Pollution in the Yealm Catchment and the Impact on Seagrass Habitats Within the Estuary

by

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Copyright Statement

Abstract

This study investigates the past, current and potential future state of the water in the River Yealm catchment and estuary. The water quality of UK rivers has been a recent topic of contention among conservationists, landowners, government bodies and NGOs, and is something that requires continuous monitoring and management.

Through the combination of data collected by the Environment Agency and field data collected in the Yealm estuary a picture of the state of water in the Yealm catchment was formed. It reinforced the importance of continuous and consistent monitoring over the entire catchment and highlighted specific areas of focus where pollutant loads were highest; namely, Newton Stream, Cofflete Creek, Long Brook, downstream of Lee Mill industrial site, and areas of water adjacent to sewage treatment facilities.

The potential for pollution in the estuary was then investigated, in particular the impact of these on seagrass beds at Cellar's Cove, Red Cove and Tomb Rock. The impact to these important habitats so far seems minimal. However, with frequent peaks of phosphate being observed in the catchment, continued monitoring is required to accurately assess potential future threats.

This study concludes by presenting recommendations for continued monitoring and management of the Yealm catchment. Attention is drawn to areas of high pollutant load and/or variability, and focuses on pollutants that exhibited a lack of control within the catchment including phosphate and *E.coli*. The need for a long-term high quality database in both the riverine and estuarine environments is also emphasised. Finally, the value of citizen science programs is highlighted, the working being done by the YEM group is vital and programs such as this allow for consistent and long-term data collection while cementing the relationship between communities and their river systems.

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Acknowledgements

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Authors Declaration

This project was conducted in association with the YEM group. It entailed the use of combined data from the Environment Agency, National River Flow Archive and seagrass coverage data from Natural England and Tim Scott; as well as data collected in fieldwork conducted on the Yealm catchment.

Fieldwork data was coordinated and collected by myself and another student. All data analysis conducted in this report is original and used to meet the aims stated in Section 1.2.

1.1 Introduction

UK rivers can be divided into 1500 individual river systems, making up 200,000km of watercourses (National River Flow Archive, 2023a) covering 3% of UK land area (Lawton, 2023). These river systems are a hub for human life. Over time they have been used as transport networks for both people and cargo, as a source of food and as drinking water (Brauman *et al.* 2007; Haidvogl, 2018). Rivers support industrial practices and are used in the production of hydroelectric power (Brauman *et al.* 2007; Haidvogl, 2018). Riverine and riparian environments are also used for leisure and have tremendous aesthetic value (Brauman *et al.* 2007). The relationship between humans and rivers is one of practicality, yet also provides a connection between people and nature.

The incredible range of benefits provided by rivers does not stop at human use. Rivers support diverse environments with a variety of habitats types (Brauman *et al.* 2007), providing links between distant pieces of land and connecting many different ecosystems (Lawton, 2023) therefore providing a wide range of biodiversity and ecosystem functioning (JNCC, 2016; Lawton, 2023). Furthermore, they are home to 10% of species found in the UK, many of which are protected including otters, eels, lampreys, feather moss and, further downstream, seagrass beds (JNCC. 2016; Lawton, 2023).

The benefits provided by rivers are extensive. An assessment of UK river natural capital provides an asset value of almost £48 billion per year (Lawton, 2023). Hydroelectric power, for example, is valued at £2.2 billion, while the asset value provided in terms of outdoor recreation is £32 billion (Lawton, 2023). Here, natural capital refers to the application of economic principles to the services provided by nature (Dominati *et al.* 2014). These estimates of natural capital are not designed to give nature a price tag but to provide a relatable context through which to understand the value of these systems.

Despite this, the management of UK rivers in the past has led to poor water quality (Environment Agency 2023a). Pollutants of every type are entering the river systems including metals, fuels, plastics, nutrients and bacteria (Robson and Neal, 1997; Uncles *et al.* 2002; Matějíček *et al.* 2003; Edwards and Withers, 2008; Neal *et al.* 2010; Tappin *et al.* 2013; Chaturvedi *et al.* 2018; van Emmerick and Schwartz, 2019; Florini *et al.* 2020; Garcia-Garcia *et* *al.* 2021). An investigation into the state of UK rivers conducted by the Environment Agency (EA) in 2019 measured the ecological and chemical status of rivers and groundwater (Environment Agency 2023a). The ecological status was determined using a set of water, habitat and biological quality tests (Environment Agency, 2023a). Only, 14% of rivers achieved good ecological status overall (Environment Agency, 2023a). Chemical status was measured by assessing 52 chemicals, in 2019 uPBTs, including mercury, brominated diphenyl ethers (pBDE), tributyltin and certain polyaromatic hydrocarbons (PAHs) (WISE Freshwater, 2023), were added to this classification (Environment Agency, 2023a). Following this addition, 0% of waterbodies achieved good chemical status (Environment Agency, 2023a). Investigations into river water quality indicate several different sources of pollution and physical modification that directly influence the status of river water bodies (Mainstone *et al.* 2011; Nie *et al.* 2018;). The most impactful sectors being agriculture, the water industry, and urban development and transport (European Environment Agency, 2021; Environment Agency,2023a). This highlights the need for continued review of water quality criteria to provide an accurate assessment of the state of UK rivers.

Under the EU Water Framework Directive all river water bodies should reach good ecological status by 2027 (European Commission, 2023), meaning the water body in question experiences only "slight change from its natural state as a result of human impact" (Environment Agency, 2023a). Improving the water quality of UK river systems is of great importance, not only to reach global and UK policy targets, but also to ensure these rivers remain highly diverse ecosystems, that can continue to provide the ecosystem services upon which humans rely.

Strategies to improve water quality of rivers in the UK, must focus on the sectors with the highest impact; agriculture, the water industry and urban development and transport. A good deal of work has already been done to tackle these issues including the Nitrate Directive and Water Framework Directive which aim to better control river pollutants (DEFRA, 2009; Maier *et al.* 2009a; Burt *et al.* 2011; European Environment Agency, 2021). However, more work and improved management strategies are still required.

In addition to scientific investigations, and those of the UK's statutory nature conservation bodies, it is important to consider the value of community groups and citizen science programs. Communication and outreach activities with local communities are important in helping to inform wider audiences on the potential threats faced by riverine environments (Walker *et al.* 2020; Metcalfe *et al.* 2022; Phillips *et al.* 2022). Citizen science can facilitate regular measurements and the creation of long-term datasets for specific parameters, where EA or other official monitoring programs are not active (Poisson *et al.* 2019; Walker *et al.* 2020; Phillips *et al.* 2022). They also allow for relationships to be built between communities and their river systems and encourage learning opportunities for individuals that may not normally interact with nature (Metcalfe *et al.* 2022; Phillips *et al.* 2022). Finally, these groups can empower communities to make change and lead to knowledge sharing between catchments, further supporting the improvement of river water bodies (Poisson *et al.* 2019; Walker *et al.* 2020; Phillips *et al.* 2022).

This project used Environment Agency data (Environment Agency, 2023b) and field study data to determine key pollutant types in the Yealm catchment, identify their sources and assess the potential impact of these on the key habitats within the estuary. In addition, the project worked with a local community group, Yealm Estuary to Moor (YEM) to provide recommendations on future management, and to highlight areas of concern. This relationship with the YEM community group has also facilitated knowledge exchange and data sharing.

1.2 Aims and Objectives

The overall aim of this project was to investigate pollutants in the Yealm estuary with a focus on those produced by sewage treatment facilities and agricultural practices. The secondary aim is to use the findings of this investigation to support the YEM community group in improving the water quality and biodiversity of the catchment through better management and nature-based solutions.

This project is guided by the following hypotheses

- **H1**: Concentrations of pollutants increase significantly downstream.
- **H2**: Concentrations of pollutants are significantly different in the first and last year of monitoring by the Environment Agency.
- **H3**: Pollutant concentrations increase at the sites of sewage treatment facilities.
- **H4**: There is a significant seasonal variation in all pollutants analysed.
- **H5:** Concentrations of pollutants at estuarine entry points reflect those in the water column at seagrass beds.
- **H6**: The health of seagrass beds is impacted by high concentrations of pollutant input from the Yealm catchment.

1.3 Literature Review

1.3.1 River Pollution

The pollution of UK rivers is well documented, with studies conducted on local catchment to national levels. Pollutant types and sources vary but are typically associated with land use changes that have occurred in the riparian environment (Hampson *et al.* 2010; Howden *et al.* 2013). In 2019, the Environment Agency stated that only 14% of English rivers were classified as having good ecological status, the highest contributors to this failure being chemical and phosphorus pollution (Environment Agency, 2023a).

Studies of riverine pollution both nationally and internationally tend to draw similar conclusions regarding the main sources of pollutants. These include agricultural practices, sewage treatment works, urban runoff, and groundwater discharges (Uncles *et al.* 2002; Matějíček *et al.* 2003; Edwards and Withers, 2008; Neal *et al.* 2010; Tappin *et al.* 2013; Florini *et al.* 2020; Garcia-Garcia *et al.* 2021).

The concern over the state of UK rivers has increased in recent years moving from a focus on the quality of drinking water, to the impact on biological systems within the river and riparian environment (Burt *et al.* 2011; Howden *et al.* 2013). Pollution in riverine systems can disrupt biological function in numerous ways. Changes in water chemistry can result in eutrophication, bacterial blooms, and reduced oxygen concentrations (Turner and Rabalais, 1994, Vitousek *et al.* 1997; Uncles *et al.* 2002; Edwards and Withers, 2008; Maier *et al.* 2009; de Klein and Koelmans, 2011; Howden *et al.* 2011; Tappin *et al.* 2013). Physical changes such as the introduction of plastics to the system can cause habitat loss and alter feeding behaviour (Bletter *et al.* 2018; van Emmerik and Schwarz, 2019; Windsor *et al.* 2019).

The behaviour of pollutants varies depending on whether they have diffuse or point sources. Diffuse pollution is defined as "pollution from widespread activities with no one discrete source" (European Environment Agency, 2023). A point source of pollution is "a stationary location or fixed facility from which pollutants are discharged; any single identifiable source of pollution" (European Environment Agency, 2023). Point and diffuse sources of pollution therefore interact differently with the underlying physical features of the catchment and vary a great deal with land use type (Hampson *et al.* 2010; Howden *et al.* 2013). For example, rural catchments typically are influenced more by diffuse pollutants from agricultural activity, while urban areas may have greater point source inputs (Richards *et al.* 2022).

Water condition, for example, flow rate and dissolved mineral content, are subject to spatial and temporal change on many levels. Varying from catchment to catchment depending on location, river hydrography and the geology of the surrounding area (Burt *et al.* 2011; Campos *et al.* 2011). Within catchment variations are driven by seasonal and interannual variability, and land use (Hannaford and Buys, 2012; Ledingham *et al.* 2019). Short term changes can also be triggered by weather events (Amirat *et al.* 2012). Subsequent fluctuations in river pollution are layered on top of these changes to water condition, thus making them difficult to predict.

Monitoring change in such environments can therefore be a challenge. An overall catchment baseline must be established and combined with a long-term dataset to ascertain changes to the system (Hannaford and Harvey, 2010; Burt *et al.* 2011; Howden *et al.* 2011). Assessments of this type are essential for developing pollution management strategies for both the riverine and riparian environments (Hannaford and Buys, 2012; Xu *et al.* 2019). Once established, these monitoring activities must be maintained to determine the success of management strategies, it may take at least 20-30 years for any real change to be observed (Burt *et al.* 2011; Howden *et al.* 2011).

The EU Water Framework Directive is a management strategy that aimed to achieve a "good ecological status" in all marine and freshwater systems by 2015 (Maier *et al.* 2009; Burt *et al.* 2011). This has now been extended to "achieve good status in all bodies of surface water and groundwater by 2027" (European Environment Agency, 2021). This goal is supported by the pre-existing 1991 Nitrate Directive, which acts to reduce nitrate pollution in EU rivers (DEFRA, 2009). As part of this directive 70% of the UK has now been designated as a Nitrate Vulnerable Zone (NVZ) (DEFRA, 2009) meaning there are strict limits on certain agricultural practices including manure and inorganic fertiliser applications (Burt *et al.* 2011; Howden *et al.* 2011). NVZs are allocated according to two factors; whether river waters are at risk of nitrate concentrations exceeding 50mg/L, and whether coastal waters are at risk of becoming eutrophic (Musacchio *et al.* 2019). The Yealm catchment is not classified as an NVZ and is therefore not subject to these strict controls (Research Centre of European Commission, 2019).

