describing areal features with a minimum mapping unit (MMU) of 25 ha or linear features with a width of 100m (Copernicus Programme 2020a). Change layers highlighting land cover change between the reference years with a smaller MMU (5 ha) were obtained to improve the thematic resolution of these Europe-wide layers (Copernicus Programme 2020d, e).

The CLC images had to be pre-processed before land cover could be analysed (Fig. A1). Both the land cover and the change layers were projected into the Swedish National Coordinate system SWEREF99. Then, the areal extent of Sweden was masked from the Europe-wide raster layers by using the DEM50m (Lantmäteriet 2020). This resulted in five raster layers depicting land cover and related changes in Sweden in 2000, 2006 and 2012. Further, these raster layers were reclassified based on literature, to collapse the 44 initial classes (Kosztra et al. 2019) into 9 broader land cover classes with relevance to TOC and TON release (Table 1). 9 of the 44 classes were not relevant to the Swedish context (212, 213, 221, 223, 241, 244, 334, 422, 423).

Table 1 Land cover reclassification based on CORINE identifiers (Kosztra et al. 2019), with overarching description and new identifier

Reclassified Identifier	Description	CORINE Identifier
1	Urban Areas	11X
		12X
		14X
2	Agriculture	21X
		22X
		24X
3	Forest	31X
		324
4	Grassland (natural)	321
		322
		323
5	Pasture (grazed)	23X
6	Wetlands	4XX
7	Mines	13X
8	Barren	33X
9	Water	5XX

The reclassified rasters were merged with the corresponding change layers to improve thematic accuracy, as the change layers have a lower MMU (5 ha) than the CLC layers (25 ha) (Fig. A1). This did not change spatial accuracy, as both CLC and change layers have the same geometric resolution (100m) (Table A1). This was done by erasing the areas in the CLC layer with the corresponding change layer and subsequently mosaicking these rasters together. As there are two land cover change layers for 2006, one belonging to the study period 2000-2006 (TO 2006) and one belonging to the study period 2006-2012 (FROM 2006) (Table A1), these layers were mosaicked together before merging with the CLC layers. When comparing to the unchanged CLC of the respective year data, 0.01%, or 3857 cells (2000), 0.02%, or 10498 cells (2006), and 0.03% 15337 cells (2012), of the image differed in (broad) land cover class.

Based on the processed CLC data, land cover in Sweden could be analyzed. The areal extent of the land cover classes was recorded for each study year. This informed about dominant land cover and enabled detection of large-scale changes in the classes. Over the whole study period, the number of land cover changes was obtained. Here, a cell would be considered if the broad land cover class differed from the previous study year. The layer resulting from the raster calculator tool showed the number of land cover changes, between 0 and 2 (Fuchs et al. 2015). With this information, ‘pristine areas’ and areas with multiple changes could be identified spatially.

Furthermore, directional land cover change was investigated (Fuchs et al. 2015). For all broad land cover classes, areal gains and losses, as well as the direction of the change, were recorded. By considering gross, or directional, changes in addition to net changes, dynamic

changes in land cover with implication for water chemistry could be detected more reliably (Fuchs et al. 2015).

3.3 Water quality data

Water quality data was retrieved from the European monitoring database WaterBase. This overarching database consists of six different databases, all maintained by the European Environmental Agency (EEA). Like Cazorla (2020), this study focuses on the 'WaterBase-Water Quality' database, which contains measurements from various national water monitoring programs, with varying timescales and methods. In the aggregated version (T_WISE4_AggregatedData), with over 3 million entries (Berggren and Al-Kharusi 2020; Cazorla 2020), annually averaged water quality parameters were collected.

In Sweden, water quality data is monitored by the Swedish university of Agricultural Sciences (SLU), together with the Swedish Environmental Protection Agency and the Swedish Agency for Marine and Water (Ahlgren 2018).

In WaterBase, standardized *TOC* data (in mg L^{-1}) is available from 1987 in Swedish freshwater systems. Since then, the measurement method for TOC changed three times, as shown by Ahlgren (2018). Since 2007, the base method following the Swedish standard SS 02 81 99 remained unchanged, using a Shimadzu TOC 500 with an ASI-502 test injector. In 1999, pre-treatment of the samples was changed, with the addition of hydrochloric acid to evaporate inorganic carbon and in 2004 another measurement instrument was introduced, the NDIR-detector (Ahlgren 2018). The latest changes in measurement method occurred in 2007. After pretreatment with hydrochloric acid, carbonic acid is removed from the sample by a catalyzer and further quantified (Ahlgren 2018). This is achieved with help of a Shimadzu TOC-VCPH, a THM-2 model and a sample changer (Ahlgren 2018).

For *TON* data (in mg L^{-1}) three measurement methods have been used in Sweden (Ahlgren, 2018) since 1987 (Wallman et al. 2009). Yet, DON and thus, TON, cannot be measured directly in the water sample (Sun et al. 2017). One method (Tot-N_sum) involves measuring Kjeldahl nitrogen together with the inorganic forms of nitrogen, nitrite, and nitrate (Wallman et al. 2009). From 1987 to 2006, spectrophotometry was used on previously potassium persulphate digested samples to determine total nitrogen in the freshwater (Tot-N_ps) (Wallman et al. 2009). This method was replaced by Tot-N_TNB, where the sample is catalytically oxidized to nitrogen oxides and further characterized by its emitted electromagnetic radiation, referred to as chemiluminescence (Wallman et al. 2009). The measurement data is homogenized by SLU before publishing, which is further indicated by a data quality identifier in WaterBase.

3.4 Site selection based on water data

The provided dataset contained 319 monitoring sites for Sweden with data for TOC from earliest 1987 to 2012 and/or TON data from 2002 to 2011.

To ensure inter-comparability in the water data, certain criteria had to be fulfilled.

1. The site needs to have data for both TOC and TON to enable calculation of the ratio between TOC and TON (TOC:TON).
2. The annual means of the site should be based on at least 10 observations per year (on average), to minimize the representation of seasonality in the data. While the spread of the data is not evident in the database, measurements at equal time intervals are assumed.
3. The measurement site should contain consecutive TON data for 10 years, to reflect the longest time series available and minimize the influence of missing years on analysis.
4. The location of the site should be known for further spatial analysis.
5. The measurement site should have TOC measurements starting in 1987, as this constitutes the earliest measurements.

These conditions yielded 44 study sites for deeper analysis.

3.5 Watershed Delineation

In accordance with Chen et al. (2016) drainage basins were created to combine land cover and water quality data. Based on the DEM_{50m}, the area of the catchment draining into the measuring point could be obtained, and further investigated regarding the land cover fractions and associated changes.

First, a depressionless DEM was created in ArcMap by filling the initial DEM (Lantmäteriet 2020) with the maximum sink depth (172.03m) (Fig. A2). This changed the minimum elevation value of the DEM from -57.31 m to -0.56 m. This standard practice minimizes errors in the catchment delineation due to artificial sinks in the DEM (Yan 2019). Without a depressionless DEM, cells with a lower value than surrounding cells that are not actual sinks might cause significantly different flow direction and flow accumulation calculations.

Based on the filled DEM, the watershed was delineated with hydrological tools. With the flow direction tool, the unidirectional flow of water could be recorded following the steepest down slope (D8 algorithm). This output was further used to calculate flow accumulation, a dimensionless value depicting the number of cells (area: 0.25 ha) that drain into the current one. Here, the maximum number of cells draining into one cell was 1146. To determine the associated catchments, the point locations of the previously determined 44 monitoring sites were used as pour points, as seen by Chen et al. (2016) (Fig. A2).

After visual evaluation, the snap distance within which the points could be moved toward DEM cells with high flow accumulation values was set to 750m (or 15 cells). The coordinates of most monitoring stations could thus be moved to cells with high flow accumulation within this radius. This ensures more reliable mapping of the catchments by reducing inaccuracies of the created catchments and potential uncertainties in the monitoring site locations. Then, the watershed tool produced the individual watersheds, which were further vectorized into simplified polygons (Fig. A2).

Subsequently, land cover was assessed on a catchment basis. Similar to Chen et al. (2016), the Zonal Histogram tool in ArcMap was used to obtain the areal extent of each land cover class as a fraction of the total catchment. In this study, distance from the stream was not considered in the land cover investigation. The analysis was conducted under the assumption that each cell in the watershed contributes equally to the measured water chemistry (Giri and Qiu 2016). Additionally, the dominating land cover class in the individual catchment was determined, seen in Cazorla (2020).

3.6 Statistical evaluation

As the Shapiro-Wilk test showed that the data only partly followed a normal distribution, non-parametric alternatives were chosen for all statistical analysis. It is noted that five TOC series, one TON series and seven TOC:TON ratios were not normally distributed and thus required non-parametric testing.

To detect temporal trends in the water data, non-parametric Man-Kendall rank correlations were calculated for the time series of TOC, TON and TOC:TON (Monteith et al. 2007; Björnerås et al. 2017; Kritzberg 2017). In accordance with literature, the Theil-Sen slope was calculated (with the Real Statistics using Excel Add-in) to characterise the magnitude and direction of temporal changes (Erlandsson et al. 2008; Björnerås et al. 2017; Skerlep et al. 2020). This non-parametric alternative calculating the slope as the median based on all pairwise slopes between the data (Erlandsson et al. 2008) was favored over linear regression (Kritzberg and Ekström 2012; Attermeyer et al. 2018) due to its robustness. In connection with that, annual change rates (in % yr^{-1}) were retrieved by dividing the significant Theil-Sen slope with the long-term median of the concentration measured at the related monitoring site (Björnerås et al. 2017;

Skerlep et al. 2020). Due to multiple comparisons and a related higher risk of the Type I error of falsely rejecting the null (no change) hypothesis, the significance level (two-tail, alpha) was adjusted by the number of comparisons (following the Bonferroni correction) to yield an overall significance level of 0.05 for the Man-Kendall test (Berggren and Al-Kharusi 2020).

The importance of physical factors, namely latitude and catchment size, on water chemistry was tested using the Spearman correlation. Here, latitude and catchment size were individually compared to absolute concentrations of TOC, TON and TOC:TON. Additionally, latitude and catchment size were inter-compared to detect potential spatial correlation between these two factors. This is done to reduce the effect of catchment size on the dilution, and thus concentration, of chemical parameters. Considering latitudinal distribution could visualize the influence of a differing climate (classification) on water chemistry. Similar considerations were made about catchment size and land cover change patterns.

To determine the influence of land cover change, non-parametric F-tests (Kruskal-Wallis tests) were performed for each land cover class. For this, the land cover classes were further combined, with the new class Combined Impervious, consisting of Urban (1), Mines (7) and Barren (8). This was done due to a similar extent of impervious areas (Giri and Qiu 2016) in these three classes, and the subsequent effects on hydrology (Chen et al. 2016). The land cover class Water was excluded from this land cover comparison, as seen in Cazorla (2020). Also, Pasture could not be included in further analysis due to mostly insignificant land cover changes in the watersheds (No Change: 43 sites; Major Increase: 1 site; Major Decrease: 0 sites). The previously calculated land cover changes for Sweden between 2000 and 2012 were the grouping criteria for the Theil-Sen slopes of the monitoring sites. If the land cover class in the watershed increased more than the Swedish average, or if there was any increase in an otherwise decreasing class, the site was considered to undergo a MAJOR INCREASE, and the Theil-Sen slope would be classed as such. If the land cover class decreased more strongly than the Swedish average in the case of a decreasing class, MAJOR DECREASE would be attributed to this site and its trend in water parameter. MAJOR DECREASE also contained trend data from sites that showed a decrease of the same strength as the increase on national level. Changes in between would be classed as NO CHANGE.

By choosing this categorization, the focus could be on monitoring sites with larger land cover changes, while minor changes potentially blurring signals could be excluded from the analysis This was achieved by focusing on changes larger than the average land cover change in Sweden in the respective class.

Subsequently, water chemistry trends at the sites were tested with the Kruskal-Wallis test for a significant difference between the groups NO CHANGE, MAJOR INCREASE and MAJOR DECREASE. A significant Kruskal-Wallis p-value would result in pairwise comparison using the Mann-Whitney U test, the non-parametric alternative to the t-test used in literature for water quality with different treatments (Kritzberg and Ekström 2012; Berggren and Al-Kharusi 2020).

4 Results

4.1 Land cover and land cover changes in Sweden

The areal extent of land cover, as well as total changes between 2000 and 2012, was obtained. It was found that 98.95% of the cells, and thus, of the land in Sweden, remained in the same broad land cover class through the whole study period (Fig. 1). Conversely, 1.00% of the area changed once, and 0.04% of the area changed twice within this 12-year period.

Overall, 1.02% of the total area in Sweden was affected by land cover change (Table 2). The most extensive land cover in Sweden was forest, expanding over 63% of the terrestrial area. However, forest decreased by 0.34% in the study period, which corresponded to an annual land cover change of 0.03%. On country level, the largest increases could be observed in the coverage of Pasture, 131 191 ha (0.28%) in 12 years.

Table 2 Areal extent of the broad land cover classes during the study period in ha and percentage of total terrestrial Sweden (total area: 46806875 ha), as well as total changes between 2000-2012

Land Cover	2000 (%)	2006 (%)	2012 (%)	Total Change (ha)	Total Change (%)
Urban	1.28%	1.32%	1.39%	51087	0.11%
Agriculture	7.89%	7.87%	7.96%	31486	0.07%
Forest	63.70%	63.64%	63.36%	-160575	-0.34%
Grassland	6.39%	6.39%	6.38%	-5087	-0.01%
Wetlands	0.58%	0.57%	0.56%	-5587	-0.01%
Pasture	6.23%	6.26%	6.51%	131191	0.28%
Mines	0.04%	0.06%	0.06%	9911	0.02%
Barren	2.58%	2.60%	2.61%	14537	0.03%
Water	11.30%	11.30%	11.16%	-66963	-0.14%
Total	100.00%	100.00%	100.00%		1.02%

Regarding land cover, spatial trends could be observed in Sweden (Fig.1). While forest was evenly spread in the country, agricultural areas were predominantly located in the southern part of the country. In the north, barren areas, as well as (natural) grasslands became more prevalent along the mountains. Urban Areas were barely visible, which complied with their extent (~1.3%) (Table 2).