1.3.2 Estuarine Eutrophication and Seagrasses

One of the criteria for the allocation of NVZ is whether the coastal waters associated with a catchment are at risk of becoming eutrophic (Musacchio *et al.* 2019). Eutrophication is the altering of water chemistry through the addition of nutrients that leads to changes in species assemblage and dynamics (Davison and Hughes, 1998; van Katwijk *et al.* 2009; Calleja *et al.* 2017; Curiel *et al.* 2021). High nutrient concentrations trigger phytoplankton and algal blooms which out compete slower growing algal and seagrass species causing a loss of coverage (van Katwijk *et al.* 2009; Calleja *et al.* 2017; Curiel *et al.* 2021). Eutrophic events can lead to dramatic changes in not only plant assemblage but can also alter animal and bacterial populations (Calleja *et al.* 2017; Curiel *et al.* 2021). The loss of key habitats such as seagrass could result in the loss of important commercial fish species as well as protected species including the long-snouted seahorse (Waycott *et al.* 2009; The Plymouth Sound and Estuaries SAC, 2021). The change in these population dynamics can lead to trophic collapse and a loss of ecosystem functioning (van Katwijk *et al.* 2009; Calleja *et al.* 2017; Curiel *et al.* 2021).

Nutrient pollution entering river water in the catchment can therefore have drastic implications for estuarine habitats. Seagrass beds are one such habitat. Seagrasses are one of the most diverse and productive coastal habitats in the UK, providing numerous benefits to their surrounding environment as well as the human population (Hemminga and Duarte, 2000; Waycott *et al.* 2009).

The importance of seagrass can be roughly grouped into three categories; their role as ecosystem engineers, as a physical barrier between estuarine and coastal waters, and as a carbon sink (Hemminga and Duarte, 2000; Nelleman *et al.* 2009; Cullen-Unsworth and Unsworth, 2013; Ramesh, *et al.* 2019).

Seagrass habitats are some of the most diverse and productive ecosystems on earth, rivalling that of coral reefs and rainforests (Waycott *et al.* 2009). They provide high quality habitat for numerous species including commercially important fish species and protected species such as seahorses (The Plymouth Sound and Estuaries SAC, 2021). They act as a source of organic matter to coastal ecosystems, are an integral part of trophic food webs (Curiel *et al.* 2021), and play a vital role in nutrient cycling and nitrogen fixation (Davison and Hughes, 1998; Diekmann *et al.* 2010; Curiel *et al.* 2021.

The physical structure of seagrass beds provides several benefits. The complex root structures stabilise the sediments, reducing erosion (Diekmann *et al.* 2010; Potouroglou *et al.* 2021). Their densely packed leaves reduce wave energy, triggering sedimentation and providing coastal protection (Paul and Amos, 2011; Curiel *et al.* 2021). Seagrass beds also help to filter water, removing both pollutants and pathogens from the water column (Short and Wyllie-Echeverria, 1996; Potouroglou *et al.* 2021).

Seagrasses act as carbon sinks, taking in and storing carbon dioxide in the form of biomass (Nelleman *et al.* 2009; Fourqurean *et al.* 2012; Duarte *et al.* 2013). As the seagrass plants grow, they take in carbon dioxide through photosynthesis, storing it within their leaves and roots as organic carbon (Nelleman *et al.* 2009; Fourqurean *et al.* 2012; Duarte *et al.* 2013). When the plants die, the organic carbon becomes stored in the root bed and sediment beneath the seagrass (Nelleman *et al.* 2009; Fourqurean *et al.* 2012; Duarte *et al.* 2013). The structural stability of the seagrass enables large amounts of carbon to be stored in this way over long periods of time (Nelleman *et al.* 2009; Fourqurean *et al.* 2012; Duarte *et al.* 2013). Seagrass beds are considered a blue carbon ecosystem with the potential to store 140 Mg C ha^{-1} (Blue Carbon Initiative, 2023).

Despite their importance, seagrass ecosystems face chemical, physical and biological threats (Duarte, 2002; Grech *et al.* 2012; Unsworth *et al.* 2019).

Physical removal of seagrasses occurs in several ways, the most common being static moorings, coastal development, extreme sea surface temperatures and storm damage (Ondiviela *et al.* 2014; Smale *et al.* 2019; Unsworth *et al.* 2022).

The chemical and biological threats to seagrass are linked. In the UK, the most influential threat to seagrass comes from agricultural runoff (Grech *et al.* 2012). The introduction of both inorganic and organic fertilisers into the estuarine system increase turbidity, reducing the light available for photosynthesis (Davison and Hughes, 1998). The reduction in photosynthetic potential then reduces seagrass coverage, lessening its ability to filter water, further increasing the turbidity within the water column (van der Heide *et al.* 2007). In addition, nutrient pollutants from agricultural and sewage infrastructure cause eutrophication leading to an increase in both phytoplankton abundance and macroalgal growth, further reducing the light and nutrients available for seagrass growth; resulting in a shift in species assemblage and ecosystem function (van Katwijk *et al.* 2009; Calleja *et al.* 2017; Curiel *et al.* 2021).

Changes in seagrass coverage are being monitored on a global scale, some papers reporting as much as a 1-7% overall loss in coverage annually (Unsworth *et al.* 2022; Dunic *et al.* 2021; Waycott *et al.* 2009). In the UK seagrass losses are at least 44% since 1936, 39% of which was since 1980 (Green *et al.* 2021). Extend this timeline and this number could be up to 92% (Green *et al.* 2021). This loss of seagrass is of great concern as seagrass beds provide numerous benefits both to the marine environment and to humans, locally and globally (Unsworth *et al.* 2022; Dunic *et al.* 2021; Cullen-Unsworth and Unsworth, 2013; Waycott *et al.* 2009).

Seagrasses are considered a high conservation priority as they are both valuable and vulnerable (Davison and Hughes, 1998; Diekmann *et al.* 2010). As such they are protected under policies including the Bern Convention, the EU Water Framework Directive and Wildlife and Countryside Act 1981 (Curiel *et al.* 2021; Green *et al.*, 2021).

The threats faced by seagrass beds become amplified in transitional environments including that of the Yealm estuary (Curiel *et al.* 2021). The seagrass beds of the Yealm are made up predominantly of *Zostera noltei* which is considered a Priority Habitat under the UK Biodiversity Action Plan (Tyler-Walters, 2005). The presence of moorings in Cellar's cove has been the topic of many discussions surrounding local seagrass management (Bunker and Green 2018). Conservation efforts are being conducted nationally to protect these ecosystems, most notably in the Plymouth Sound and Estuaries SAC is the Life ReMEDIES project. This project aims to increase seagrass coverage through, out-planting, education and alternatives to traditional static moorings. However, the main sites of out-planting include Jennycliff Bay and Cawsand Bay and do not currently cover the Yealm estuary (Life Creation ReMEDIES, 2023).

1.3.3 The Yealm Estuary

The Yealm catchment is an ideal study site for several reasons. The catchment comprises many habitat types from blanket moorland to riparian woodland and estuarine seagrass beds (Yealm Estuary to Moor, 2022). It also has a wide variety of land use types including small towns, agricultural land and is home to several industrial activities including China Clay quarries and sewage treatment facilities (Yealm Estuary to Moor, 2022). The Yealm catchment holds several designations including being part of the South Devon Area of Natural Beauty (AONB), the Plymouth Sound and Estuaries SAC and has SSSI regions throughout the catchment (Yealm Estuary to Moor, 2022). The combination of protected/valuable habitats and the potential for pollution in this small catchment makes it an interesting area for research (JNCC, 2016; Yealm Estuary to Moor, 2022).

In addition, the Environment Agency has been monitoring many sites throughout the catchment since the year 2000 (Environment Agency, 2023b). A range of parameters have been measured at these sites which will provide an overview of the dominant pollutant types within the catchment and the change in water quality over time.

The final reason for the selection of the Yealm catchment is the activities of the Yealm Estuary to Moor (YEM) group. This community group aims "to link fragmented habitats, such as wetlands, woodlands and species rich grassland, along the River Yealm from coastal estuary to moorland source, to create a continuous in-river and riparian wildlife corridor" (Yealm Estuary to Moor, 2022). Through the hard work of community members, a citizen science program has been established and a continuous recorder installed to measure water quality, a schools' initiative to grow tree saplings has been established, land management through the planting of trees and communication with landowners is ongoing, and numerous individuals have become involved to spread their message of improving the biodiversity within the catchment (YEM corridor, 2023).

As such, the Yealm provides an excellent study location, not only because of the wealth of data available for such a project, but because of the wide variety of valuable habitat in close proximity to potentially damaging land-use practices in both the industrial and agricultural sectors.

2.1 Environment Agency Data Analysis

2.1.1 Data sources

The Environment Agency (EA) has a national network of river stations at which they take regular samples of several parameters. Throughout the Yealm catchment there are 69 of these stations. Monitoring at these stations varies both in the parameters measured and the timescales measurements are taken. Data is free to download and a list of station ID numbers in the Yealm catchment is also available (Environment Agency, 2023b).

Measurements of rainfall within the catchment also proved a useful tool. This data is free to download through the National River Flow Archive (National River Flow Archive, 2023b). Measurements were taken daily at the Puslinch Bridge monitoring station, which is situated at the base of the River Yealm, before it joins the estuary.

2.1.2 Station selection

When selecting stations from the EA database it was important to provide a representative picture of the state of the water throughout the Yealm catchment. In addition, stations with long timescales were vital to analyse changes over time. Furthermore, a wide variety of parameters needed to be measured at chosen stations to allow for an in-depth investigation into pollutant types within the catchment.

The following process was undertaken to select nine stations and ten parameters of interest (Figure 1). The five-year cut off was chosen as any dataset shorter than this would not be sufficient to demonstrate changes in parameters over time, in fact, stations with the longest datasets were prioritised. Parameters of interest were narrowed down by both the data available, and their association with pollutant sources and land use types found throughout the Yealm catchment.

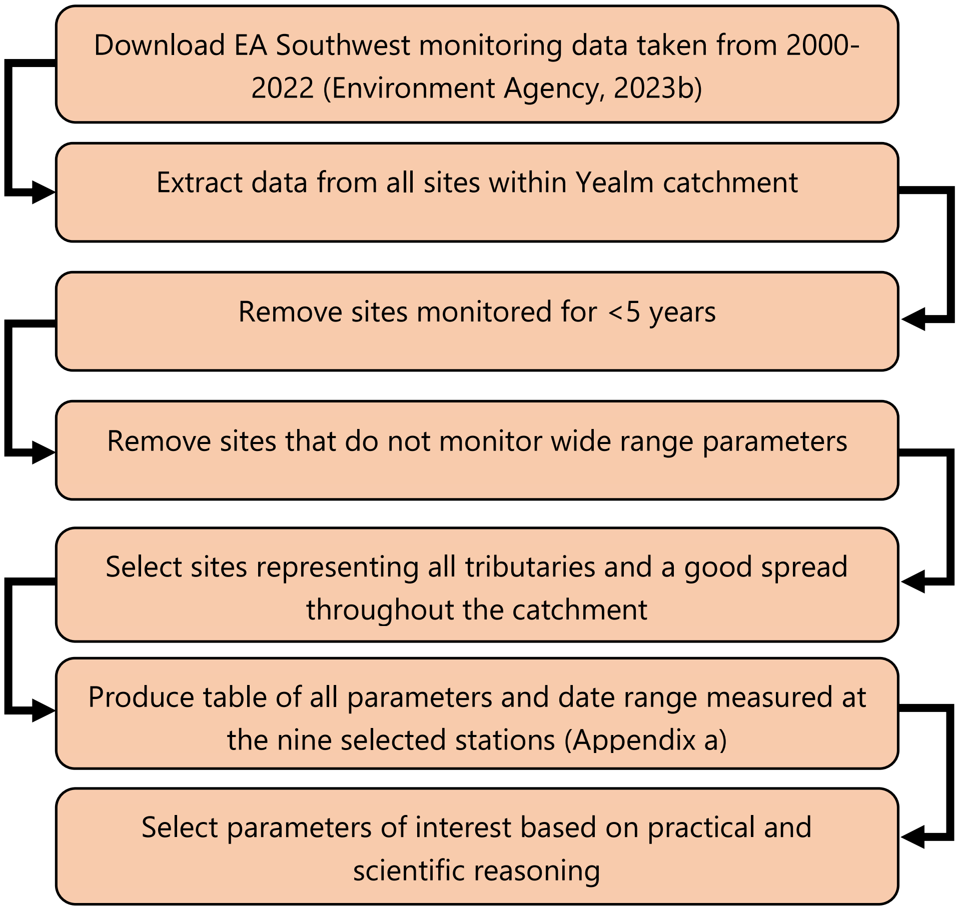


Figure 1: *Flow chart describing the process by which nine stations and ten parameters of interest were selected.*

The nine stations selected are plotted in Figure 2. In addition to covering a representative area within the catchment, eight of the nine stations align with those monitored by the YEM group citizen science program. The numbering of stations going forward will be consistent with the YEM group stations; with the exception of YLM25 which represents the furthest upstream sampling point and is not monitored by the YEM group.