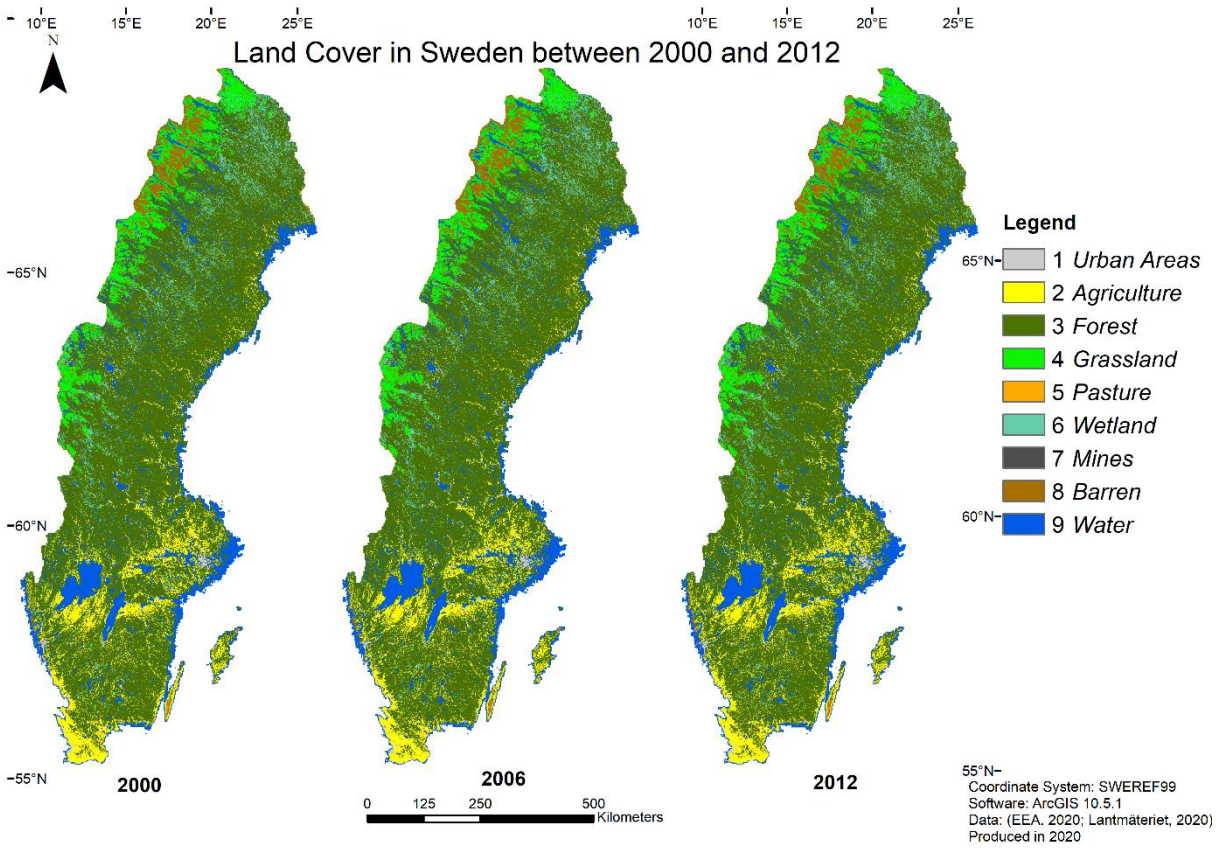


Figure 1 Merged land cover data for Sweden, reclassified based on CORINE data for the study years 2000 (EEA, 2020a, 2020d), 2006 (EEA, 2020b; 2020d; 2020e) and 2012(EEA, 2020c;2020e)

Additionally, directional land cover changes were considered (Table 3; Table 4). It was noted that the total areal change was four times higher between 2006 and 2012, with 400 782 ha of the surface changing. Afforestation was identified as the largest conversion between 2000 and 2006, with 24 463 ha of Sweden being transformed (Table 3). At the same time, 55 385 ha of forest were lost, the largest losses during that period. Between 2006 and 2012, afforestation accounted for a transformation of 91 214 ha (Table 4). From 2006 to 2012, the largest areal losses (220 867 ha) occurred for forested areas (Table 4). In general, the areal losses of forest accounted for more than double the areal gain between 2000 and 2012.

Table 3 Directional land cover changes for the time period between 2000 and 2006 in ha, depicting the initial land cover class in 2000 and the area that transformed into the respective other land cover classes in 2006.

		T	O	2006	(ha)						
		Urban	Agriculture	Forest	Grassland	Wetland	Pasture	Mine	Barren	Water	Total
F	Urban		330	912	0	53	3	326	71	44	1739
R	Agriculture	7374		15342	0	2483	193	1862	101	644	27999
O	Forest	8734	14923		471	721	16964	6329	3360	3883	55385
M	Grassland	0	0	1454		0	737	4	3963	284	6442
	Wetland	1361	3134	331	0		1	252	60	25	5164
2	Pasture	68	68	3048	138	48		268	62	242	3942
0	Mine	1702	130	100	1	34	0		0	0	1967
0	Barren	107	0	217	1038	60	87	78		117	1704
0	Water	176	98	3059	398	76	1388	0	268		5463
(ha)	Total	19522	18683	24463	2046	3475	19373	9119	7885	5239	109805

Both Urban areas and Pastures showed large net gains from 2000 to 2006, expanding by 19 522 ha and 19 373 ha, respectively (Table 3). In 2012, further 54 514 ha were converted to Urban areas, while the largest areal gains were noted for Pastures (127 091 ha) (Table 4).

Agricultural land predominantly decreased (-27999 ha) between 2000 and 2006 (Table3). Conversely, areal increase was dominating in the later study period, with 76 449 ha changing to agricultural land (Table 4).

Table 4 Directional land cover changes for the time period between 2006 and 20012 in ha, depicting the initial land cover class in 2006 and the area that transformed into the respective other land cover classes in 2012.

		T	O	2012	(ha)						
		Urban	Agriculture	Forest	Grassland	Wetland	Pasture	Mine	Barren	Water	Total
F	Urban		9116	11065	25	386	30	343	0	245	21210
R	Agriculture	19762		10651	42	1683	923	1255	248	1083	35647
O	Forest	28364	58569		2444	3119	103621	7226	6755	10769	220867
M	Grassland	230	52	4221		141	1013	29	1230	546	7462
	Wetland	2262	3613	1190	0		446	63	2627	172	10373
2	Pasture	169	265	6059	194	43	0	376	280	3945	11331
0	Mine	2786	444	3370	10	34	10		0	37	6691
0	Barren	177	356	1216	1158	19	58	69		306	3359
6	Water	764	4034	53442	2898	1050	20990	89	575		83842
(ha)	Total	54514	76449	91214	6771	6475	127091	9450	11715	17103	400782

4.2 Analysis of the watersheds

4.2.1 Trends in water chemistry at the monitoring sites

At the study sites, TOC concentrations in the range between 2.4 and 29.4 mg L^{-1} were measured, with an average TOC concentration (Mean ± Standard Deviation) of 8.74 ± 4.00 mg L^{-1}. For TON, the annual average concentrations ranged between 0.105 and 1.392 mg L^{-1} and averaged at 0.47 ± 0.28 mg L^{-1}. The annually averaged C:N ratio varied from 6.01 to 43.41, with a mean ratio of 22.71 ± 7.95.

Both TOC and TON exhibited higher chemical concentrations in the southern half of the country (Fig. 2a; b). Yet, the ratio TOC:TON did not show this gradient (Fig. 2c). Here, the lowest C:N ratios were found in the South, while the largest C:N values were located in the central South. To test these relationships, non-parametric Spearman correlation coefficients between chemical parameters, catchment size and latitude were calculated. While TOC showed no significant relationship to catchment size (rho=0.05; p-value=0.72), a negative correlation between TOC and latitude could be found (rho=-0.34; p-value=0.023). On the other hand, TON showed a significant negative correlation for both catchment size (rho=-0.34; p-value=0.025) and latitude (rho=-0.70; p-value<0.001). The ratio TOC:TON appeared to be positively related to catchment size (rho=0.46; p-value=0.0015) as well as latitude (rho=0.69; p-value<0.001).

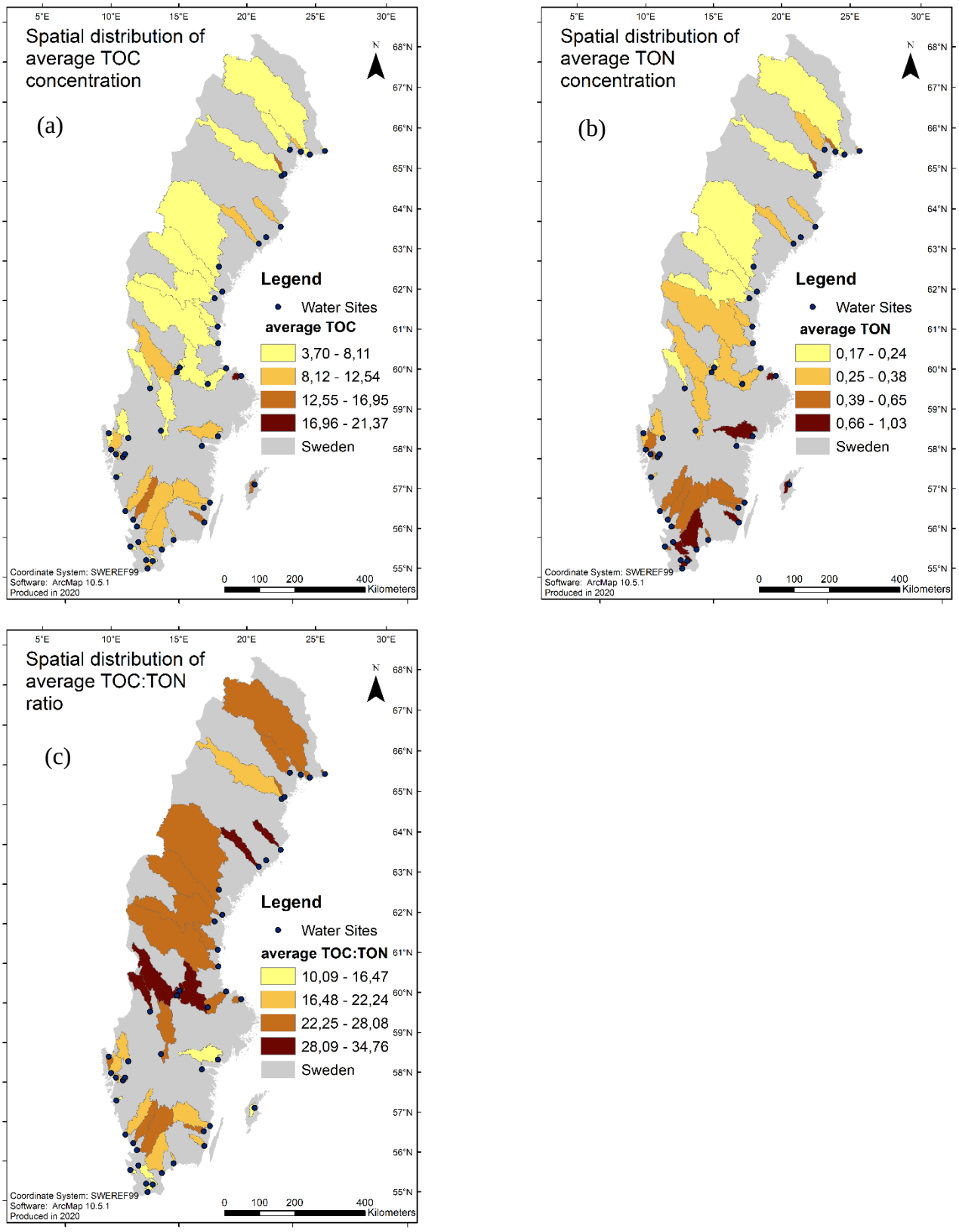


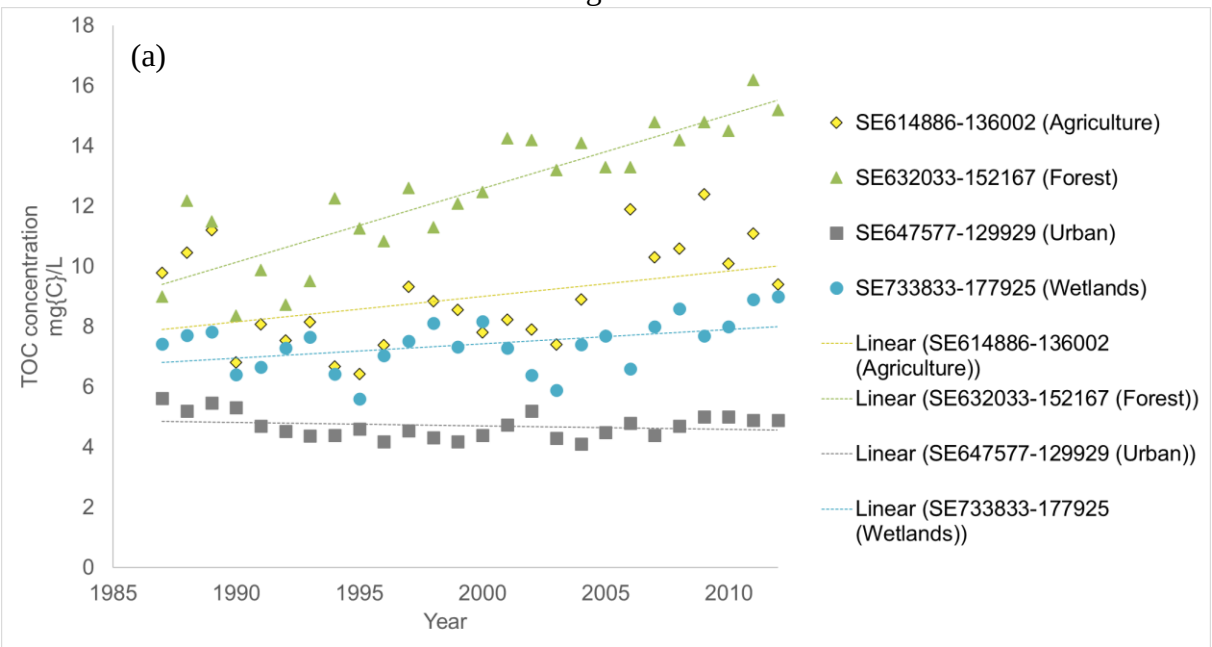
Figure 2 Spatial distribution of the 44 water monitoring sites and the associated, delineated catchments, with (a) the mean TOC concentration in each watershed (in mg L^{-1}); (b) the mean TON concentration in each watershed (in mg L^{-1}); and (c) the mean TOC:TON ratio in each watershed