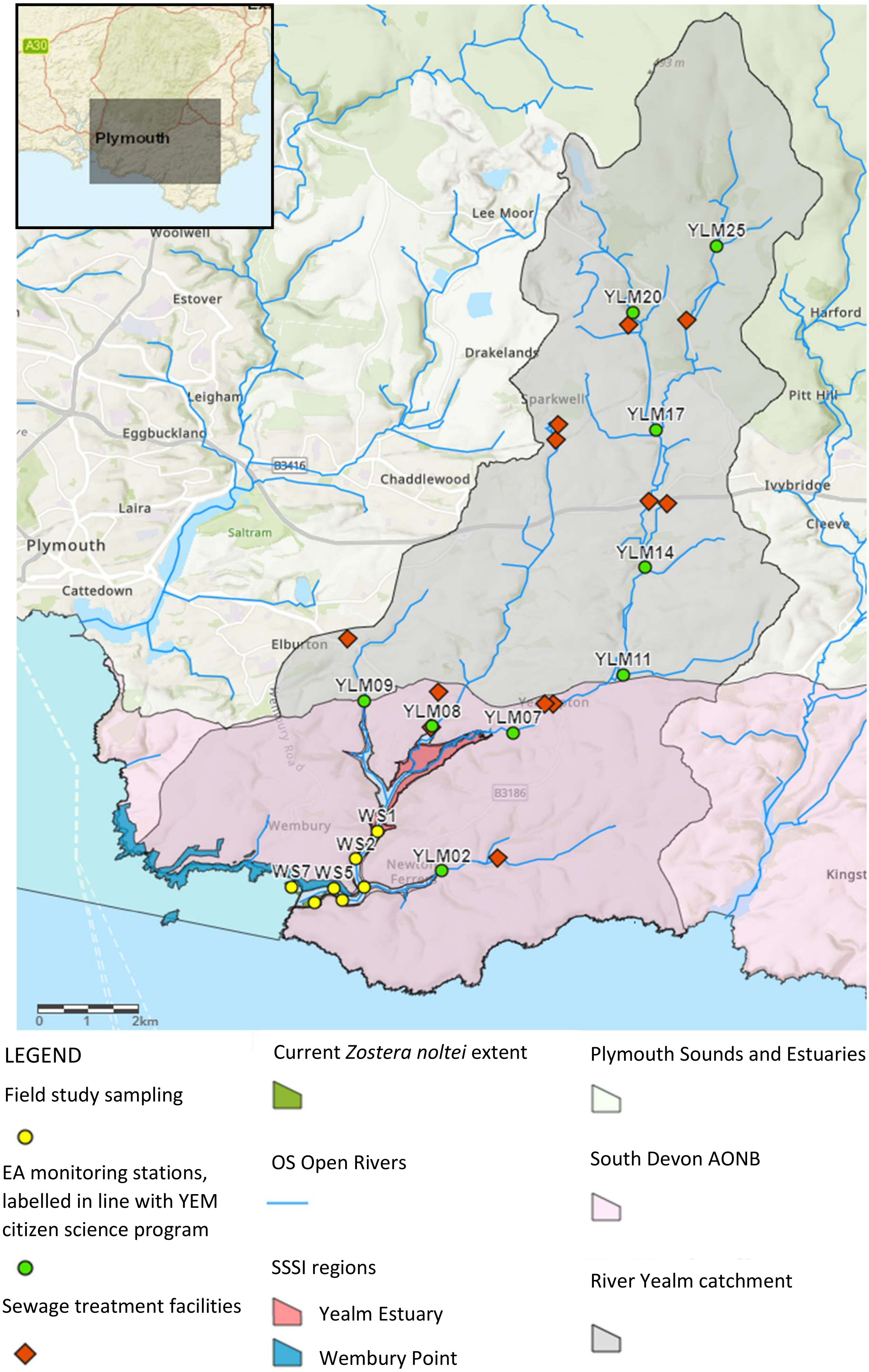


***Figure 2**: Map the Yealm catchment, highlighting SAC, SSSI, AONB designations, sewage treatment facilities and sampling stations.*

2.1.3 Parameter selection

The ten parameters of interest selected are listed below. A brief investigation into metal and chemical concentrations was also included for completeness, however, data on these parameters were taken over short and irregular intervals.

- Ammoniacal nitrogen as N (mg/L)
- *Enterococci*: intestinal (no/100ml)
- *Escherichia coli*: (no/100ml)
- Nitrate as N (mg/L)
- Orthophosphate, filtered as P (mg/L)
- Solids, suspended at 105°C (mg/L)
- Temperature (°C)
- Dissolved oxygen (mg/L)
- % oxygen saturation (%)
- BOD 5-day (mg/L)

Ammoniacal nitrogen is a measure of the ammonia concentration in the water column. Ammonia is a toxic pollutant associated with the presence of faecal matter and other waste products (Uncles *et al.* 2002). High concentrations of ammoniacal nitrogen in the water column could result in eutrophication and can be toxic to aquatic life (Li *et al.* 2020).

Enterococci and *Escherichia coli* (*E.coli*) are bacteria found in both animal and human faecal matter (Suzuki *et al.* 2011; Florini *et al.* 2020; Garcia-Garcia *et al.* 2021). The contamination of shellfish with both *E.coli* and *Enterococci* can be damaging not only to the shellfish but also to those farming, selling and consuming them (Garcia-Garcia *et al.* 2021).

The presence of nitrate in the water is part of the natural chemistry of the river. However, increases in the concentration can be indicative of pollution from wastewater treatment plants, agricultural waste and run off and urban runoff (Uncles *et al.* 2002; Matějíček *et al.* 2003; Edwards and Withers, 2008). While nitrate is important for plant growth, high concentrations can result in an imbalance leading to eutrophication (Uncles *et al.* 2002; Matějíček *et al.* 2003; Edwards and Withers, 2008).

Orthophosphate is the simplest and most common form of phosphorus dissolved in water. Like nitrate, orthophosphate varies naturally though increased concentrations indicating pollution from several potential sources (Tappin *et al.* 2013). Such sources include agricultural fertilisers, industrial and urban waste, and soil erosion (Neal *et al.* 2010; Tappin *et al.* 2013). Like nitrate, high orthophosphate concentrations can result in eutrophic events (Uncles *et al.* 2002; Matějíček *et al.* 2003; Edwards and Withers, 2008).

The presence of suspended solids in the water column is also a natural process, building up through sediment resuspension and runoff over soils, the concentrations fluctuate according to river flow and precipitation (Edwards and Withers, 2008; Nnane *et al.* 2011). However, high concentrations can also suggest input into the water column including clay and sewage (Edwards and Withers, 2008). High suspended solids concentrations increase turbidity, reducing the light available for photosynthesizing organisms, and extreme cases maybe result in reduced dissolved oxygen content (Bilotta and Brazier, 2008).

The concentration of oxygen and % oxygen saturation within the water column act as an indicator of water quality (Braukmann and Böhme, 2011; Bozorg-Haddad *et al.* 2021).

Biological oxygen demand (BOD) measures the amount oxygen required to decompose organic substances by aerobic microorganisms in a water sample, thus, lowering dissolved oxygen concentrations (Nemerow, 1974; Tchobanoglous and Schroeder, 1985).

2.2 Methods

Data were downloaded from the Environment Agency and manipulated in Excel. Data visualisation and analysis were conducted using Minitab, RStudio, ArcGIS, PRIMER and QGIS. Data were not normally distributed, exhibiting strong positive skew as many values did not exceed the detection limit of monitoring equipment. All data below the detection limit were recorded as half the detection limit, this value varied with each parameter. Data remained skewed following transformations, as such non-parametric testing was used. Figure 3 shows a summary of data processing and analysis.

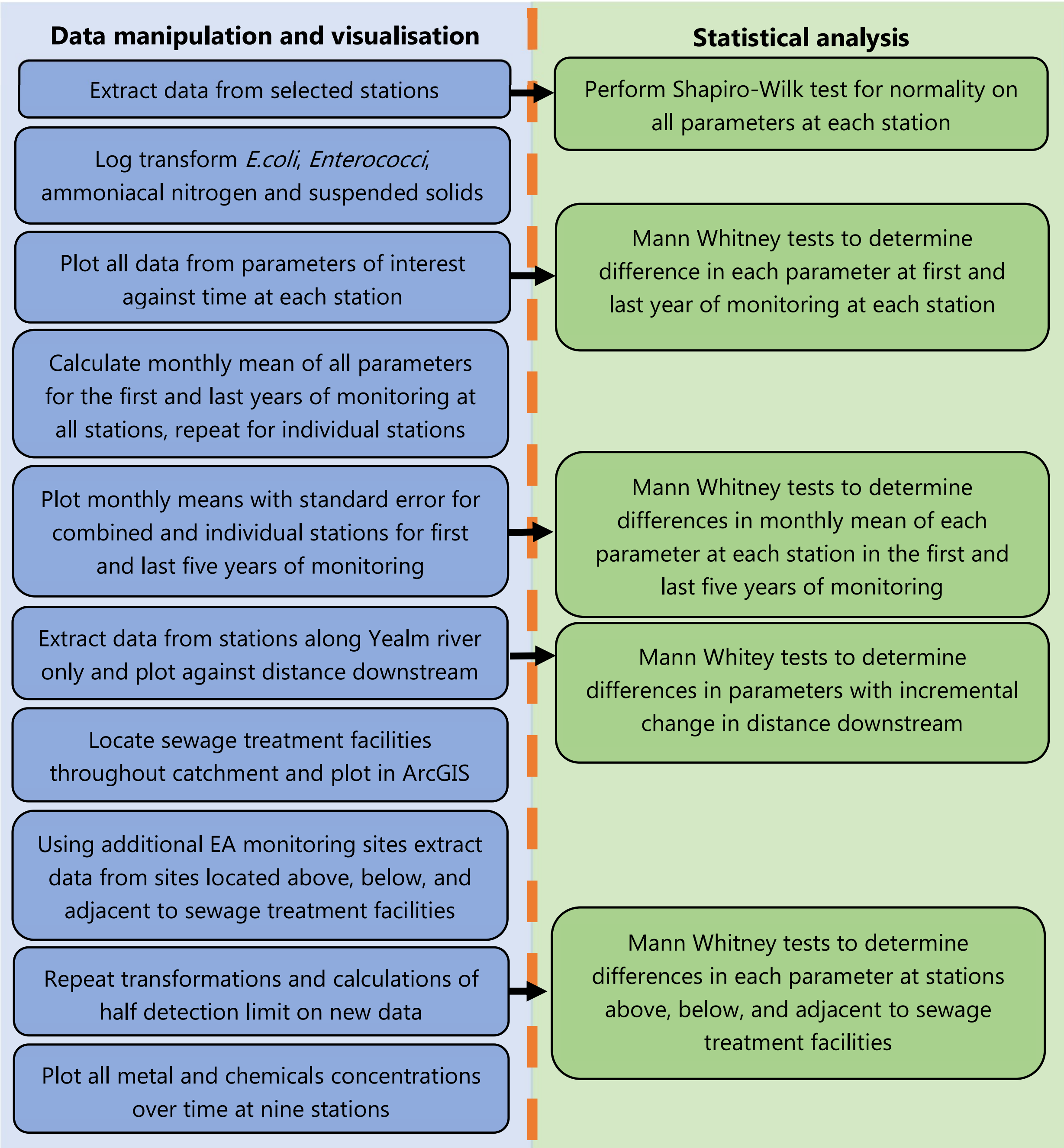


Figure 3: *Flow chart describing the EA process by which data were processed and analysed.*

2.3 Results

The results of the EA data investigation are broken into six sections. The findings presented generate a picture of the current state of the water within the Yealm catchment, highlight how this has changed in the past 20 years, and indicate what pollutants are entering the estuarine system.

2.3.1 Annual variation of parameters

Investigating the annual variation in parameters provides a picture of how the inputs and water quality of the rivers and tributaries in the Yealm catchment have changed over time. The complete dataset from each of the nine selected Environment Agency monitoring stations was used in this investigation.