4.2.2 Trends in land cover in the catchments

After site selection and delineation, 44 monitoring sites with associated watersheds were investigated. The watersheds had a mean size of 36 338 ha, with the largest watershed being 2 911 865 ha (WaterBase identifier: SE70773-157350). The smallest watershed had a size of 198 ha (SE649673-151838). Further, catchment size distribution was considered: the ten largest catchments varied from 504 137 ha to 2 911 865 ha, while the ten smallest catchments extended between 198 ha and 21 882 ha (Table A2). Considering the geographical location of the monitoring stations, a latitudinal range between 55° and 66° was covered, with 29 sites located in the South (up until 60° latitude). In the catchments, 14.0% of the area changed land cover once, and 1.3% experienced land cover change twice during the study period.

Regarding land cover in these catchments, forests were dominating 37 of the 44 sites (Fig. A3; A4; A5). Further five sites were classed as agricultural. It was noted that urban areas and pasture were dominant in one watershed each, SE647577-129929 and SE649673-151838, respectively. In general, the largest land cover changes in the catchments occurred in forested areas, with least of the changes in grassland areas. (Fig. A3; A5). Contrary to nation-wide land cover change trends, pasture coverage remained stable in the catchments.

The most prevalent land cover was forest, covering on average 65.8% of each catchment. The most extensive forest cover (~89.2%) was found in the catchment at monitoring site SE632033-152167 (Fig. 3a). This river exhibited both the largest absolute TOC values and the strongest increase between 1987 and 2012. Absolute TON concentrations were generally highest at the agriculturally dominated (~89.2%) station SE614886-136002 (Fig. 3b). Moreover, this site recorded the strongest decrease in TON concentrations between 2002 and 2011. The lowest absolute concentrations of both TOC and TON were found in the catchment SE647577-129929, which was surrounded by urban areas (between 47.8% and 50.1%) (Fig. 3a; b). The catchment with most wetlands (~26.4%) detected the highest absolute C:N ratios, and thus the lowest quality of organic matter (Fig. 3c). Organic matter quality was observed to increase the most in both the wetland and the agricultural site.



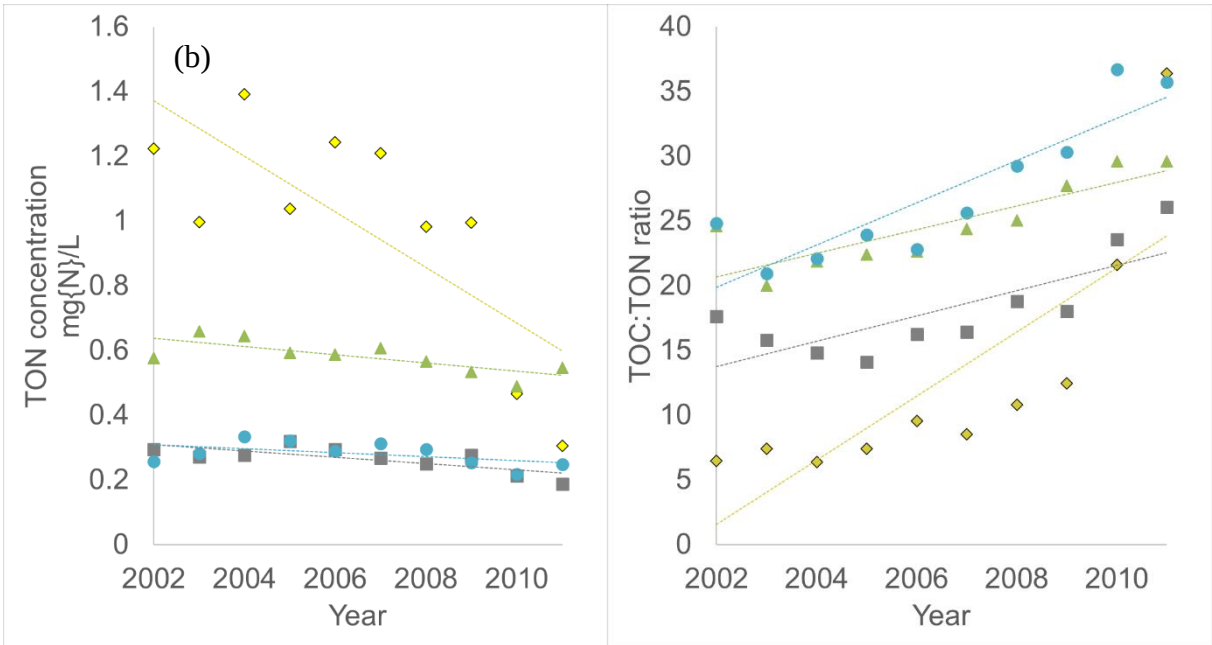
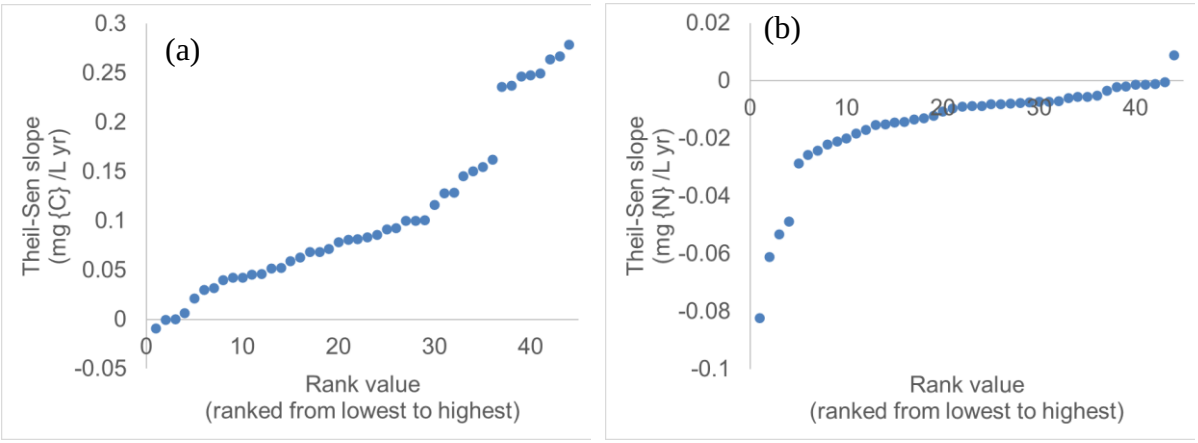


Figure 3 Exemplary depiction of temporal trends of absolute water chemistry values at 4 sites which have the largest coverage of the respective land cover class (Agriculture, Forest, Urban, Wetlands); showing data points and linear trendlines for (a) the TOC concentrations between 1987-2012; (b) the TON concentration between 2002-2011; and (c) the TOC:TON ratios between 2002-2011.

4.3 Temporal analysis of water quality

Further, water quality data was statistically analyzed to detect temporal trends. A positive trend was found for TOC in 25 of the 44 sites, and 12 of these 25 had a p-value below the Bonferroni-corrected significance level of 0.0006 (Table A3). Only one site showed a (statistically not significant) negative Theil-Sen slope for TOC (Fig. 4a). The remaining 19 sites showed no significant p-value for the Man-Kendall trend test. Taking these 25 sites with significant TOC trends into account, concentrations changed between 0.043 and 0.267 mg L^{-1} y^{-1}, which corresponded to relative change rates from 0.78% to 2.15% (Mean: 1.41% ± 0.48%). Considering all 44 sites, organic C measurements derived from the WaterBase data varied between 2.4 and 29.4 mg L^{-1} (Mean: 8.74 ± 4.00 mg L^{-1}). This translated into annual change rates between -0.19% and 2.15% (Mean: 1.10% yr^{-1} ± 0.59% yr^{-1}).



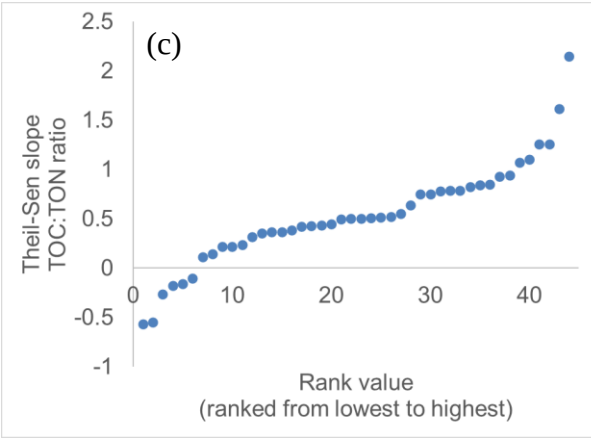


Figure 4 Visual presentation of the distribution of changes in water quality parameters by ranking of the Theil-Sen slopes from lowest (Rank=1) to highest (Rank=44) for (a) annual TOC data (1987-2012); (b) annual TON data (2002-2011) and (c) TOC:TON data (2002-2011).

For TON, 9 of the 44 sites showed a significant trend, with predominantly negative Theil-Sen slopes (Fig. 4b; Table A3). The TON trends observed at monitoring Site SE646771-129330 were significant after Bonferroni-correction. In terms of concentrations, the annual average TON value aggregated by WaterBase ranged between 0.105 and 1.392 mg L^{-1} and averaged at 0.47 ± 0.28 mg L^{-1}. Between 2002 and 2011, annual TON concentrations decreased by -2.83% ± 1.86%, from -8.09% yr^{-1} to 0.99% yr^{-1}. Focusing on the 9 sites exhibiting significant temporal patterns, annual TON values continuously changed by -4.53% ± 2.01%, with annual decreases varying between -8.09% to -2.43%.

There was a clear positive trend in the TOC:TON data, with 37 of the 44 sites having a significant p-value at alpha, and 5 of these after adjusting the significance level (Fig. 4c; Table A3). Generally, organic matter in the rivers had a TOC:TON ratio of 22.71 ± 7.95, with a minimum of 6.01 and a maximum ratio of 43.41. This corresponded to a relative annual increase of 2.82% ± 2.69%. However, the range of TOC:TON across all sites stretched from decreases of -1.94% yr^{-1} to increases of 13.91% yr^{-1}. At the 37 sites with significant Man-Kendall trend p-value, only positive annual change rates were recorded. The TOC:TON ratio informing about organic matter quality increased by 3.51% ± 2.32% yr^{-1} (from 0.86% to 13.91% yr^{-1}).

Furthermore, three sites without any significant trends could be identified (SE672117-145779, SE683661-156793 and SE732407-183604).

4.4 Land cover and water quality trends

The comparison of land cover and water quality parameters showed the influence of land cover change on water quality parameters. Here, it could be seen that only two changes in land covers led to differences in slopes (Table 5). However, none of the p-values were significant after bonferroni-correction ($p_{bonferroni\text{-}corrected}$=0.003) (Table 5). It was found that temporal trends in TOC differed depending on changes in agricultural extent (p=0.009). The slopes of TON showed significant differences based on urbanization (p=0.011). Forest dynamics did not yield significantly different slope-values. Also, temporal trends in water quality seemed to be unaffected by wetland changes. The TOC:TON ratio development exhibited no connection to land cover changes, signified in p-values between 0.097 and 0.521.

*Table 5 P-values of the Kruskal-Wallis test where the Theil-Sen slope values were grouped based on changes in land cover in the 44 catchments. Significant p-values (two-tailed, 0.05) are indicated by **

	TOC p-value	TON p-value	TOC:TON p-value
Combined Impervious	0.489	0.011*	0.521
Agriculture	0.009*	0.089	0.489
Forest	0.453	0.650	0.978
Grassland	0.405	0.087	0.192
Wetlands	0.612	0.153	0.097

Further inter-comparison between the three treatment groups No Change (NC), Major Decrease (MD) and Major Increase (MI) was conducted if significant differences could be detected via the Kruskal-Wallis test. The resulting Mann-Whitney U test showed which type of treatment could lead to differences in water chemistry at the monitoring sites.

Generally, the Theil-Sen slopes of the retrieved TOC:TON ratios seemed uncoupled from land cover changes, even after pairwise Man-Whitney U testing (Table A4; A5; A6).

A connection between urban areas and N-leakage could be found (Table 5). In the catchments, urbanization was associated with a larger decrease in TON concentrations, signified by a more negative Theil-Sen slope, than in constant areas ($Median_{MI}$=-0.015; $Median_{NC}$=-0.007; p_{NC-MI}=0.001) (Fig. 3). No difference in TON slopes could be recorded between other directional changes of the urban land cover class (p_{MI-MD}=0.223; p_{NC-MD}=0.157) (Table A5). Urbanization could not be linked to changes in TOC or TOC:TON trends (Table A4; A6). There were distinct differences in combined impervious changes in combination with catchment size distribution, with No Change occurring predominantly in small catchments. Six of the largest catchments (>504 000 ha) recorded an increase in impervious land cover (Table A2).

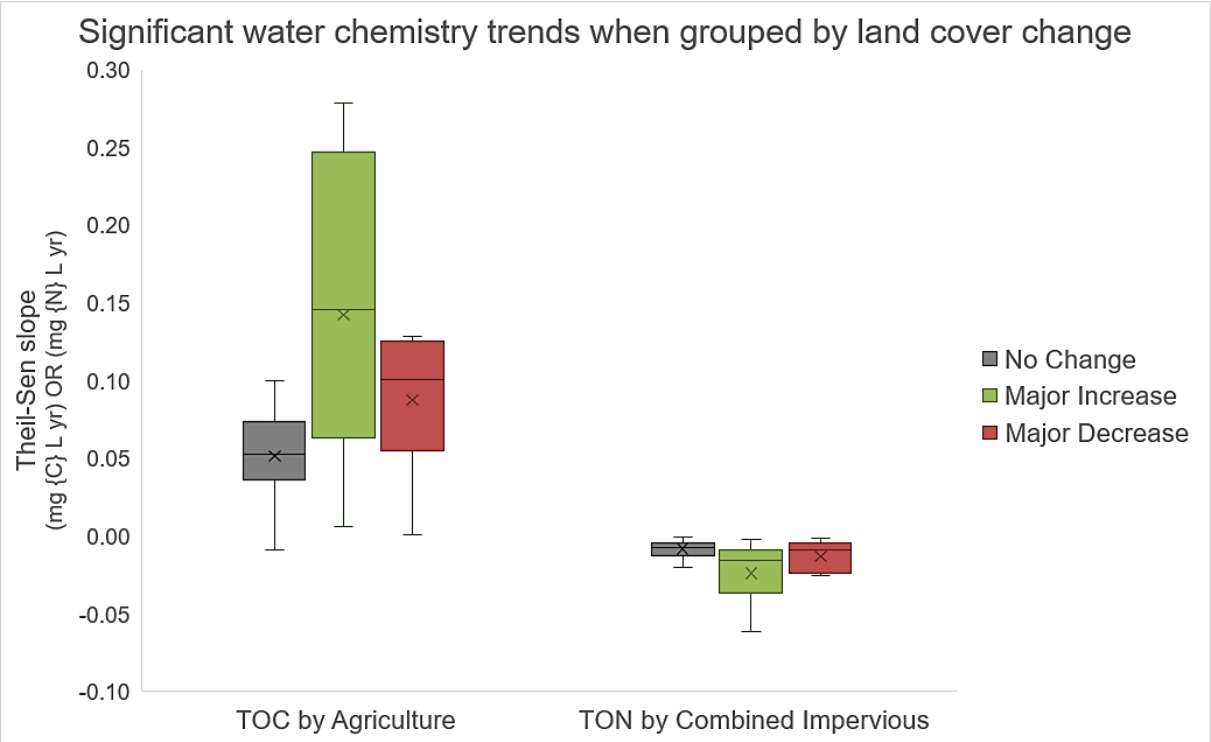


Figure 3 Boxplot showing the significant (alpha=0.05) groupings of the Kruskal-Wallis test with box as 25th and 75th percentile, centre line as median, x marker as mean, top and bottom of whiskers as maximum and minimum value and individual points as outliers; on the left, Theil-Sen slopes (in mg C L^{-1}) of absolute TOC concentrations were grouped by changes in Agriculture between 2000-2012; on the right, Theil-Sen slopes (in mg N L^{-1}) of absolute TON concentrations were grouped by changes in Combined Impervious (combination of the land cover classes urban areas, mines and barren)

While the differences in TOC concentration between the treatments Major Increase and Major Decrease in agricultural areas showed no significance (p_{MI-MD}=0.137), a comparison with catchments having constant agricultural coverage yielded significant results (p_{NC-MI}=0.002; p_{NC-MD}=0.015) (Table A4). Catchments with increasing agriculture observed stronger trends in TOC increase ($Median_{NC}$=0.053; $Median_{MI}$=0.145) (Fig. 3). In agricultural areas, the Kruskal-Wallis test results implied that no agricultural treatment group influenced the slope for TON (p=0.089) (Table 5). However, inter-comparison with the Man-Whitney U test revealed that TON trends in decreasing agricultural coverage marginally differed from the other two groups (p_{MI-MD}=0.030; p_{NC-MD}=0.045), with Major Decrease showing a more negative trend ($Median_{NC}$= -0.007 > $Median_{MD}$=-0.033) (Table A5). It was seen that catchment size influenced the grouping by agricultural changes (Table A2). Agricultural expansion dominated in the largest sites (6 of 10), and in the two smallest catchments. Most of the smaller catchments (5 of 10) experienced no change in agricultural extent.

In forested areas, the comparably high p-values derived from the Kruskal-Wallis test indicated no difference between the treatment groups (Table 5). This was further supported by p-values from the Man-Whitney U tests (Table A4; A5; A6). Hence, no effect of forest cover change on temporal trends in water chemistry could be detected. Further looking at the catchment size distribution in the groups, the largest group Major Decrease (n=25) contained most of the largest (6 of 10) and the smallest (7 of 10) catchments (Table A2). However, the two largest catchments (SE733351-187900, SE617263-135608) had an increase in forest.

Grassland dynamics could not be connected to developments in water chemistry by the Kruskal-Wallis test (Table 5). The lower p-value for differences in TON slopes between the three treatment groups could entail a weak albeit not significant relationship between certain land cover changes (Table 5). Such weak relationships were found between increasing and

constant grassland coverage (p_{NC-MI}=0.060) as well as decreasing and constant grassland coverage (p_{NC-MD}=0.053). Due to large differences in sample sizes, all of the largest catchments and most of the smaller catchments (7 of 10) belonged to group No Change (n=38). Decreasing grassland coverage affected two of three catchments (n=3).

The lack of significant p-values from the Kruskal-Wallis test suggests that changes in wetland coverage did not affect any of the investigated aspects of water chemistry (Table 5). Yet, subsequent Man-Whitney U tests showed a minor difference in C:N slopes between constant and decreasing wetland extent (p_{NC-MD}=0.044) (Table A6). Catchments characterized by a decrease in Wetland areas had stronger C:N developments than catchments with constant Wetland coverage ($Median_{MD}$=1.468; $Median_{NC}$=0.379) (Table A5). Increasing wetland coverage led to TON trends that were nearly statistically significant ($p=0.055 > p_{significant}=0.05$). Here, catchments with an increase in wetland area exhibited a weaker decrease in TON ($Median_{NC}$=-0.016; $Median_{MI}$=-0.008) (Table A5). The catchment size comparison showed that unequal sample sizes influenced land cover grouping. Therefore, most of the (6 of 10 for the largest; 9 of 10 for the smallest) sites could be found in the group with increasing wetlands.

5 Discussion

Overall, the proposed hypotheses are partly supported by the findings in this study. The water data exhibited clear temporal trends. Despite relatively stable land cover in Sweden, relationships between water chemistry trends and land cover changes could be detected in the catchments. The following section will interpret causes and implications of these findings.

5.1 Temporal trends in water quality

In agreement with the first hypothesis, the findings indicate that TOC concentrations increased since 1987. This trend of increasing TOC concentrations further aligns with literature (Kritzberg and Ekström 2012; Weyhenmeyer et al. 2014; Björnerås et al. 2017; Ahlgren 2018; Berggren and Al-Kharusi 2020; Cazorla 2020; Deininger et al. 2020; Skerlep et al. 2020).

It appears that the absolute concentrations retrieved from WaterBase follow general trends for Swedish running waters, as shown through median values between 2.6 and 16.8 mg L^{-1} by Ahlgren (2018), respectively 2.7 to 24.2 mg L^{-1} by Attermeyer et al. (2018). In the highly studied Svartberget catchment, average DOC concentrations revolved around 24.3 mg L^{-1} (Oni et al. 2013). A similar spread of concentrations (3.0 to 23.8 mg L^{-1}) was observed for lakes in Sweden (Attermeyer et al. 2018). Despite a larger range (0.1-332 mg L^{-1}), TOC loads in rivers and streams correspond to average global lake DOC concentration of 7.58 ± 0.19 mg L^{-1}, based on a study of 7 500 lakes from Sobek et al. (2007). Considering annual changes in organic C, the rates based on the Theil-Sen slopes (Mean: 1.41% ± 0.48%) line up with the relative increases of DOC presented in literature, which range from 1.1% yr^{-1} (Berggren and Al-Kharusi 2020; Skerlep et al. 2020) to nearly 1.6% yr^{-1} (Björnerås et al. 2017; Kritzberg 2017). It is noted, however, that these DOC trends were derived from different base conditions, such as study location and time. Both Kritzberg (2017) and Skerlep et al. (2020) investigated nearly 80 years of organic C data from water bodies located in southern Sweden, namely lakes around the Aneboda Field station and the Lyckeby river respectively. The study by Björnerås et al. (2017) presents organic C data ranging from 1990 to 2013, focusing on 315 freshwater bodies in northern Europe (90 in Sweden) and North America. The analysis of WaterBase data for central Europe by Berggren and Al-Kharusi (2020) does not include Sweden. Nevertheless, the detected organic C trends align with values found for Swedish freshwaters in this study.

According to Erlandsson et al. (2008), less annual TOC change was detected in large catchments in Sweden (210-26800 km^2), showing a median annual increase of 0.27%. In the context of this study, especially catchment size needs to be discussed, as 35 catchments could be considered ‘large’ (218-29000 km^2). The observed spatial gradients in concentrations might

rather be influenced by catchment size than by latitude. Due to longer water residence times in larger catchments, more TOC could be degraded along the river (Skerlep et al. 2020), resulting in lower TOC concentrations at the monitoring site. Similarly, nutrients and organic compounds have a higher potential of being sedimented and mineralized in larger watersheds, thus disappearing from the water column (Kritzberg et al. 2020). Therefore, absolute concentrations at the monitoring sites might be skewed by the catchment size. The N-S gradient observed in the data rather reflects catchment size distribution in Sweden, with northern catchments having a larger area and thus lower absolute TOC and TON concentrations and larger areas. This was further supported by correlation between catchment size and latitude (rho=0.32; p-value=0.035).

Similar assumptions can be made about the connection between catchment size and land cover changes, due to a discrepancy between the significance of land cover changes in the catchments (Table A2). While larger catchments showed changes in more classes between 2000 and 2012, the relative magnitude of change (in % of the catchment area) was lower than in average-sized watersheds. This trend is seen in most of the land cover classes (Agriculture, Forest, Combined Impervious) but less distinctly in Wetland changes. In the selected catchments, smaller watersheds (< 7128 ha) recorded little to no change in the land cover classes. Though, trends in the form of annual change rates reduce the bias of varying catchment sizes and allow intercomparison of both water chemistry trends and land cover changes.

Conversely, this dataset presented generally decreasing TON concentrations in Swedish freshwaters. While this agrees with findings from WaterBase by Cazorla (2020), boreal regions have been predominantly reporting rising organic N concentrations, with an annual increase of 2.11% yr^{-1} in Norwegian rivers (Deininger et al. 2020) and increases between 0.01% to 2.20% yr^{-1} in Swedish rivers (Ahlgren 2018). At the 44 selected monitoring sites in Sweden, N concentrations changed by -2.83% yr^{-1}, which aligns with observations of total nitrogen decrease rates in central Europe by Berggren and Al-Kharusi (2020).

Notably, average TON concentrations in this study are lower than reported from WaterBase data, with averages for central Europe between 1.18 and 1.21 mg L^{-1} (Cazorla 2020), respectively averaging at 2.2 mg L^{-1} (Berggren and Al-Kharusi 2020). Yet, the observed TON values are within the range of median TON retrieved directly from Swedish authorities (0.12 to 0.87 mg L^{-1}) (Ahlgren 2018). Due to an overall lack of anthropogenic N inputs in Sweden (Berggren and Al-Kharusi 2020), there is a greater dependency of plants on efficient soil nutrient cycling as the major N source. Simultaneously, global warming and the subsequent acceleration of growth might result in stronger N retention and utilization by trees (Erlandsson et al. 2008; Fröberg et al. 2011). Hence, decreasing TON concentrations in the water might be caused by increasing N demands of plants, as well as higher consumption rates by microbial organisms. In WaterBase studies focused on central Europe, anthropogenic N addition through agriculture plays a larger role (Berggren and Al-Kharusi 2020; Cazorla 2020) than in Sweden, which might cause the differences in absolute values.

As opposed to Ahlgren (2018) and Deininger et al. (2020), TOC:TON ratios were observed to be increasing in Swedish freshwater systems. The disparity between rising TOC concentrations and decreasing TOC concentrations resulted in an annual increase in TOC:TON ratio by 2.82%, ranging from -1.94% to 13.91% yr^{-1} in the individual catchments. This stands in contrast to C:N ratios declining by 1.09% yr^{-1} in Norwegian rivers (Deininger et al. 2020). The quality of organic matter in the water was decreasing between 2002 and 2011, expressed in a higher average TOC:TON ratio (22.71 ± 7.95). This value is remarkably higher than boreal C:N ratios recorded by Attermeyer et al. (2018) in catchments in central and northern Sweden, ranging between 4.6 to 13.6. Compared to larger-scale studies, TOC:TON ratios detected here exceed the average C:N ratio of 17.09 retrieved for Europe via WaterBase (Cazorla 2020). The overall high C:N values in the monitoring sites could partly be explained by stream morphology

(Cazorla 2020), as sites in WaterBase generally conduct measurements on smaller streams closer to the headwaters, carrying higher carbon loads than the rivers in Norway (Deininger et al. 2020) or Sweden (Attermeyer et al. 2018). As these sites tend to be less affected by human activities, N fluxes from the soil are comparably low. Therefore, total organic matter in the waters is characterized by low quality with poor degradation potential, expressed in higher values.