Data are presented in scatter plots with overall trend lines at each station to provide a visual indication of change (Figure 4). Figure 4a clearly indicates a decrease in nitrate concentration over time at most stations. It also shows that stations further upstream (YLM25 and YLM20) have more consistent, and lower concentrations that may not have changed significantly over time. Orthophosphate concentrations are more variable, exhibiting both increases and decreases over time depending on the station. Downstream stations appear more variable.

A series of Mann Whitney tests were conducted to better determine statistically significant differences between monitoring years. Tests were conducted using all data from the first and last years of monitoring at each station. Results are presented in Table 2.

Figure 4: *Scatter plots of all EA monitoring data collected between 2000 and 2022. Stations distinguished with different colours. Overall trend plotted for each station. a) Nitrate b) Orthophosphate.*

Table 2: *Results from a series of Mann Whitney tests to determine differences in parameters at each station in their first and last year of monitoring. Statistically significant results in bold are highlighted blue for increase and yellow for decrease.*

Parameter	Station ID	Year range	Median	Median	p-value
Nitrate	YLM02	2007-2022	**5.965**	**5.145**	**0.000**
	YLM07	2000-2021	**2.65**	**1.99**	**0.025**
	YLM08	2007-2019	**3.8**	**2.8**	**0.000**
	YLM09	2007-2019	**6.64**	**4.80**	**0.000**
	YLM11	2000-2019	**3.930**	**3.115**	**0.005**
	YLM14	2000-2016	**1.975**	**1.560**	**0.006**
	YLM17	2000-2022	1.085	1.300	0.055
	YLM20	2009-2022	**0.506**	**0.856**	**0.003**
	YLM25	2000-2022	**0.471**	**0.266**	**0.002**
Orthophosphate	YLM02	2007-2022	**0.1095**	**0.1400**	**0.013**
	YLM07	2000-2021	0.0365	0.0770	0.310
	YLM08	2007-2019	0.020	0.021	0.154
	YLM09	2007-2019	**0.060**	**0.385**	**0.000**
	YLM11	2000-2019	0.0575	0.061	0.831
	YLM14	2000-2016	**0.034**	**0.024**	**0.032**
	YLM17	2000-2022	0.032	0.040	0.704
	YLM20	2009-2022	na	na	na
	YLM25	2000-2022	0.005	0.005	0.580
Ammoniacal nitrogen	YLM02	2007-2022	0.015	0.015	0.389
	YLM07	2000-2021	0.0235	0.015	0.767
	YLM08	2007-2019	**0.015**	**0.0465**	**0.001**
	YLM09	2007-2019	**0.068**	**0.038**	**0.008**
	YLM11	2000-2019	na	na	na
	YLM14	2000-2016	0.033	0.015	0.269
	YLM17	2000-2022	0.042	0.015	0.204
	YLM20	2009-2022	0.015	0.015	0.769
	YLM25	2000-2022	0.015	0.015	0.769
E.coli	YLM02	2007-2022	930.5	1100	0.254
	YLM08	2007-2019	**205**	**435**	**0.029**
	YLM09	2007-2019	**5000**	**1477.5**	**0.000**
	YLM11	2007-2019	**1458**	**425**	**0.000**
	YLM14	2007-2016	1326	2204.5	0.611
	YLM17	2007-2022	**1095.5**	**2300**	**0.010**
	YLM20	2009-2015	121	135	0.847
	YLM25	2007-2016	**18**	**5**	**0.046**
Enterococci	YLM02	2012-2022	270	480	0.395
	YLM08	2012-2019	108	153	0.681
	YLM09	2012-2019	710	785	0.631
	YLM11	2012-2019	243	215	0.608
	YLM14	2012-2016	270	325	0.726
	YLM17	2012-2022	390	730	0.351
	YLM20	2012-2015	45	54	0.474
	YLM25	2012-2016	na	na	na
Suspended solids	YLM02	2008-2022	11.2	12.0	0.933
	YLM08	2014-2019	**8.23**	**16.58**	**0.001**

	YLM09	2008-2019	6.50	9.75	0.179
	YLM11	2007-2019	4.9	4.6	0.850
	YLM14	2007-2016	1.5	3.415	0.536
	YLM17	2005-2022	6.2	5.8	0.460
	YLM20	2009-2015	1.5	4.53	0.276
	YLM25	2007-2022	1.5	1.5	0.383
Temperature	YLM02	2007-2022	12.39	12.55	0.729
	YLM07	2000-2021	11.75	12.65	0.908
	YLM08	2007-2019	14.71	11.55	0.590
	YLM09	2007-2019	11.89	11.45	0.679
	YLM11	2000-2019	13.00	11.55	0.339
	YLM14	2000-2016	**11.7**	**8.5**	**0.022**
	YLM17	2000-2022	11.8	12.8	0.820
	YLM20	2009-2022	11.5	13.4	0.064
	YLM25	2000-2022	10.70	12.05	0.212
Dissolved oxygen	YLM02	2013-2018	11.60	10.25	0.224
	YLM07	2000-2021	10.5	10.3	0.869
	YLM11	2000-2006	10.3	10.5	0.712
	YLM14	2000-2016	10.35	10.45	1.000
	YLM17	2000-2016	10.35	10.70	0.716
	YLM20	2014-2022	10.65	10.50	0.247
	YLM25	2000-2022	10.7	11.1	0.193
% oxygen saturation	YLM02	2007-2018	**102.45**	**95.75**	**0.002**
	YLM07	2000-2021	98.0	97.8	0.773
	YLM08	2000-2007	98	100	0.166
	YLM14	2000-2016	97.5	97.9	0.671
	YLM17	2000-2016	96.5	98.9	0.275
	YLM20	2014-2022	100.65	100.50	0.969
	YLM25	2000-2022	**97**	**101.15**	**0.000**
BOD 5-day	YLM07	2000-2006	1.15	0.5	0.312
	YLM11	2000-2006	**1.15**	**0.5**	**0.026**
	YLM14	2000-2006	1.2	0.5	0.277
	YLM17	2000-2013	1.200	0.825	0.335
	YLM25	2000-2006	0.5	0.5	0.751

Using both the Figure 4 and Mann Whitney tests it is clear that few parameters change between the first and last year of monitoring. While there were fluctuations in some parameters over time, for the most part these were not statistically significant and therefore did not indicate a change in water quality.

Nitrate was the only parameter to exhibit an overall decrease in concentration, with only two exceptions. This could be the result of stricter regulations to reduce the amount of nitrate entering riverine systems (DEFRA, 2009; European Commission, 2023).

Orthophosphate concentrations increased significantly at stations YLM02 and YLM09 suggesting between that 2007 and 2019/2022 a new source of orthophosphate has entered the system.

The concentrations of *E.coli* showed variable changes over time exhibiting both significant increases and decreases. Further investigations into station specific changes are required. In addition, it is important to note that for *E.coli* and *Enterococci*, 48.8% and 18.1% of measurements were greater than the bathing water standards for each bacterium respectively. The majority of these high values were found at stations YLM02, YLM09 and YLM17, in total, measurements at these stations accounted for 65% of values above the safe bathing limit for both *E.coli* and *Enterococci*.

Little significant change has occurred over time for most parameters indicating that water quality in the Yealm catchment has been relatively stable. Monitoring of this kind must continue to monitor any future changes. Detail in the results may have been missed for three reasons. Firstly, that the dataset may not yet be long enough to exhibit any real change over time, secondly, the large variability in the raw data may have skewed the results causing a loss of some of the detail, and thirdly, many values did not exceed the detection limit of monitoring equipment.

2.3.2 Seasonal variation

Monthly nitrate, orthophosphate, suspended solids and *E.coli* concentrations were averaged over the first and last five years of monitoring. Nitrate, orthophosphate and suspended solids time frames are 2005-2009 and 2018-2022, *E.coli* time frames were 2007-2011 and 2018-2022 as monitoring began later. The monthly averaged concentrations can be compared to determine changes over time both on an interannual and seasonal basis. The standard error for each was also plotted to observe the differences in variance between months. A series of Mann Whitney tests was also conducted (Table 3).

Nitrate concentration appears to follow slight a seasonal pattern, declining during the summer months (Figure 5). This pattern is consistent between the time periods measured, though during the 2018-2022 period the summer low is extended, concentrations remained low in August and September. In addition, there was a drop in nitrate concentration in January 2005-2009 compared to higher concentrations in 2018-2022. There was little significant difference between months in each time period, indicating at though a seasonal change can be seen, it is not significant (Table 3). Additionally, when comparing months from each time period, only one significant difference was highlighted, this difference was measured in August, providing further evidence of an extended summer in 2018-2022.

In Figure 6 the mean monthly concentrations were plotted at each station allowing further comparisons to be made. The nitrate concentrations during the 2005-2009 period were higher at stations YLM02, YLM07, YLM08, YLM09, YLM11 and YLM20. The greatest variability in the concentrations was observed at stations YLM07, YLM08 and YLM09. During the 2018-2022 period the stations with highest variability were YLM07 and YLM09. Measurements taken at YLM25 remained low in both timeframes, this station was the furthest upstream.

Therefore, it is evident that nitrate concentrations exhibit some seasonal variation but that variation between stations must also be monitored. The overall concentrations of nitrate have decreased over time however, some stations continue to exhibit a great deal of variation, while stations further upstream change very little.

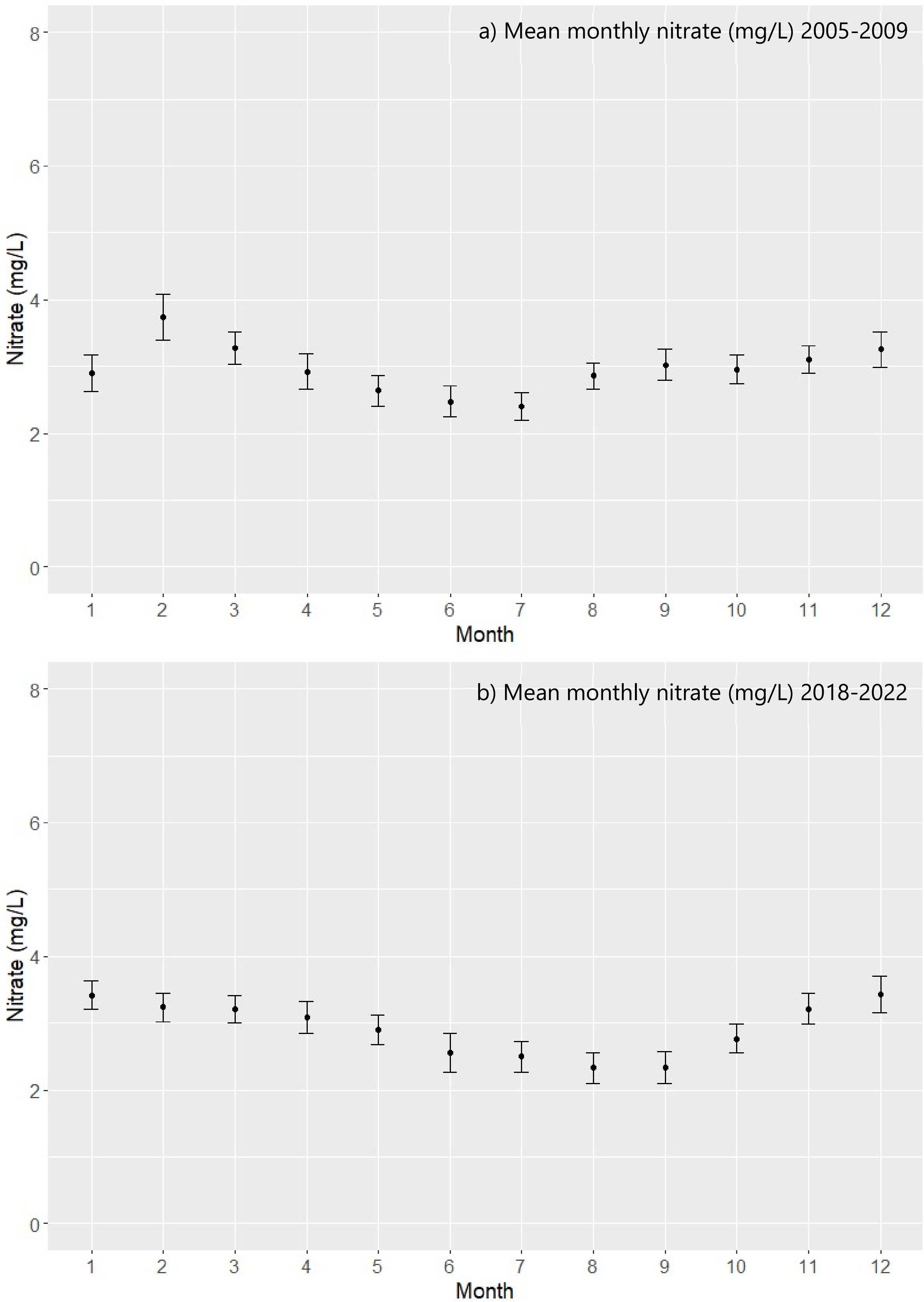
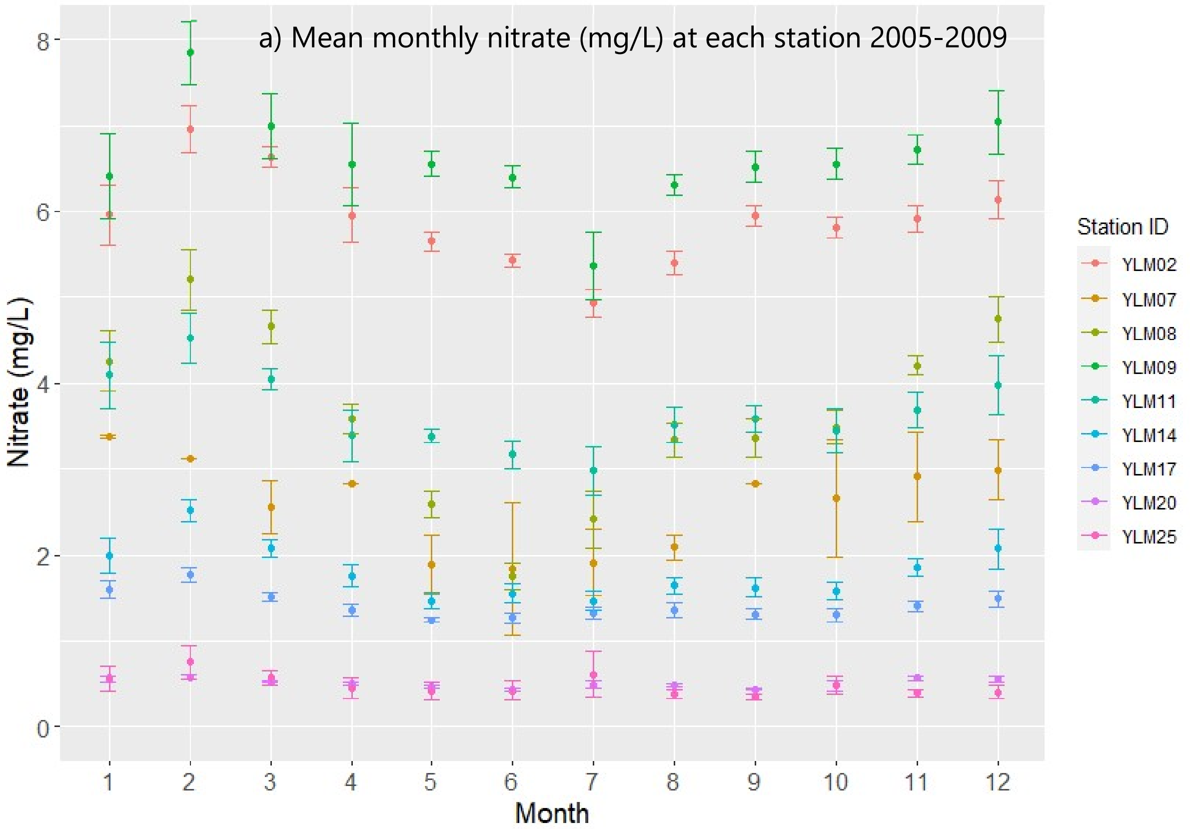


Figure 5: *Mean monthly nitrate concentrations (mg/L) averaged from EA data collected at nine stations from a) 2005-2009 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*



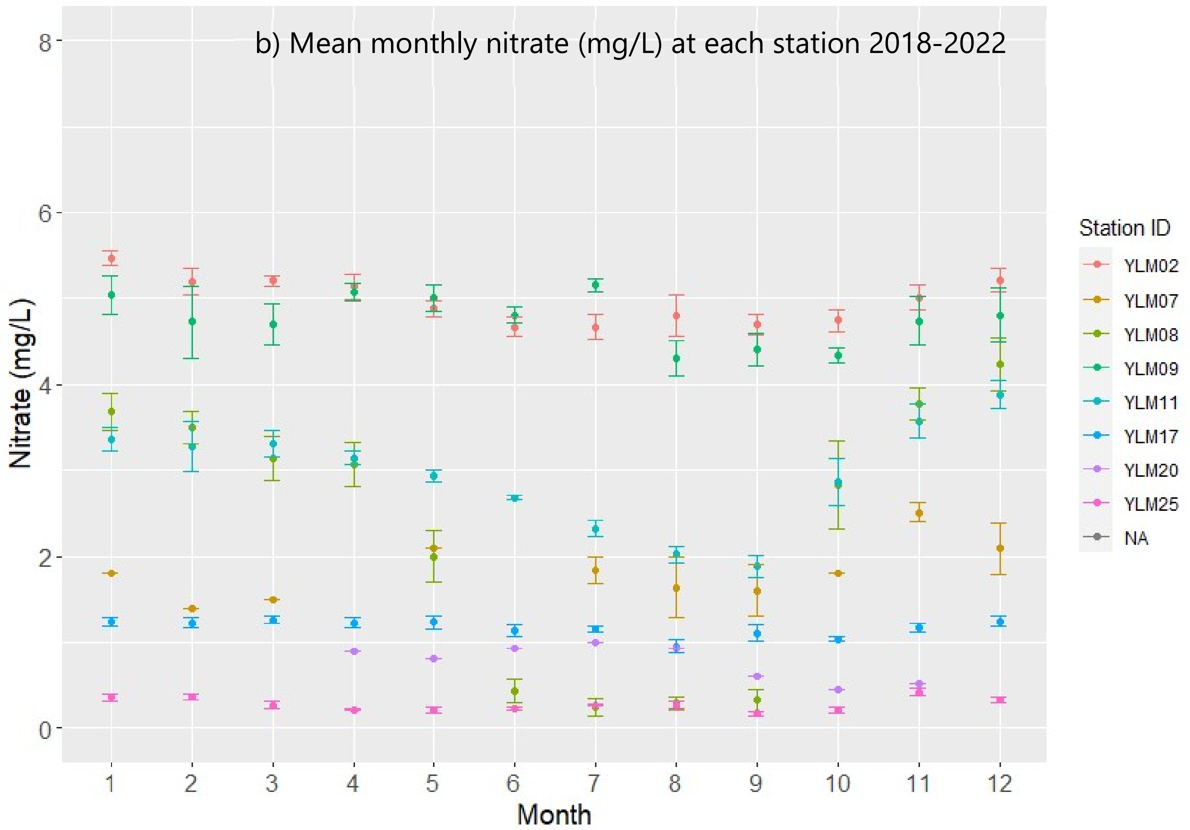


Figure 6: *Mean monthly nitrate concentrations (mg/L) averaged at each of the nine preselected stations measured by the EA in a) 2005-2009 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*

Mean orthophosphate concentrations exhibit an increase during summer and autumn during both time periods (Figure 7). A gradual increase during the spring is clear in 2018-2022 while a more abrupt increase is evident in 2005-2009.

In 2005-2009 orthophosphate concentration is much higher in January than in 2018-2022, however, looking at the station breakdown (Figure 8), it is evident that this high mean concentration can be explained by high concentrations with high variability measured at YLM02, YLM07 and YLM09.

Additionally, during the 2018-2022 period the variation was greater in the summer and autumn months when concentrations are at their highest, 2005-2009 exhibits a similar pattern though to a lesser extent. In both time periods the stations with the highest variability are YLM02 and YLM07, these stations also represent the highest concentrations suggesting there are orthophosphate inputs in these areas. YLM25 also exhibits high variability during the 2018-2022 period. Similarly to nitrate, the seasonal patterns in orthophosphate were not significant within either time period (Table 3). However, when comparing the two, there were significant increases in concentration between 2005-2009 and 2018-2022 in May, July, August, and September.

To gain a better understanding of the orthophosphate concentrations and thus produce effective management strategies, focus needs to be drawn to highly variable, high concentration regions. YLM02 and YLM07 located at Newton stream and at Puslinch Bridge are two such regions. It would also be valuable to take additional measurements of spring and summer orthophosphate concentrations as this is where the greatest increases have occurred between the two time periods.

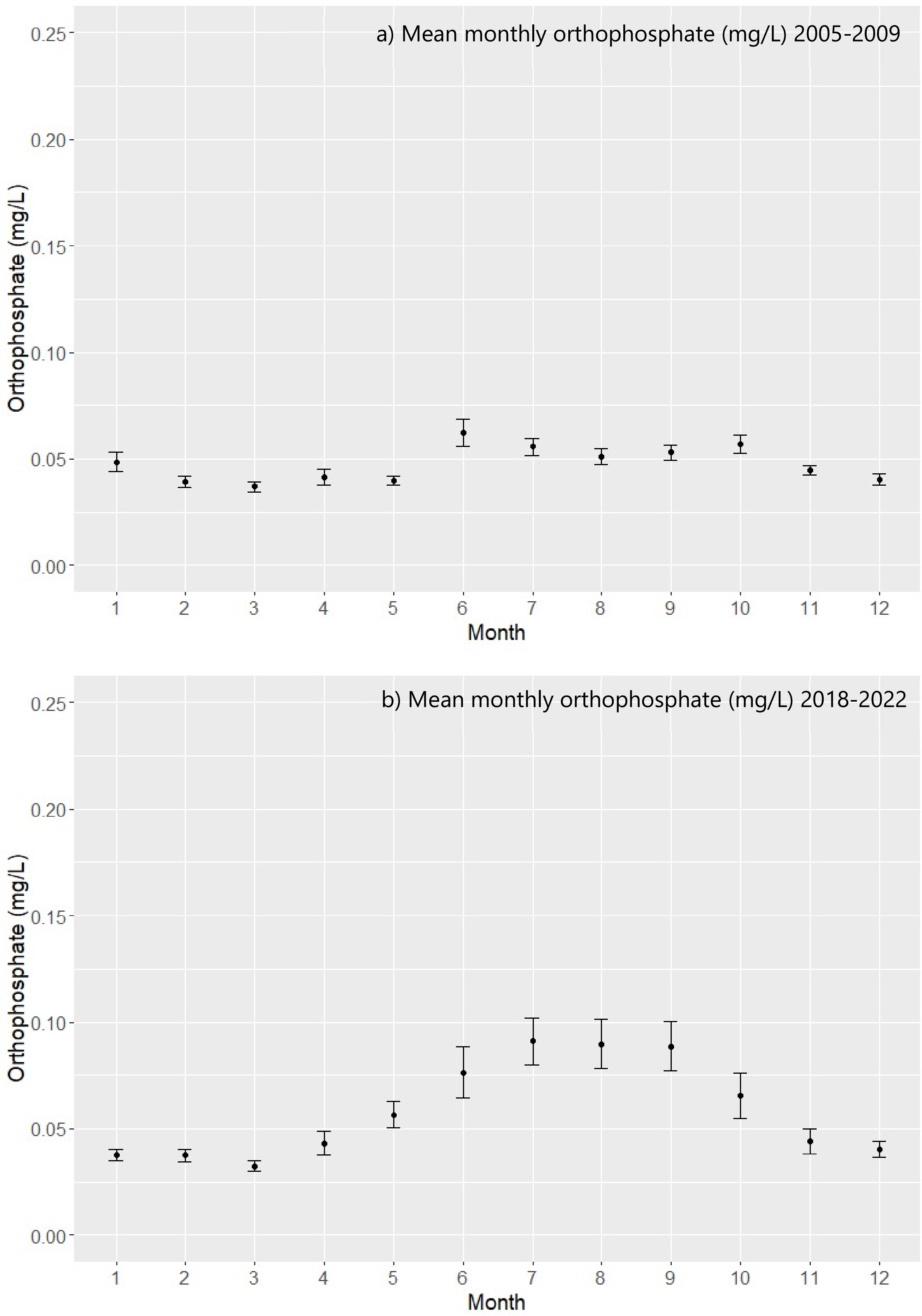


Figure 7: *Mean monthly orthophosphate concentrations (mg/L) averaged from EA data collected at nine stations from a) 2005-2009 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*