5.2 How does urbanization affect water quality changes?

In compliance with the second hypothesis, differences in TON slopes could be found between directional urbanization. Catchments with increasing urban or impervious areas showed a significantly stronger decrease in TON than catchments with constant or decreasing impervious coverage.

This might reflect efforts to reduce eutrophication originating in urban areas. Especially industrial areas and wastewater treatment plants function as point sources of N (European Environment Agency 2018), with industry contributing 5% and treatment of municipal and individual wastewater contributing ~27% to the total anthropogenic N release in Sweden (Carpenter 2008; Naturvårdsverket 2014; Chen et al. 2016). The proposed findings suggest, however, that newly built urban areas do not coincide with more TON release. As concluded by Cazorla (2020), decreasing TON concentrations in urban areas might be related to stricter regulations regarding treatment of private and industrial wastewater (European Environment Agency 2018). This is further supported by a decrease in N export from urban sources since 1995, as observed by the Swedish environmental protection agency (Naturvårdsverket 2014). It was found that urbanization occurred at the expense of forests, agriculture, and wetlands in Sweden. Conversion from land covers with higher N accumulation and export to more impervious surfaces leads to less TON transport into rivers. This corresponds to the observed more negative TON trends in catchments with a net urban gain. Thus, improved wastewater treatment and regulations might explain the connection between urbanization and a stronger decrease in TON concentrations (Naturvårdsverket 2014; European Environment Agency 2018).

Contrastingly, no relationship could be detected between TOC slopes and impervious expansion. This finding might be related to the focus of mitigation measures. On both EU and national level, the release and export of N and P from anthropogenic structures is regulated to reduce eutrophication (European Environment Agency 2018; Naturvårdsverket 2020). However, there are no similar regulations for organic carbon in urban wastewater. This might be reflected in the lack of trend between urbanisation and TOC trends. Generally, urban catchments were characterized by comparably high concentrations of more stable and less degradable (aromatic) TOC (European Environment Agency 2018; Berggren and Al-Kharusi 2020).

The increase in TOC:TON ratio across Sweden could not be attributed to impervious area changes. This complies with findings that determined the influence of urban areas on organic matter quality and thus, bioreactivity being low in boreal regions such as Sweden (Berggren and Al-Kharusi 2020), potentially due to the low spatial extent (~1.3% of Sweden).

5.3 What are the effects of forest changes on water quality development?

In contrast to prominent literature findings (Rosenqvist et al. 2010; Björnerås et al. 2017; Kritzberg et al. 2020; Skerlep et al. 2020), this study found no relationship between changes in TOC and forest dynamics. Increasing forest cover could not be determined to predict TOC trends, as shown by Weyhenmeyer et al. (2014) and Kritzberg (2017). Hence, the third hypothesis is not supported.

This might be connected to the timescales of TOC release and land cover changes. As found by Skerlep et al. (2020), DOC concentration changes caused by afforestation along the Lyckeby river were recorded with a lag time of around 40 years. During this period, the organic horizon was generated through a built-up of organic matter in the soil (Rosenqvist et al. 2010; Kritzberg 2017). This implies that trends observed in the current dataset could be associated with land cover changes occurring from the 1950s and not within the time period based on CORINE data (2000-2012). The overall increasing TOC concentrations across the catchments might be a result of afforestation efforts in Sweden since the 1970s (Rosenqvist et al. 2010). As land cover was rather stable between 2000 and 2012 (Kritzberg 2017), the signals between land cover changes and water chemistry development might be weak and less detectable.

Generally, Swedish forests accumulate large amounts of soil organic matter (Rosenqvist et al. 2010; Björnerås et al. 2017; Skerlep et al. 2020), with conversion to forest increasing soil carbon by 18% (industrial forest) to 53% (forest developing on abandoned land without interference) (Guo and Gifford 2002). Especially coniferous forests, such as Spruce (*Picea abies*), are characterized by a thick organic soil horizon, formed through podzolization processes (Rosenqvist et al. 2010; Weyhenmeyer et al. 2014). A positive relationship between organic layer thickness and TOC export was established in such podzols (Andersson et al. 2000). While afforestation with focus on coniferous forests also had some TOC export-inhibiting effects on soil properties (Rosenqvist et al. 2010), this soil acidification was counteracted by liming, which raised soil pH again and increased organic matter solubility and transport into freshwaters (Andersson et al. 2000). Thus, the relationship between TOC trends and land cover changes might be constrained by the temporal extent of the data rather than a lack of actual linkages.

Further, literature suggests that deforestation is a major disturbance to the ecosystem (Schelker et al. 2012; Kritzberg 2017). As observed by Guo and Gifford (2002), the conversion from forest to another land cover resulted in soil carbon losses up to 43%. This might be linked to the impacts of forestry operations on biogeochemical properties in the soil (Schelker et al. 2012; Dunn et al. 2015). According to Schelker et al. (2012), each harvesting measure (clear cut, site preparation) increased the organic C flux from the (previously) forested site, by a magnitude of 8-10% of the total Net Ecosystem Exchange. This is connected to changes in local hydrology toward shorter water residence time and higher litter inputs with subsequent faster decomposition, potentially caused by higher soil temperatures due to more insolation (Schelker et al. 2012). Yet, this is not reflected in the data.

Similarly, grouping by forest dynamics did not yield any differences in TON trends. This could be attributed to the tree species composition in Swedish forests (Cronan and Aiken 1985; Fröberg et al. 2011). Afforestation increases N retention in the soil, which was strongest in Norway Spruce dominated stands (Fröberg et al. 2011). Forests with more Birch (*Betula pendula; Betula pubescens*) or Pine (*Pinus sylvestris*) had larger N leakage from the soil (Fröberg et al. 2011). Based on this, it could be assumed that forest gains in the study period consisted mainly of coniferous species. This complies with the dominance of industrial forestry in Sweden, as coniferous species make up over 60% of productive forest (Fredh et al. 2012; Lindbladh et al. 2014) and Norway Spruce accounts for 41% of the standing volume (Fröberg et al. 2011; Skerlep et al. 2020). In addition to the previously discussed lag time, afforestation with focus on Spruce might have minimized potential effects of forest cover changes on TON trends.

Slow decomposition rates in the soil further link to the quality of organic matter in forest stands. The positive C:N trend observed in the catchments could not be attributed to changes in forest coverage. This is directly contradicting findings from Rosenqvist et al. (2010), where afforestation led to organic matter with higher C:N ratios leaching from the soil. However, the relatively short study period of 12 years might not capture TOC:TON developments on longer

timescales (Rosenqvist et al. 2010; Kritzberg 2017; Skerlep et al. 2020). As observed for TOC, the relationship between organic matter quality and directional forest changes is masked by the delayed response of forest soils.

5.4 How does wetland coverage influence trends in water chemistry?

Contradicting the fourth hypothesis, changes in wetland extent did not coincide with different TON trends. This stands in contrast to prevalent findings, where literature observed a positive relationship between the extent of wetlands and Nitrogen concentrations in comparable catchments in the north-eastern (Pellerin et al. 2004) and Midwestern (Carpenter 2008) US, and in a relatively urbanized catchment in eastern China (Chen et al. 2016).

This discrepancy between literature and presented findings could be partly connected to nitrogen cycling in wetlands (Zhou et al. 2010). Saunders and Kalff (2001) observed that wetlands are characterized by high nitrogen retention, which is achieved through denitrification in oxygen-poor environments such as wetland soils. Denitrification describes the conversion from (inorganic) nitrate to N-containing gases facilitated by bacteria in the soil (Zhou et al. 2010). As a large fraction of organic N is microbially converted to inorganic N compounds for further uptake (Berman and Bronk 2003; Berggren et al. 2015), denitrification might act upon these particles, thus reducing the total nitrogen content in the soil by adding nitrous oxide (N_2O) or N_2 to the atmosphere (Zhou et al. 2010). Additionally, sedimentation processes might retain nitrogen in the soil and reduce the magnitude of nitrogen export to freshwaters (Kritzberg et al. 2020; Skerlep et al. 2020). The nitrogen content in wetland soils further depends on the prevalence of vegetation, with more densely vegetated areas having higher uptake and subsequent binding of nitrogen by (aquatic and terrestrial) plants (Saunders and Kalff 2001; Zhou et al. 2010). Based on this, it is assumed that wetlands with less vegetation have a higher nitrogen leakage (Saunders and Kalff 2001; Zhou et al. 2010). Wetlands could release and/or retain more nitrogen, depending on the strength of denitrification and sedimentation processes. In the catchments, variability in vegetation density and subsequent nitrogen retention of the wetland areas could have contributed to the lack of (significant) relationship between wetland changes and TON trends found in this study.

Moreover, the applied methods might have obscured potential linkages. Especially the coverage within the catchments needs to be considered, as wetlands covered rather small parts of the catchments (on average ~4.57%). Even the site with the largest extent of wetlands (~26.4%) was dominated by another land cover class, namely forests (~70.5%), which might have masked water chemistry development caused by wetland changes. While wetland extent changed more in the catchments (0.03% yr^{-1}) than in Sweden (-0.001% yr^{-1}), the land cover changes were comparably small, which might be reflected in the lack of relationship. The short time period and the marginal changes in wetland extent did not coincide with leakage of large amounts of TOC, which occurred during large-scale drainage and/or conversion of wetlands in earlier times (Meyer-Jacob et al. 2015; Kritzberg et al. 2020).

Additionally, the proposed findings did not reveal any influence of changing wetland extent between 2000 and 2012 on changes in TOC concentrations. This appears counterintuitive considering that wetlands are associated with higher TOC release. This was observed in catchments in continental Europe, where natural sites (dominated by wetlands and/or forests) show higher (Berggren and Al-Kharusi 2020) or even the highest TOC concentrations (Cazorla 2020). These larger-scale trends imply connections between wetland coverage and TOC development not detected in this study. Besides previously addressed shortcomings in the methodology, it is assumed that these differences are caused by land cover considerations in this study. As pointed out by Solomon et al. (2015), TOC export from wetlands is dependent on the distance to the water body, as constantly saturated wetland soils mainly release organic carbon from the shallow topsoil (Stepanauskas et al. 2000). With increasing distance to the

water body, and thus, increasing water residence time, more wetland derived TOC could be processed and respired before leaching into the water (Kritzberg et al. 2020; Skerlep et al. 2020). The non-weighted land cover attribution applied here might skew wetland-TOC interactions, thus weakening the influence of increasing wetland cover on trends in TOC concentration. Changes in wetland cover did not explain the positive trend in organic matter quality.

5.5 What is the influence of agriculture on water quality trends?

Changes in agricultural extent did not significantly influence the observed decrease in TON concentrations. The fifth hypothesis is therefore not supported. However, the Kruskal-Wallis test statistic indicates a weak relationship between agricultural land cover changes and TON, albeit not significant at the chosen significance level ($p=0.089 > p_{alpha}=0.05$). Nevertheless, this is considered as an indicator for trends observed in literature (Wasserstein et al. 2019), where TON concentrations in the river correspond with the extent of arable fields within the catchment (Rosenqvist et al. 2010; Solomon et al. 2015).

This potential dynamic could be linked to increased N use efficiency in Swedish agriculture (Hellsten et al. 2017). More agriculture in the catchment could lead to more N being added to the soils, with (mineral) fertilizers (Solomon et al. 2015) contributing up to 55% to the total N input in Swedish soils (Hellsten et al. 2017). Yet, the observed reduction in riverine TON concentrations could partly be attributed to Swedish and EU-wide regulations regarding N concentrations in agricultural runoff (Hellsten et al. 2017; European Environment Agency 2018). These regulations might limit the impact of increasing agricultural coverage on TON concentrations in the water, with newly converted agricultural areas exporting less additional TON to the rivers than established fields. This assumption is furthered by intercomparison of directional agricultural changes and the related TON trends in the catchments, where no difference in TON trends between increasing ($Median_{MI}$=-0.009 mg L^{-1} yr-1) or constant ($Median_{NC}$=-0.007 mg L^{-1} yr^{-1}) agricultural coverage could be found.

In line with nutrient-rich runoff, there is a stronger increase in organic C concentrations transported from areas with changing agricultural coverage than from continuous agricultural fields ($Median_{NC}$=0.053 mg L^{-1} yr^{-1}). The direction of agricultural change was not found to be influential on TOC trends ($Median_{MI}$=0.145 mg L^{-1} yr^{-1}; $Median_{MD}$=0.100 mg L^{-1} yr^{-1}). These findings align with Guo et al. (2017), who observed that increasing DOC concentrations were driven by agricultural expansion in the urbanized catchment of Dianchi Lake in China. It is assumed that directional land cover changes within the catchments govern TOC export to the rivers. In the catchments, agricultural expansion (classed as Major Increase) occurred partly at the expense of another 'natural' land cover class, such as grassland or pasture with stable soil carbon in the mineral soil layer (Puissant et al. 2017). Conversion from such classes to cropland might release larger quantities of carbon into the water than unchanged land cover. As shown in a meta-analysis with focus on Australia, Brazil, New Zealand and USA by Guo and Gifford (2002), change from natural land cover to agriculture might result in soil organic carbon losses of up to 59%. This decrease in soil organic carbon might be reflected in temporary increased TOC export in the studied catchments. Similar observations can be made from the more prevalent natural forest-agriculture dynamics, with a change from forest toward cropland reducing soil organic carbon by up to 42% (Guo and Gifford 2002). Therefore, the conversion from forest, pasture or grassland to cropland depleted organic carbon pools in the soil, and further transported more TOC into rivers.