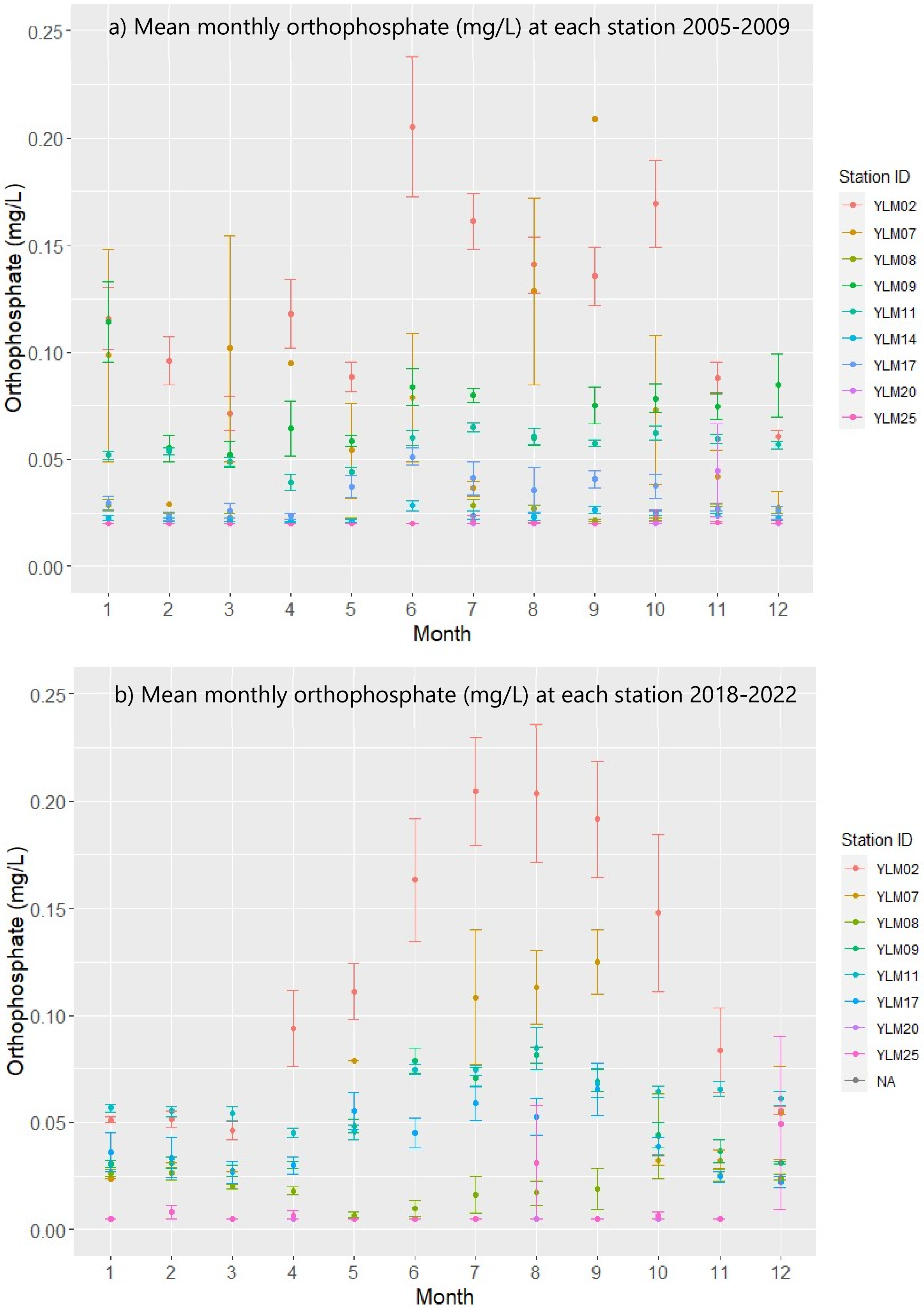


Figure 8: *Mean monthly orthophosphate concentrations (mg/L) averaged at each of the nine preselected stations measured by the EA in a) 2005-2009 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*

Mean suspended solids concentrations did not exhibit a strong seasonal variation except for a slight increase during the winter months, likely explained by greater rainfall (Figure 9).

During the 2018-2022 period the variablity of measurements was lower in general than 2005-2009, with the exception of February and May which exhibit a great deal of variation. Using the station breakdown (Figure 10), it was evident that this variation came from measurements taken at YLM09, YLM11 and YLM17. During the 2005-2009 period the greatest variability in measurements was also observed at YLM09, and at stations YLM02 and YLM20. The concentrations of suspended solids showed very little significant difference between monthly measurements in 2005-2009 or 2018-2022 (Table 3). However, when comparing the two time periods there was a significant difference. In ten of the twelve months, the concentration measured in 2018-2022 was significantly higher than that of 2005-2009.

There was no clear seasonal change in the suspended solids concentrations, however, a clear increase between the two time periods is evident. As such, work must continue to reduce suspended solids, particularly targeting large input events. Such events are likely caused by excessive rainfall, and/or are associated with industrial activities such as the China Clay works at Lee Mill.

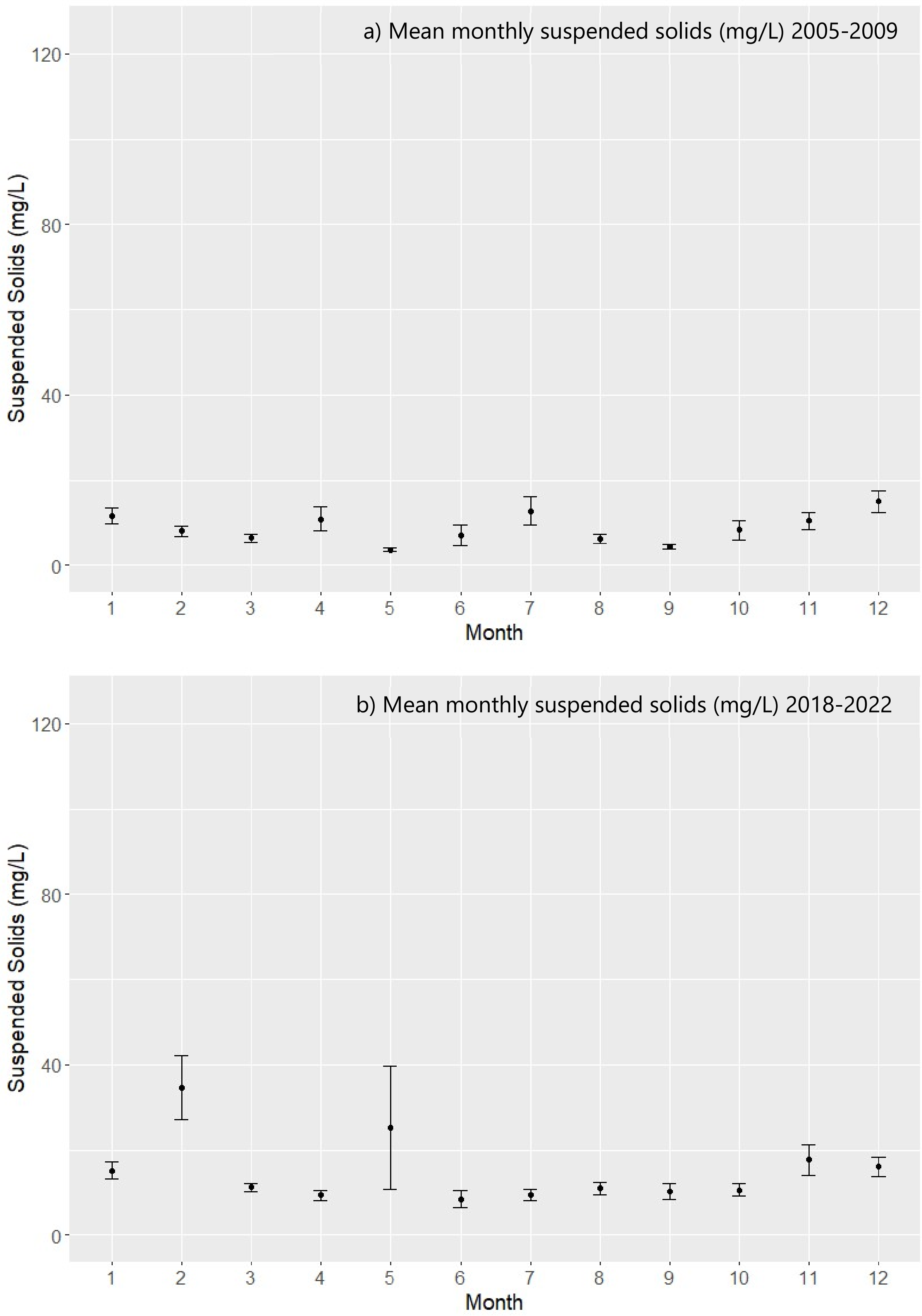
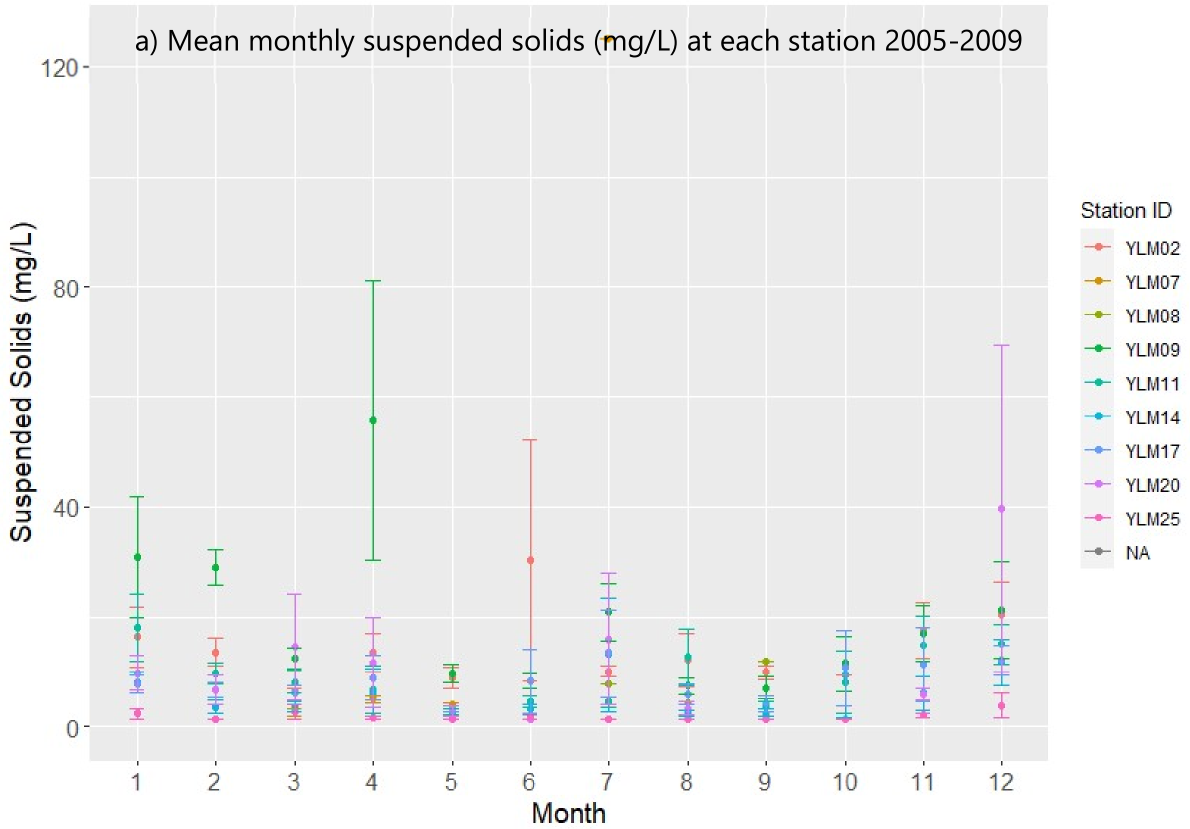


Figure 9: *Mean monthly suspended solids concentrations (mg/L) averaged from EA data collected at nine stations from a) 2005-2009 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*



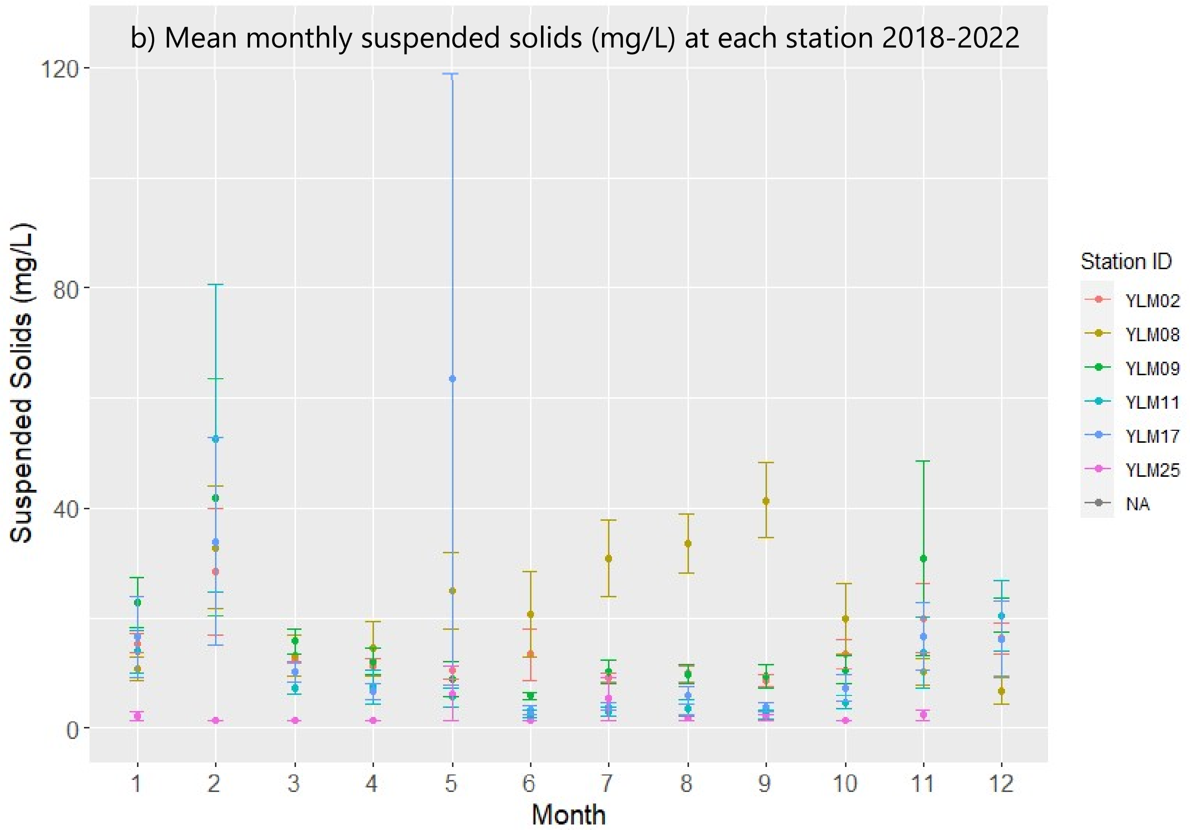


Figure 10: *Mean monthly suspended solids concentrations (mg/L) averaged at each of the 9nine preselected stations measured by the EA in a) 2005-2009 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*

E.coli concentrations were measured between 2007-2022, as such the first time period was shifted to 2007-2011.

During the 2007-2011 period there were two very large peaks in mean *E.coli* concentration with very high variability in April and July (Figure 11). Using the station breakdown (Figure 12), it was clear that these high *E.coli* concentrations were measured at YLM09. Aside from these peaks mean concentrations were relatively consistent throughout 2007-2011. *E.coli* concentrations exhibited very few significant differences between months in either time period, or when the two were compared (Table 3).

The variability in measurements during 2018-2022 was greatest in June, August and November and could be explained by stations YLM17 and YLM09. Both of which are downstream of sewage treatment facilities, Lutton STW and Elburton STW.

Management of *E.coli* concentrations must be a priority in this catchment. As stated previously over 48.8% of concentrations measured were greater than the bathing standard limit of 900 no/100ml (DEFRA, 2023).

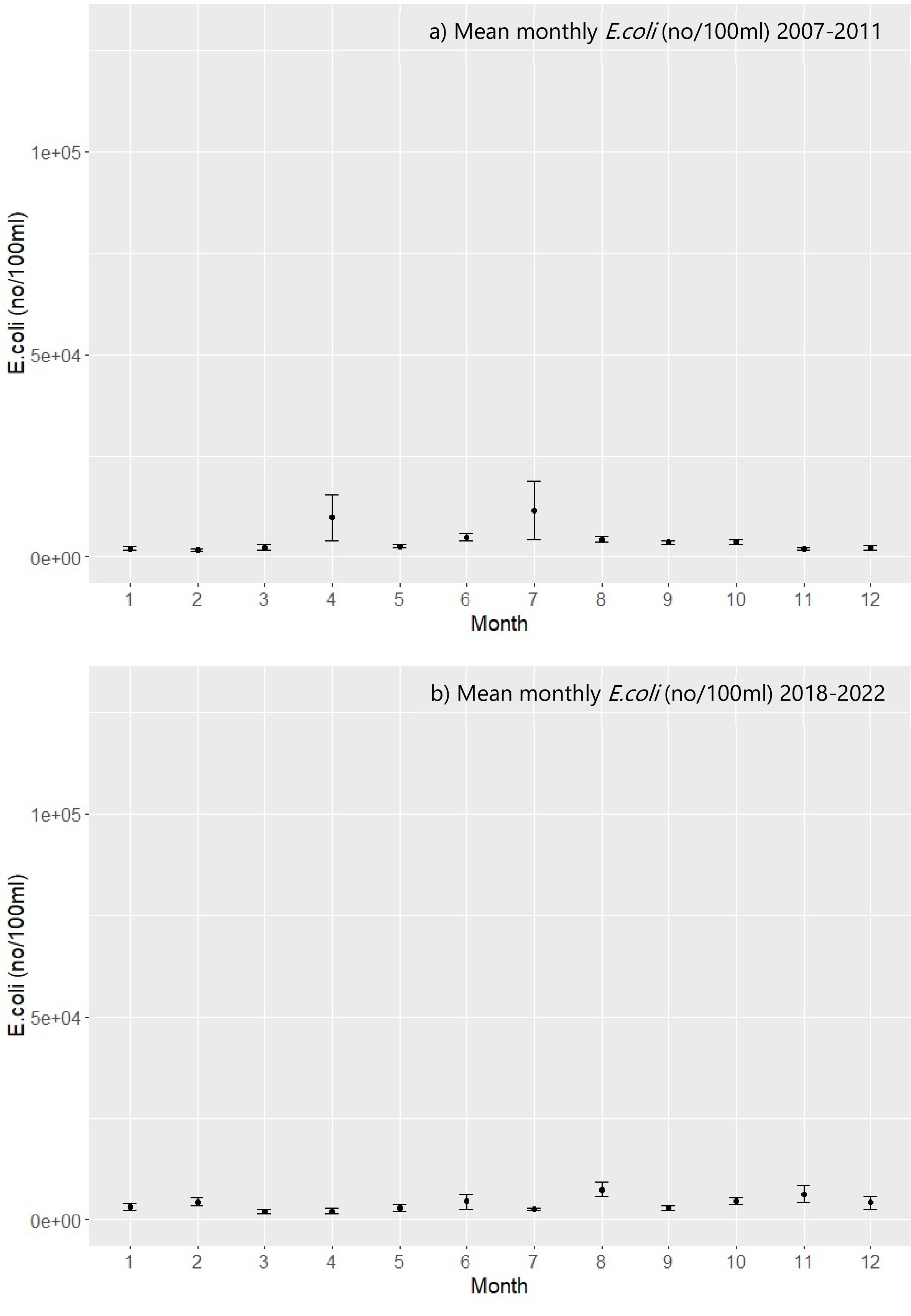


Figure 11: *Mean monthly E.coli concentrations (no/100ml) averaged from EA data collected at nine stations from a) 2007-2011 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*

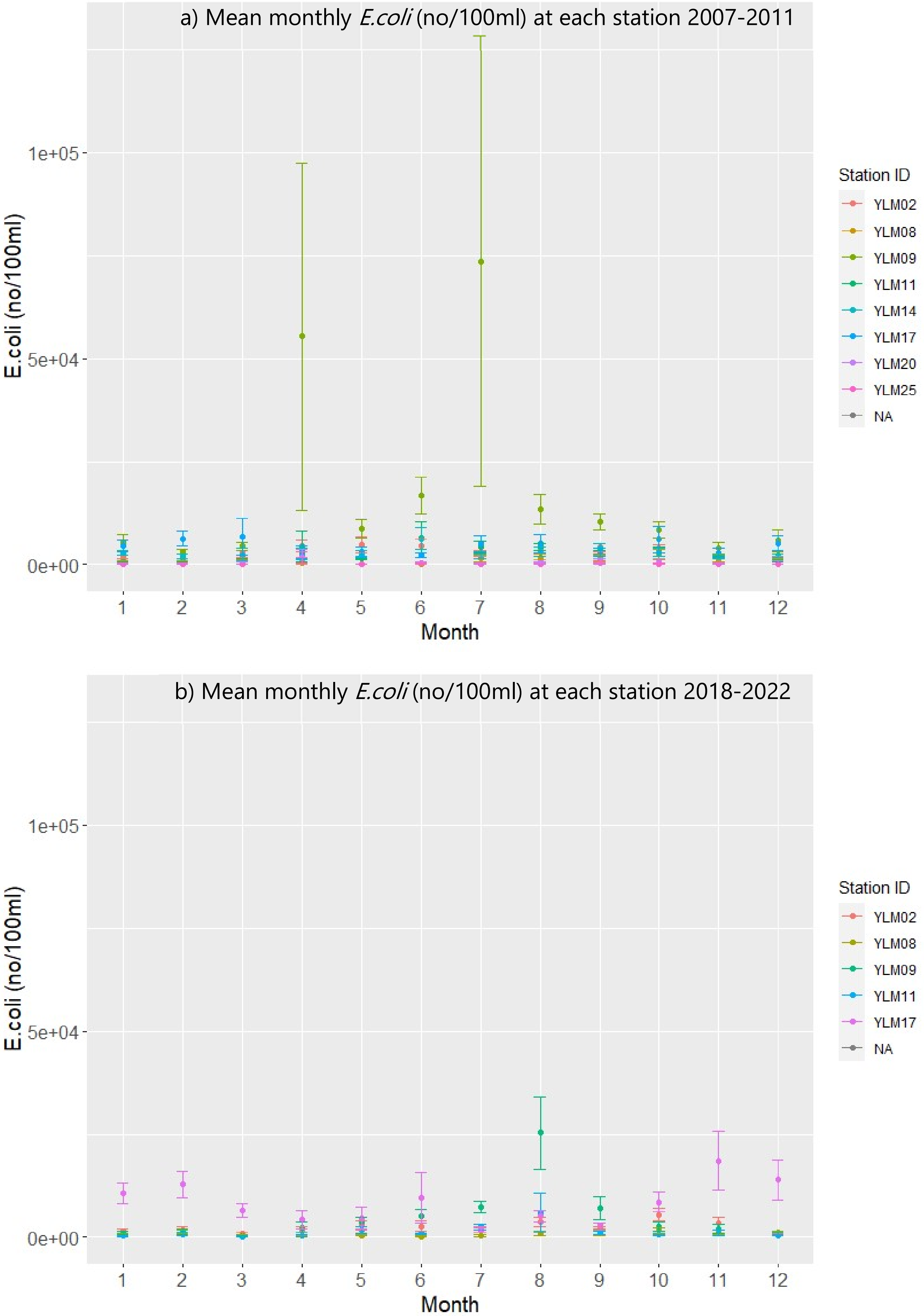


Figure 12: *Mean monthly E.coli concentrations (no/100ml) averaged at each of the nine preselected stations measured by the EA in a) 2007-2011 and b) 2018-2022. Standard error plotted as error bars (STD/√n).*

Table 3: *Results from a series of Mann Whitney tests to determine monthly differences in parameters in the first and last five years of monitoring, and between these two time periods. Statistically significant results in bold are highlighted blue for increase and yellow for decrease.*