The analysis of directional land cover changes highlighted the conversion from agriculture to forest and urban areas, grouped as Major Decrease (Fuchs et al. 2015). While not visible in the data, urban areas are associated with higher TOC release (Berggren and Al-Kharusi 2020), which could influence the TOC trends in the catchments. Afforestation on previous agricultural

land leads to increases in soil organic carbon stocks, between 18% for industrial forests and 53% for natural (secondary) forest (Guo and Gifford 2002). However, boreal forests and especially Spruce forests were also found to export more labile TOC from the soil (Oni et al. 2013; Weyhenmeyer et al. 2014; Kritzberg et al. 2020), which complies with stronger TOC trends after conversion from agricultural areas. Across the catchments, no connection between agricultural dynamics and organic matter quality could be established. However, special focus needs to be applied to the bioavailability of N derived from agricultural areas, as up to 80% of DON in runoff from livestock could be degradable by microorganisms (Sun et al. 2017).

Changes in agricultural management can be inferred to explain the seeming uncoupling of agricultural coverage and TON dynamics. This concerns efforts to mitigate organic matter input from agricultural sites through limitations on artificial fertilizers (Carpenter 2008; Kritzberg 2017), that endanger the nutrient balance in the soil (Fredh et al. 2012). Simultaneously, improvements in wastewater and manure treatment were made (Carpenter 2008; Berggren and Al-Kharusi 2020; Cazorla 2020). Therefore, the general trend derived from WaterBase suggests that N-addition by agricultural runoff was reduced or mitigated through N-limitations (Cazorla 2020).

5.6 What are the implications of these findings?

Generally, the findings in this study inform about larger developments in water chemistry. Increases in surface browning (Kritzberg 2017; Skerlep et al. 2020) coincided with an overall decrease in TON concentrations in Sweden. This implies that TON concentrations and associated eutrophication events did not drive brownification of freshwaters. On the other hand, increases in water colour caused by more stable (aromatic) DOC impeded light penetration and thus primary productivity in the waters (Fredh et al. 2012; Kritzberg et al. 2020), with negative consequences for benthic vegetation (Schindler and Scheuerell 2002; Cremona et al. 2016).

The strong increase in TOC:TON ratio suggests a change in relative contribution of different organic C sources, with decreasing quantity of DOC generated by autotrophs in the water (autochthonous DOC) (Berggren and Al-Kharusi 2020). It appears that most organic matter comes from the surrounding soils (allochthonous DOC) (Kim et al. 2014). This shift toward more stable and less degradable (aromatic) DOC leads to more transport of recalcitrant DOC into coastal waters and the Baltic Sea (Monteith et al. 2007; Nebbioso and Piccolo 2013; Naturvårdsverket 2020).

5.7 Limitations and uncertainties

Furthermore, the reliability of the findings in this study needs to be assessed. Baseline differences in concentration due to physical properties (catchment size, latitude) could be omitted by comparing change rates (Theil-Sen slopes) of water chemistry.

The accuracy of the datasets constrains the presented results. According to the Copernicus Programme (2020a, 2020b, 2020c, 2020d, 2020e), all CORINE datasets and associated change layers achieved a thematic accuracy of over 85% in all years. The European Environment Agency (2006) found that only 5% of these erroneous 15% occurred on a class 1 level (Kosztra et al. 2019), which suggests a potential thematic accuracy of 95% in this study Yet, spatial accuracy differs depending on land cover class, with overestimation of larger classes (e.g. urban) and underestimation of classes with lower areal extent (e.g. grassland) (Pflugmacher et al. 2019). These inaccuracies are furthered by the large MMU of CORINE layers (Pflugmacher et al. 2019), and can only partly be reduced by incorporating the change layers with smaller MMU. In this context, the smaller wetland class might be affected by underrepresentation in the catchments, which would explain the obscured relationship between wetlands and TON. While land cover trends might be less biased than absolute land cover, they might be more

impacted by noise in the land cover data. A small error in land cover attribution could make up a relatively large part of the land cover change.

Uncertainties in the water quality data were reduced by using annual averages of TOC and TON concentrations. This minimized the impact of interannual variability (due to e.g. land cover, seasonality) (Erlandsson et al. 2008; Chen et al. 2016; Deininger et al. 2020), and systematic measurement uncertainties (Tepuš and Simonič 2007; Wallman et al. 2009) on the data. To ensure coherence between the three different measurement methods for TOC and TON, corrections are applied by Swedish water quality monitoring programmes (Wallman et al. 2009; Ahlgren 2018). The water quality database subsequently indicates individual data points that could be outliers. While three individual C measurements were flagged as outliers in this study, the effect is smoothed if not eliminated by considering annually aggregated TOC values.

Watershed delineation based on the DEM_{50m} introduced the largest uncertainty into this study. While commonly applied, the sink-filling process in this study levelled all sinks, thus modifying elevation values within the DEM, and altering flow paths (Yan 2019). This way, not only errors in the data but also natural sinks such as lakes were removed (Yan 2019). By filling the DEM with the maximum sink depth, elevation data of 20 656 107 cells, equivalent to 11% of the DEM, was altered. It is assumed that the arbitrary choice of snap distance constitutes the largest uncertainty in the watershed delineation process. Based on visual evaluation, a snap distance of 15 cells yielded the best watershed results. This relatively high value ensured that monitoring site locations coincide with high-flow cells. Otherwise, catchments might only extend over one cell (0.25 ha). Despite reducing discrepancies between DEM derived flow values and measuring sites, this step might modify the initial data and the resulting catchment sizes tremendously. The validity of the presented results and conclusions depends largely on accurate catchment representation, which is constrained by the accuracy of the delineation process.

Land cover was considered non-spatially, therefore, each cell with associated land cover was assumed influence water chemistry equally (Giri and Qiu 2016). However, distance to the water body plays an important role in organic C and organic N dynamics, especially the increased degradation potential and enhanced flocculation and sedimentation processes with longer water residence time (Berman and Bronk 2003; Erlandsson et al. 2008; Kritzberg et al. 2020; Skerlep et al. 2020). Thus, the non-spatial assumption introduced a bias depending on catchment size. To improve the results, spatial considerations, focusing for example on the importance of the riparian zone for organic matter export (Schelker et al. 2012; Oni et al. 2013) would be needed. The non-spatial approach in this study might have particularly underestimated the importance of wetlands for water chemistry trends. This assumption aligns with literature findings that underline the close proximity of wetlands and water bodies, with fast interactions through surface and subsurface flows (Ågren et al. 2008; Laudon et al. 2012; Oni et al. 2013).

It was found that the strength of a relationship between water chemistry and land cover changes depends on the temporal extent of water quality data (Skerlep et al. 2020). This was demonstrated along the Lyckeby river, where DOC concentration changes caused by afforestation were recorded with a lag time of around 40 years (Skerlep et al. 2020). Such lag times were not detectable in the datasets, with a time span of 26 years (TOC) respectively 10 years (TON, TOC:TON). The slow update times of WaterBase further constrained the temporal extent of this study, as concentrations were only available until 2011 (TON, TOC:TON) or 2012 (TOC). Comparable land change information for Sweden was only available from 2000 (Copernicus Programme 2020a, b, c), which limited information about historical land cover and related soil organic matter pools (Fuchs et al. 2015). This could mean that the presented water chemistry trends reflect land cover changes beginning as early as the 1950s (TOC) or 1960s (TON, TOC:TON). Therefore, relationships between land cover changes and water quality trends might be stronger when considering appropriate lag times.

The uncertainties of statistical testing are more quantifiable. Applying a Bonferroni correction to reduce the risk of type 1 errors in the Man-Kendall trend test might lead to rejection of weaker trends in the data (Cortés et al. 2020). Therefore, the significance of TOC, TON and TOC:TON trends might be higher than indicated in this study. However, nearly significant relationships between land cover change and water chemistry trends (e.g. agriculture and TON) are considered as indicators of a connection and reduce the distortion by the chosen and/or Bonferroni-corrected significance level (Wasserstein et al. 2019). On the other hand, the unequal groupings might skew comparison via the Mann-Whitney U test. This could be most prevalent in the wetland class, with different sample sizes for increasing (n=30), decreasing (n=2) and constant (n=12) coverage obscuring potential trends. As all groupings are affected by asymmetry to a certain degree, the presented relationships (or lack thereof) could be caused by more extreme trends in groups with small sample sizes. Thus, sample sizes need to be considered when investigating potential linkages in the data.

Finally, the interconnectedness of TOC and TON dynamics in the ecosystem complicates the interpretation of the results. The interplay of biological and chemical factors (Andersson et al. 2000) might not follow the simplified, linear structures (Solomon et al. 2015) proposed in this study. There is a need for further understanding of organic N in aquatic ecosystems (Berman and Bronk 2003).

6 Conclusion

Water chemistry in selected monitoring sites in Sweden exhibited clear temporal trends. Annually averaged organic carbon concentrations increased between 1987 and 2012 for most sites, with significant trends in over half of the sites. Organic nitrogen concentrations generally decreased between 2002 to 2011, despite the signal being less distinct.

The temporal trends in organic matter loading at the measuring sites differed significantly when grouped by land cover changes in urban areas and agricultural areas. Urbanization led to a stronger decrease in TON concentrations. Contrary to the hypothesis, trends in TOC showed no connection to forest dynamics in the catchment. Wetland coverage changes did not affect the hypothesised stronger rise in TON concentrations. Catchments with increasing agricultural areas did not show a significantly stronger trend in TON concentrations than unchanged or decreasing agricultural areas. However, TOC trends increased significantly more in increasing and decreasing agricultural areas compared to unchanged catchments.

Future studies could refine the methodology by considering the influence of land cover classes combined instead of individually. Further, considerations regarding catchment size, geometry, and distance of land cover features to streams could inform about spatial patterns in the analysis. The accuracy of the results could be improved by using water chemistry data with higher temporal data (e.g., monthly data).

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8 Appendix

8.1 Flow charts of GIS operations

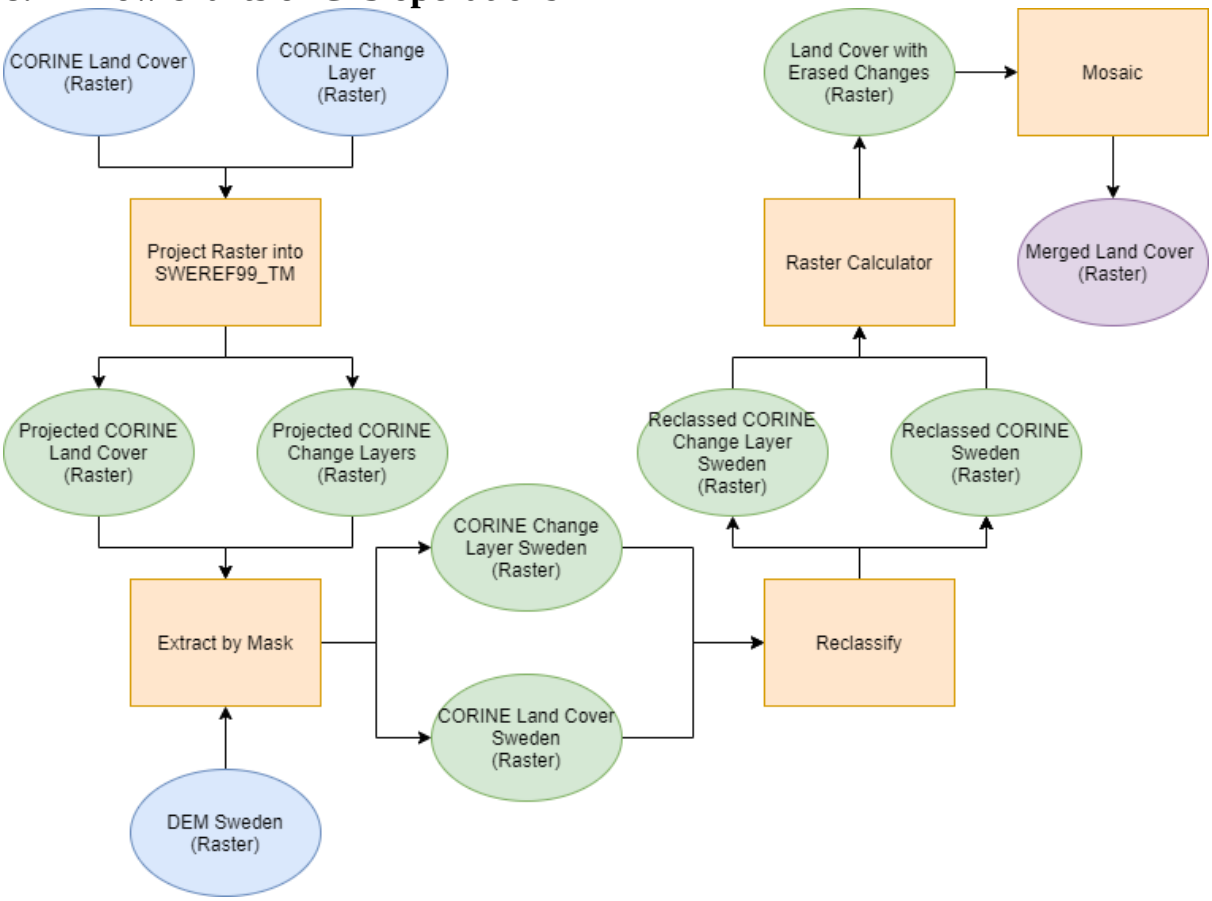

Figure A1 Flow chart depicting the pre-processing steps of the land cover and land cover change raster layers, with help of the DEM, in ArcMap.

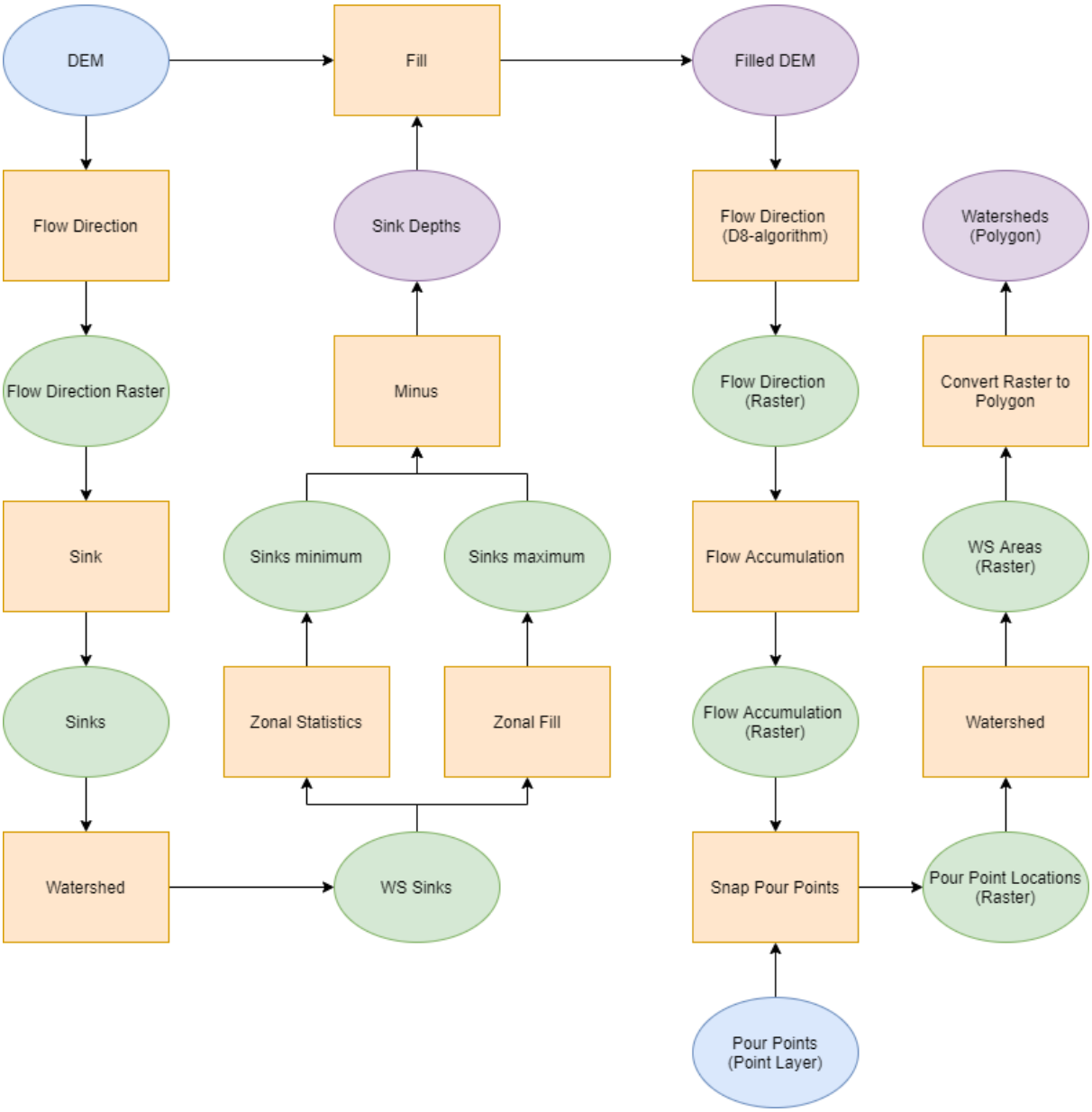

Figure A2 Flowchart depicting the watershed delineation based on the DEM, including the process to determine maximum sink depth with the Sink tool in ArcMap. The pour point layer refers to the point layer of the measurement sites.

8.2 Data

Table A1 Overview of the data used in this study, with information about data type, temporal and spatial resolution, geographic reference system and data source

Variable Name	Data Type	Spatial Resolution (m)	Version	Temporal Resolution	Geographic Reference System	Source
CORINE Land Cover 2000	GeoTIFF (Raster data)	100m	Version 2020_20u1	1999-2001	EPSG:3035 (ETRS89, LAEA)	(Copernicus Programme 2020a)
CORINE Land Cover 2006	GeoTIFF (Raster data)	100m	Version 2020_20u1	2005-2007	EPSG:3035 (ETRS89, LAEA)	(Copernicus Programme 2020b)
CORINE Land Cover 2012	GeoTIFF (Raster data)	100m	Version 2020_20u1	2011-2012	EPSG:3035 (ETRS89, LAEA)	(Copernicus Programme 2020c)
CORINE Change Layers 2000-2006	GeoTIFF (Raster data)	100m	Version 2020_20u1	1999-2007	EPSG:3035 (ETRS89, LAEA)	(Copernicus Programme 2020d)
CORINE Change Layers 2006-2012	GeoTIFF (Raster data)	100m	Version 2020_20u1	2005-2013	EPSG:3035 (ETRS89, LAEA)	(Copernicus Programme 2020e)
DEM	GeoTIFF (Raster data)	50m	-	Fall 2010	SWEREF99_ TM	(Lantmäteriet 2020)
WaterBase Sites Sweden	CSV File	-	-	-	-	WaterBase via Cazorla (2020)

8.3 Analysis of the watersheds

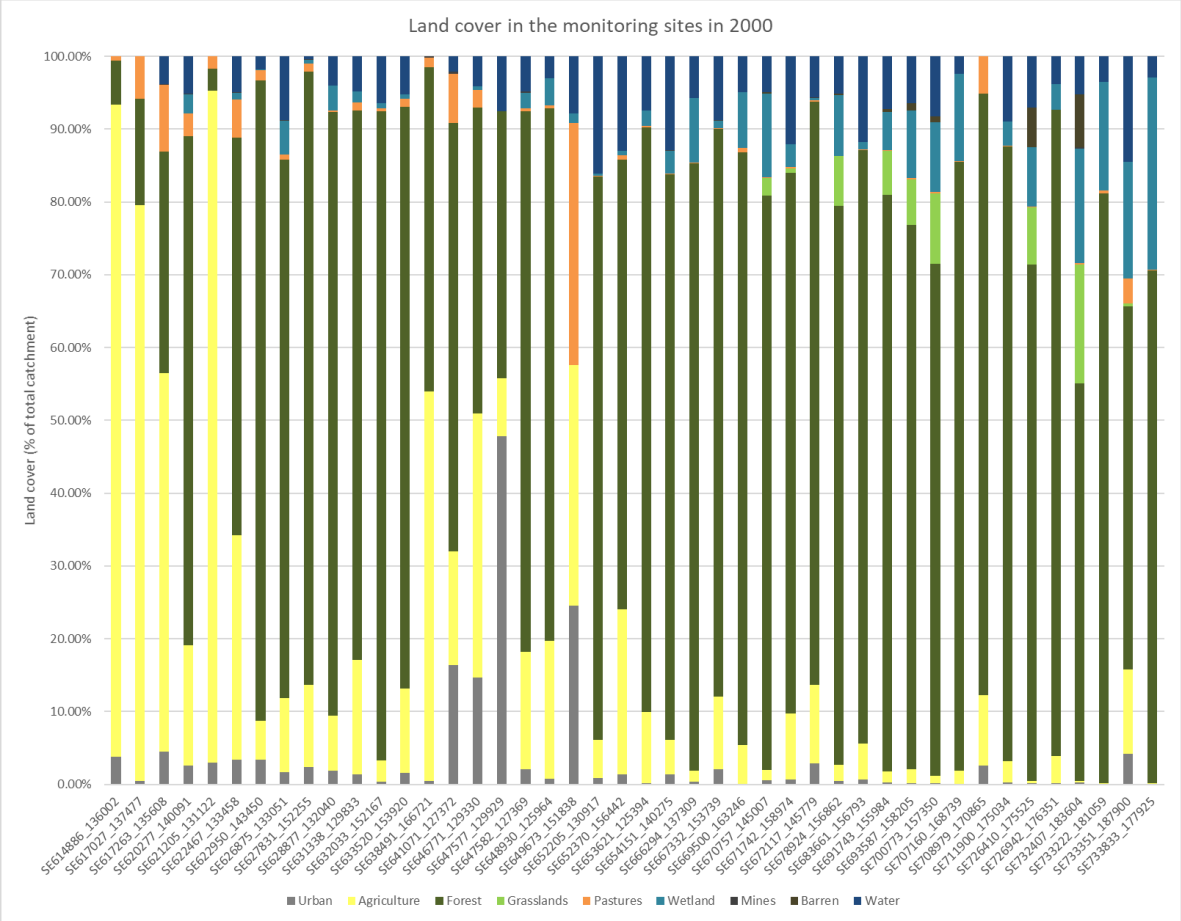

Figure A3 Stacked column chart showing the land cover classes distribution in the respective 44 catchments in 2000.

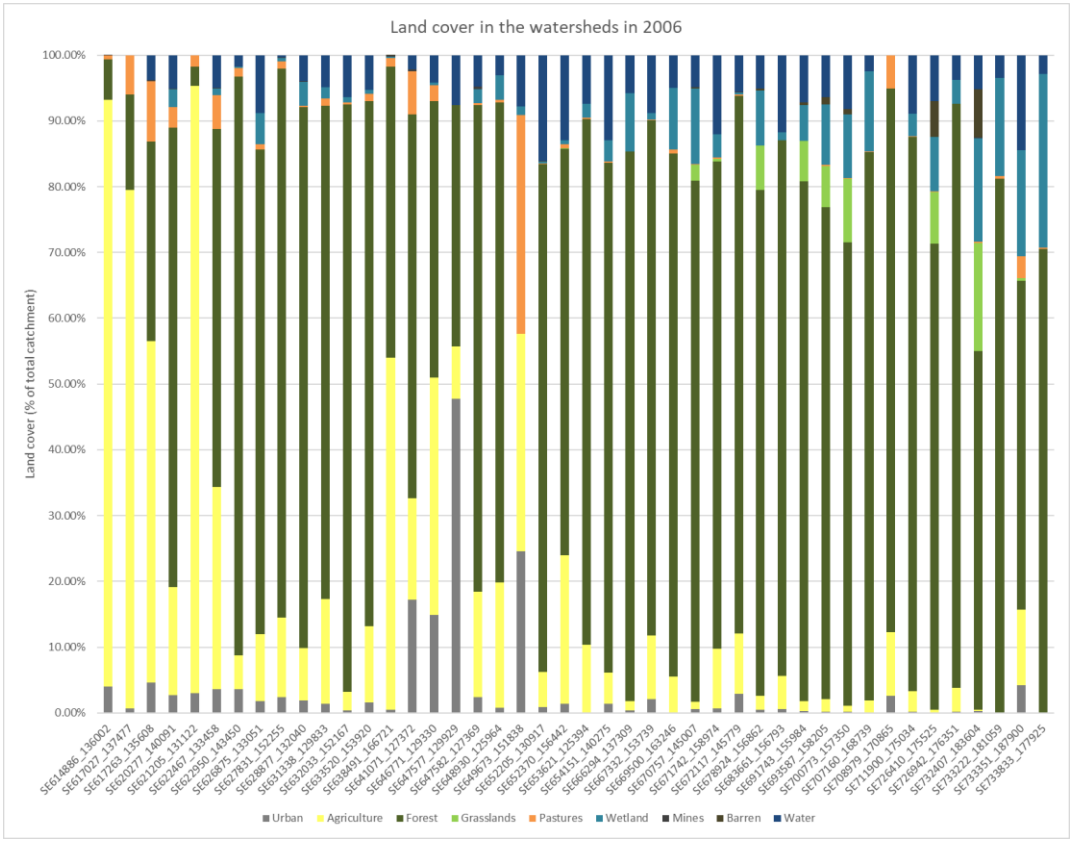

Figure A4 Stacked column chart showing the land cover classes distribution in the respective 44 catchments in 2006.

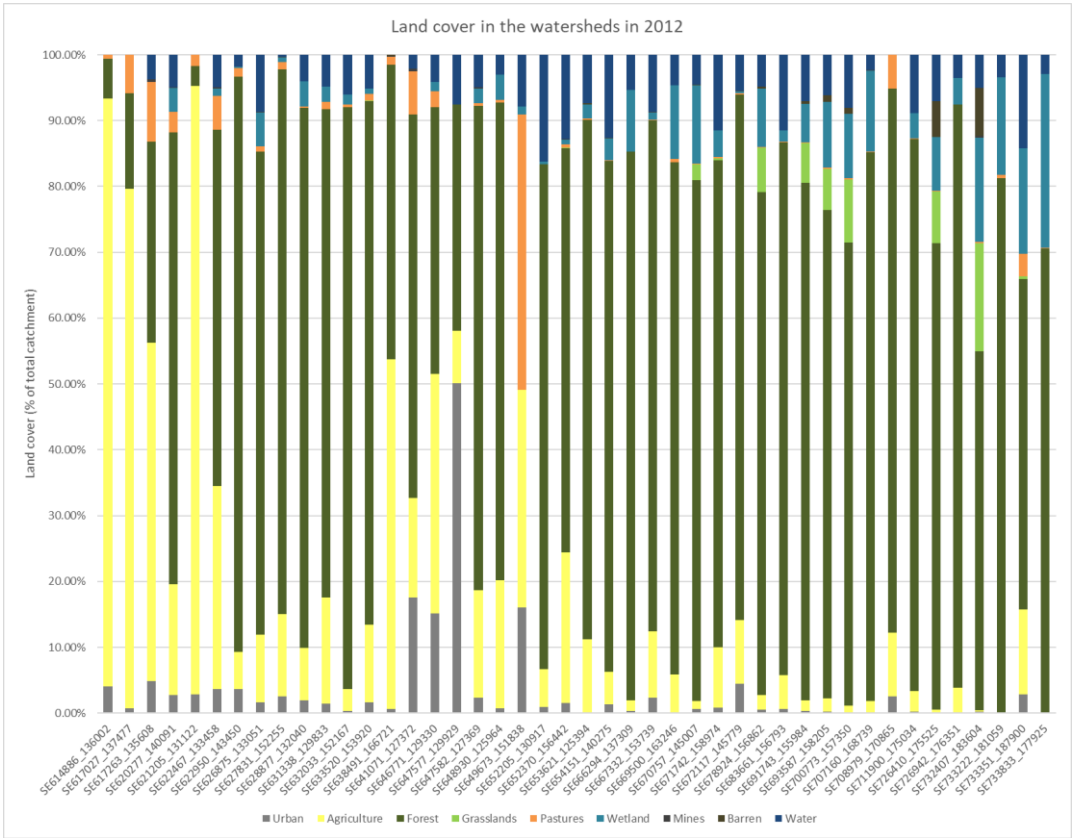

Figure A5 Stacked column chart showing the land cover classes distribution in the respective 44 catchments in 2012.

Table A2 Overview of the monitoring sites, the respective catchment size in ha and the net changes in land cover between 2000-2012, with + indicating a net gain, - indicating a net loss and 0 signifying no change in the study period; land cover changes that are not significantly higher or lower than the national average (in accordance with the grouping in Table 5) are shown in grey font

SiteID	Catchment Size (ha)	Agriculture	Forest	Grasslands	Pastures	Wetland	Combined Impervious
SE614886-136002	11213	-	0	0	+	0	+
SE617027-137477	24581	-	-	0	+	0	+
SE617263-135608	21882	-	+	0	-	0	+
SE620277-140091	413755	+	-	0	-	+	+
SE621205-131122	15547	+	+	0	0	0	-
SE622467-133458	93992	-	-	0	-	+	+
SE622950-143450	18238	+	-	0	0	0	+
SE626875-133051	616275	+	-	0	+	+	+
SE627831-152255	73038	+	-	0	-	+	+
SE628877-132040	269187	+	-	0	0	+	+
SE631338-129833	332209	+	-	0	+	+	+
SE632033-152167	73881	+	-	0	-	+	+
SE633520-153920	439632	+	-	+	-	+	+
SE638491-166721	42981	-	+	0	-	0	+
SE641071-127372	12264	-	-	0	-	0	+
SE646771-129330	15619	+	-	0	+	+	+
SE647577-129929	455	0	-	0	0	0	+
SE647582-127369	30014	+	-	0	+	+	+
SE648930-125964	132500	+	-	0	-	+	+
SE649673-151838	198	0	0	0	+	0	-
SE652205-130917	204208	+	-	0	0	+	+
SE652370-156442	334549	+	-	0	-	+	+
SE653621-125394	47871	+	-	0	+	-	+
SE654151-140275	504137	+	-	0	+	+	+
SE666294-137309	269832	+	-	0	0	+	+
SE667332-153739	609791	+	-	0	-	+	+
SE669500-163246	37198	+	-	0	-	+	0
SE670757-145007	749849	-	+	+	-	+	+
SE671742-158974	204617	+	-	-	+	+	+
SE672117-145779	30649	-	-	0	0	0	+
SE678924-156862	1981505	+	-	-	-	+	+
SE683661-156793	198136	+	-	0	+	+	+
SE691743-155984	1206157	+	-	-	-	+	+
SE693587-158205	1236285	+	-	+	-	+	+
SE700773-157350	2911865	+	-	-	-	+	+
SE707160-168739	285659	+	-	0	0	+	+
SE708979-170865	1175	0	0	0	0	0	0
SE711900-175034	165243	+	-	0	+	+	-

SE726410-175525	1074095	+	-	-	+	+	+
SE726942-176351	45887	+	-	0	0	+	-
SE732407-183604	2797126	+	-	-	-	+	+
SE733222-181059	43637	0	+	0	0	-	0
SE733351-187900	7128	+	+	0	0	0	-
SE733833-177925	376711	+	-	-	+	+	+

8.4 Statistical Test Results

Table A3 Temporal trends in the water quality data (TOC, TON, TOC:TON) indicated by the p-value (rounded to 3 digits after the comma) of the Man-Kendall rank correlation and the Theil-Sen slope. Significant p-values (two-tailed, 0.05) are indicated by [*]; significant p-values (Bonferroni-corrected, 0.0006) are indicated by [a]; not significant values are signified by grey font colour

	p-value			Slope		
Site ID	TOC	TON	TOC:TON	TOC	TON	TOC:TON
SE614886-136002	0.064	0.020*	0.001*	0.101	-0.082	1.258
SE617027-137477	0.006*	0.107	0.001*	0.100	-0.053	0.435
SE617263-135608	0.029	0.152	0.002*	0.128	-0.049	0.506
SE620277-140091	0.000a	0.419	0.007*	0.267	-0.018	0.424
SE621205-131122	0.085	0.107	0.004*	0.032	-0.027	0.217
SE622467-133458	0.015*	0.012*	0.000*a	0.117	-0.061	0.641
SE622950-143450	0.000 *a	0.107	0.007*	0.248	-0.009	0.522
SE626875-133051	0.000 *a	0.283	0.000*a	0.236	-0.012	1.075
SE627831-152255	0.000 *a	0.107	0.007*	0.279	-0.021	0.752
SE628877-132040	0.000 *a	0.323	0.002*	0.238	-0.008	0.829
SE631338-129833	0.000 *a	0.049	0.002*	0.162	-0.020	0.944
SE632033-152167	0.000 *a	0.020*	0.002*	0.250	-0.014	0.556
SE633520-153920	0.000 *a	0.074	0.007*	0.247	-0.013	0.446
SE638491-166721	0.010 *	0.721	0.001*	0.129	-0.017	0.370
SE641071-127372	0.912	0.032	0.004*	0.001	-0.015	0.240
SE646771-129330	0.982	0.000*a	0.002*	0.000	-0.015	0.511
SE647577-129929	0.627	0.030	0.020*	-0.009	-0.011	0.147
SE647582-127369	0.000*a	0.007	0.001*	0.150	-0.013	0.933
SE648930-125964	0.000*a	0.020*	0.000*a	0.145	-0.015	0.518
SE649673-151838	0.003*	0.020*	0.020*	0.060	-0.022	0.217
SE652205-130917	0.004*	0.074	0.012*	0.043	-0.007	0.369
SE652370-156442	0.008*	0.032	0.001*	0.093	-0.024	0.354
SE653621-125394	0.000*a	0.032	0.001*	0.155	-0.009	0.788
SE654151-140275	0.003*	0.007*	0.004*	0.063	-0.010	0.753
SE666294-137309	0.002*	0.107	0.012*	0.072	-0.008	0.848
SE667332-153739	0.002*	0.474	0.152	0.078	-0.002	-0.567
SE669500-163246	0.000*a	0.210	0.074	0.264	0.009	-0.160
SE670757-145007	0.006*	0.530	0.074	0.081	-0.001	-0.265
SE671742-158974	0.001*	0.178	0.007*	0.083	-0.007	0.502
SE672117-145779	0.050	0.592	0.210	0.046	-0.002	-0.547
SE678924-156862	0.045	0.152	0.007*	0.043	-0.006	0.496

SE683661-156793	0.112	0.178	0.049	0.040	-0.006	-0.099
SE691743-155984	0.774	0.039	0.001*	0.006	-0.007	1.256
SE693587-158205	0.260	0.788	0.032	0.021	-0.000	0.111
SE700773-157350	0.050	0.371	0.004*	0.047	-0.005	0.433
SE707160-168739	0.043	0.283	0.000*a	0.082	-0.006	1.614
SE708979-170865	0.047	0.323	0.020*	0.053	-0.001	0.387
SE711900-175034	0.003*	0.152	0.012*	0.092	-0.009	0.316
SE726410-175525	0.208	0.049	0.001*	0.030	-0.007	1.102
SE726942-176351	0.040	0.152	0.002*	0.100	-0.008	0.784
SE732407-183604	0.094	0.419	0.049	0.069	-0.003	-0.179
SE733222-181059	0.178	0.007*	0.000*a	0.069	-0.029	2.148
SE733351-187900	0.019*	0.721	0.012*	0.086	-0.001	0.845
SE733833-177925	0.034	0.152	0.004*	0.052	-0.008	0.787

Table A4 Results from Mann-Whitney U test for TOC, with Sample Size, Median value of TOC concentration (mg L^{-1}), z-value and p-value; significant p-values (one-tailed, 0.05) indicated by *; significant p-values (bonferroni-corrected, 0.003) indicated by ^{a}; statistically not significant p-values indicated by grey font colour

TOC Land Cover	Group	Sample Size	Median	U-value	z-value	p-value
Combined Impervious	No Change	22	0.069			
	Increase	17	0.101	154	0.920	0.181
	Increase	17	0.101			
	Decrease	5	0.086	26	1.254	0.109
	No Change	22	0.069			
	Decrease	5	0.086	53	0.094	0.464
Agriculture	No Change	13	0.053			
	Increase	23	0.145	64	2.799	0.002^{*a}
	Increase	23	0.145			
	Decrease	8	0.100	67	1.106	0.137
	No Change	13	0.053			
	Decrease	8	0.100	22	2.136	0.015*
Forest	No Change	13	0.063			
	Increase	6	0.084	27	1.009	0.161
	Increase	6	0.084			
	Decrease	25	0.093	61	0.675	0.255
	No Change	13	0.063			
	Decrease	25	0.093	128	1.046	0.150
Grassland	No Change	38	0.089			
	Increase	3	0.081	53	0.175	0.435
	Increase	3	0.081			
	Decrease	3	0.047	3	0.436	0.350
	No Change	38	0.089			
	Decrease	3	0.047	30	1.327	0.098
Wetland	No Change	12	0.073			
	Increase	30	0.083	150	0.821	0.208
	Increase	30	0.083			
	Decrease	2	0.122	27	0.195	0.423
	No Change	12	0.073			
	Decrease	2	0.112	7	0.922	0.220

Table A5 Results from the Mann-Whitney U test for TON, with Sample Size, Median value of TON concentration (mg L^{-1}), z-value and p-value; significant p-values (one-tailed, 0.05) indicated by *; significant p-values (bonferroni-corrected, 0.003) indicated by ^{a}; statistically not significant p-values indicated by grey font colour

TON Land Cover	Group	Sample Size	Median	U-value	z-value	p-value
Combined Impervious	No Change	22	-0.007			
	Increase	17	-0.015	81.5	2.974	0.001^{*a}
	Increase	17	-0.015			
	Decrease	5	-0.009	32	0.783	0.223
	No Change	22	-0.007			
	Decrease	5	-0.009	38	1.030	0.157
Agriculture	No Change	13	-0.007			
	Increase	23	-0.009	115.5	1.103	0.133
	Increase	23	-0.009			
	Decrease	8	-0.033	50	1.874	0.030*
	No Change	13	-0.007			
	Decrease	8	-0.033	28	1.702	0.045*
Forest	No Change	13	-0.008			
	Increase	6	-0.021	34	0.395	0.351
	Increase	6	-0.021			
	Decrease	25	-0.009	54	1.025	0.157
	No Change	13	-0.008			
	Decrease	25	-0.009	148.5	0.415	0.335
Grassland	No Change	38	-0.010			
	Increase	3	-0.001	25	1.577	0.060
	Increase	3	-0.001			
	Decrease	3	-0.007	3	0.436	0.350
	No Change	38	-0.010			
	Decrease	3	-0.007	24.5	1.602	0.054
Wetland	No Change	12	-0.016			
	Increase	30	-0.008	122	1.601	0.055
	Increase	30	-0.008			
	Decrease	2	-0.019	13	1.285	0.113
	No Change	12	-0.016			
	Decrease	2	-0.019	11	0.091	0.462

*Table A6 Results from the Mann-Whitney U test for TOC:TON, with Sample Size, Median value of TOC:TON, z-value and p-value; significant p-values (one-tailed, 0.05) indicated by *; statistically not significant p-values indicated by grey font colour*

TOC:TON Land Cover	Group	Sample Size	Median	U-value	z-value	p-value
Combined Impervious	No Change	22	0.537			
	Increase	17	0.502	151	1.005	0.159
	Increase	17	0.502			
	Decrease	5	0.316	39	0.235	0.410
	No Change	22	0.537			
	Decrease	5	0.316	43	0.718	0.242
Agriculture	No Change	13	0.496			
	Increase	23	0.522	138	0.362	0.360
	Increase	23	0.522			
	Decrease	8	0.402	65	1.196	0.118
	No Change	13	0.496			
	Decrease	8	0.402	42	0.688	0.250
Forest	No Change	13	0.446			
	Increase	6	0.438	37	0.132	0.449
	Increase	6	0.438			
	Decrease	25	0.511	72	0.125	0.452
	No Change	13	0.446			
	Decrease	25	0.511	158	0.123	0.452
Grassland	No Change	38	0.515			
	Increase	3	0.111	23	1.677	0.048*
	Increase	3	0.111			
	Decrease	3	0.502	1	1.309	0.100
	No Change	38	0.515			
	Decrease	3	0.502	47	0.476	0.326
Wetland	No Change	12	0.379			
	Increase	30	0.515	136	1.211	0.115
	Increase	30	0.515			
	Decrease	2	1.468	8	1.674	0.050
	No Change	12	0.379			
	Decrease	2	1.468	2	1.734	0.044*