Month: Years	Nitrate	n	Orthophosphate	n	Suspended: Solids	n	Month: Years	E.coli	n
1: 05-09	2.19	60	0.027	107	9.10	44	1: 07-11	818	101
2: 05-09	**2.96**	57	0.024	107	6.40	40	2: 07-11	495	114
3: 05-09	2.52	93	0.020	168	4.05	66	3: 07-11	422	152
4: 05-09	2.04	69	0.021	129	3.10	53	4: 07-11	507	126
5: 05-09	1.82	84	0.025	151	1.50	55	5: 07-11	936	131
6: 05-09	1.66	74	**0.043**	134	1.50	50	6: 07-11	**1272**	134
7: 05-09	1.79	81	0.032	149	4.30	61	7: 07-11	1150	140
8: 05-09	2.34	108	0.030	203	1.50	81	8: 07-11	1288	162
9: 05-09	2.80	100	0.032	194	1.50	81	9: 07-11	1260	180
10: 05-09	2.49	108	0.030	203	1.50	79	10: 07-11	1309	161
11: 05-09	2.67	113	0.030	208	**4.80**	78	11: 07-11	**743**	162
12: 05-09	2.61	82	0.028	149	**9.20**	58	12: 07-11	765	126
1: 18-22	3.80	77	0.035	77	10.90	74	1: 18-22	550	70
2: 18-22	3.59	77	0.030	77	12.55	74	2: 18-22	745	70
3: 18-22	3.41	75	0.026	75	**10.25**	70	3: 18-22	440	68
4: 18-22	3.23	59	0.029	59	**7.13**	56	4: 18-22	570	53
5: 18-22	2.82	68	**0.050**	68	6.90	65	5: 18-22	**910**	61
6: 18-22	2.62	41	0.067	41	5.30	39	6: 18-22	1091	37
7: 18-22	1.95	70	0.073	70	6.40	65	7: 18-22	1750	58
8: 18-22	1.70	72	0.071	73	6.42	68	8: 18-22	2000	62
9: 18-22	1.70	59	0.066	59	5.88	55	9: 18-22	1600	51
10: 18-22	2.90	68	**0.047**	68	7.71	62	10: 18-22	1600	59
11: 18-22	3.79	59	0.036	59	8.38	53	11: 18-22	1182	51
12: 18-22	4.00	41	0.031	41	11.00	36	12: 18-22	1400	36

1: 05-09 vs 18-22	2.19/3.80	60/77	0.027/0.035	107/77	**9.10/10.90**	44/74	1: 07-11 vs 18-22	818/550	101/70
2: 05-09 vs 18-22	2.96/3.59	57/77	0.024/0.030	107/77	**6.40/12.55**	40/74	2: 07-11 vs 18-22	**495/745**	114/70
3: 05-09 vs 18-22	2.52/3.41	93/75	0.020/0.026	168/75	**4.05/10.25**	66/70	3: 07-11 vs 18-22	422/440	152/68
4: 05-09 vs 18-22	2.04/3.23	69/59	0.021/0.029	129/59	**3.10/7.13**	53/56	4: 07-11 vs 18-22	507/570	126/53
5: 05-09 vs 18-22	1.82/2.82	84/68	**0.025/0.050**	151/68	**1.50/6.87**	55/65	5: 07-11 vs 18-22	936/910	131/61
6: 05-09 vs 18-22	1.66/2.62	74/41	0.043/0.067	134/41	**1.50/5.30**	50/39	6: 07-11 vs 18-22	1272/1091	134/37
7: 05-09 vs 18-22	1.79/1.95	81/70	**0.032/0.073**	149/70	4.30/6.40	61/65	7: 07-11 vs 18-22	1150/1750	140/58
8: 05-09 vs 18-22	**2.34/1.70**	108/72	**0.030/0.071**	203/73	**1.50/6.42**	81/68	8: 07-11 vs 18-22	**1288/2000**	162/62
9: 05-09 vs 18-22	2.80/1.70	100/59	**0.032/0.066**	194/59	**1.50/5.88**	81/55	9: 07-11 vs 18-22	1260/1600	180/51
10: 05-09 vs 18-22	2.49/2.90	108/68	0.030/0.047	203/68	**1.50/7.71**	79/62	10: 07-11 vs 18-22	**1309/1600**	161/59
11: 05-09 vs 18-22	2.67/3.79	113/59	0.030/0.036	208/59	**4.80/8.38**	78/53	11: 07-11 vs 18-22	**743/1182**	162/51
12: 05-09 vs 18-22	2.61/4.00	82/41	0.028/0.031	149/41	9.20/11.00	58/36	12: 07-11 vs 18-22	765/1400	126/36

2.3.3 Downstream variation

This section investigates the changes in parameters with distance downstream. The analysis focused on all data collected at five stations spread along the Yealm river, stations located along other tributaries were not included.

Data are presented as boxplots to highlight any changes in parameter concentrations with distance downstream (Figure 13). A series of Mann Whitney tests were then conducted to determine significant differences between the medians of each parameter with distance downstream, the results are presented in Table 4.

The downstream change of parameters measured was variable, some exhibit conservative behaviour while others vary considerably.

The most marked downstream change is the increase in nitrate concentration. Both Figure 13a and the Mann Whitney tests indicate significant increases in nitrate concentration between each station progressing downstream. The greatest increases occur at stations YLM20 and YLM11, these represent the joining of the River Piall and Long Brook, providing evidence of nitrate inputs along these tributaries.

Orthophosphate follows much the same pattern except for a significant decrease at station YLM14, coinciding with the joining of Brook Lake. The decrease exhibited at YLM14 could be explained by an addition of 'cleaner' water from the Brook Lake tributary diluting the concentrations measured upstream. A significant decrease in suspended solids was also evident at YLM14.

E.coli and *Enterococci* concentrations increased sharply to YLM17 where they then begin to decrease further downstream. This indicates that both *E.coli* and *Enterococci* sources lie between YLM25 and YLM17 with concentrations decaying below this point.

Table 4: *Results from a series of Mann Whitney tests to determine differences in parameters with distance downstream. Statistically significant results in bold and highlighted blue for increase and yellow for decrease.*

Parameter	***Km downstream***	***Station ID***	***N***	***Median***	***p-value***
Nitrate	0.00	YLM25	562	0.296	
	2.10	YLM20	376	**0.446**	**0.000**
	3.65	YLM17	809	**1.200**	**0.000**
	5.72	YLM14	508	**1.610**	**0.000**
	7.29	YLM11	684	**3.045**	**0.000**
Orthophosphate	0.00	YLM25	685	0.020	
	2.10	YLM20	429	**0.020**	**0.007**
	3.65	YLM17	931	**0.031**	**0.000**
	5.72	YLM14	628	**0.022**	**0.000**
	7.29	YLM11	806	**0.056**	**0.000**
Ammoniacal nitrogen	0.00	YLM25	563	0.015	
	2.10	YLM20	376	0.015	0.145
	3.65	YLM17	841	**0.015**	**0.000**
	5.72	YLM14	513	**0.015**	**0.000**
	7.29	YLM11	684	0.015	0.119
E.coli	0.00	YLM25	420	18.0	
	2.10	YLM20	336	**112.5**	**0.000**
	3.65	YLM17	680	**1598**	**0.000**
	5.72	YLM14	419	**1440**	**0.032**
	7.29	YLM11	601	**692**	**0.000**
Enterococci	0.00	YLM25	181	5	
	2.10	YLM20	165	**36**	**0.000**
	3.65	YLM17	440	**575**	**0.000**
	5.72	YLM14	181	**360**	**0.001**
	7.29	YLM11	363	**230**	**0.000**
Suspended solids	0.00	YLM25	482	1.5	
	2.10	YLM20	357	**3.8**	**0.000**
	3.65	YLM17	797	4.1	0.388
	5.72	YLM14	447	**1.5**	**0.000**
	7.29	YLM11	603	**4.5**	**0.000**
Temperature	0.00	YLM25	586	10.80	
	2.10	YLM20	401	**11.63**	**0.001**
	3.65	YLM17	860	11.40	0.774
	5.72	YLM14	526	11.39	0.360
	7.29	YLM11	678	**11.80**	**0.001**
Dissolved oxygen	0.00	YLM25	113	10.6	
	2.10	YLM20	50	10.8	0.191
	3.65	YLM17	178	**10.5**	**0.007**
	5.72	YLM14	99	10.4	0.626
	7.29	YLM11	79	10.3	0.391
% oxygen saturation	0.00	YLM25	167	98.00	
	2.10	YLM20	50	**99.85**	**0.013**
	3.65	YLM17	231	**97.60**	**0.000**
	5.72	YLM14	149	97.00	0.154
	7.29	YLM11	128	97.00	0.223

BOD 5-day	0.00	YLM25	79	0.5	
	3.65	YLM17	159	0.5	0.453
	5.72	YLM14	84	1.2	0.086
	7.29	YLM11	79	0.5	0.083

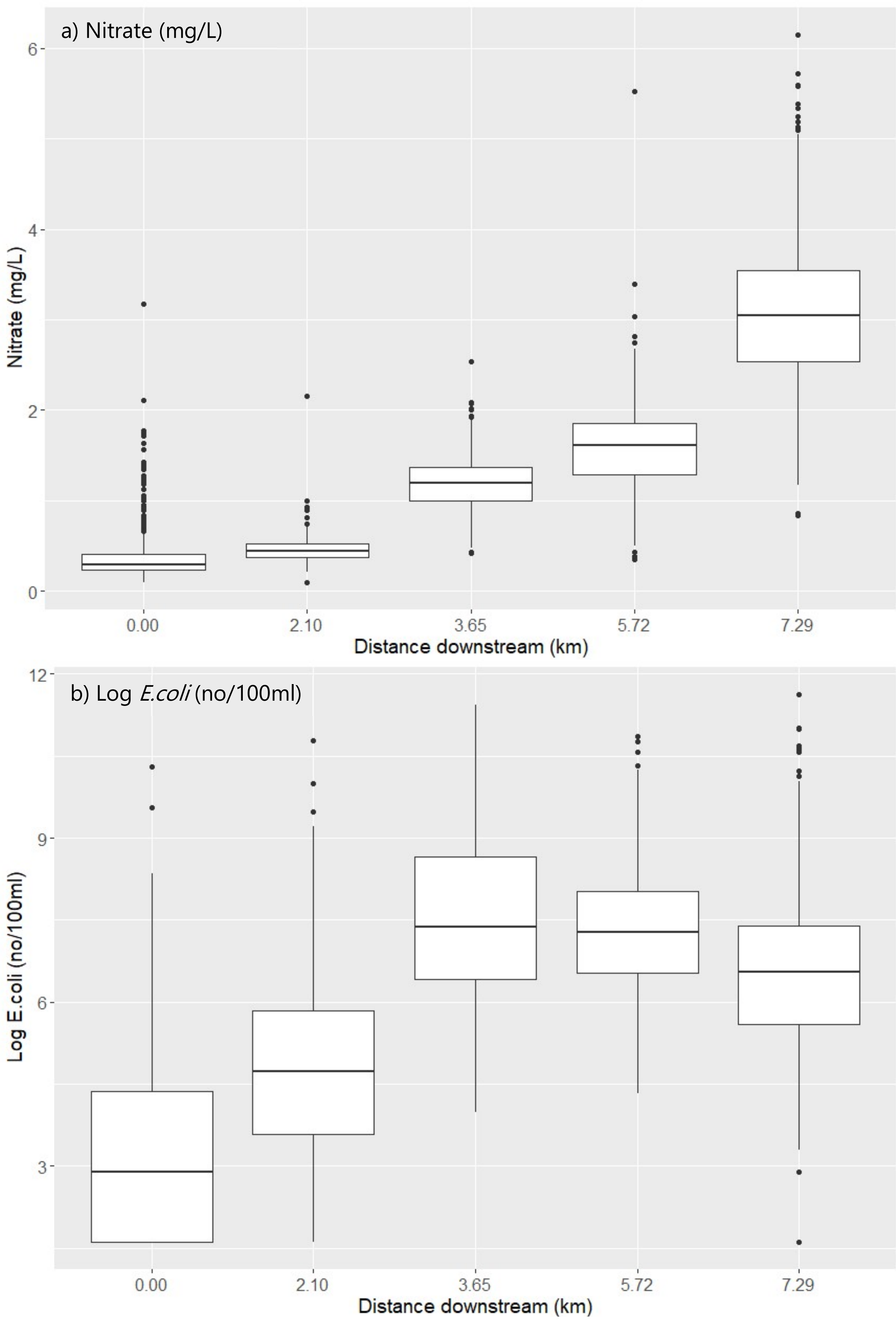


Figure 13: *Boxplots of all EA data at stations along the River Yealm (YLM25, YLM20, YLM17, YLM14 and YLM11; in downstream order). Distance downstream in kilometres from YLM25 (the furthest station upstream). a) Nitrate (mg/L), b) Log E.coli (no/100ml), data logged to better visualise patterns.*

2.3.4 Sewage treatment works

This section aims to determine whether the presence of sewage treatment facilities along the Yealm impact the water quality.

The locations of wastewater treatment plants were plotted alongside a map of EA monitoring stations. Widening the station search to include all EA monitoring sites enabled new stations to be selected to provide information about the water quality above and below sewage treatment plants. Many of the sites had very limited data meaning they were unable to be compared with the YLM stations. For this reason, only two areas along the River Yealm were selected for further study. Stations YLM07 and YLM11 are located either side of the Yealmpton Waste Water Treatment Works and stations YLM14 and YLM17 are either side of Lee Mill Sewage Treatment Works (Figure 14). This provides information on the state of the river water before and after the sewage treatment facilities and indicates whether these sites are a direct input of pollutants into the riverine system.

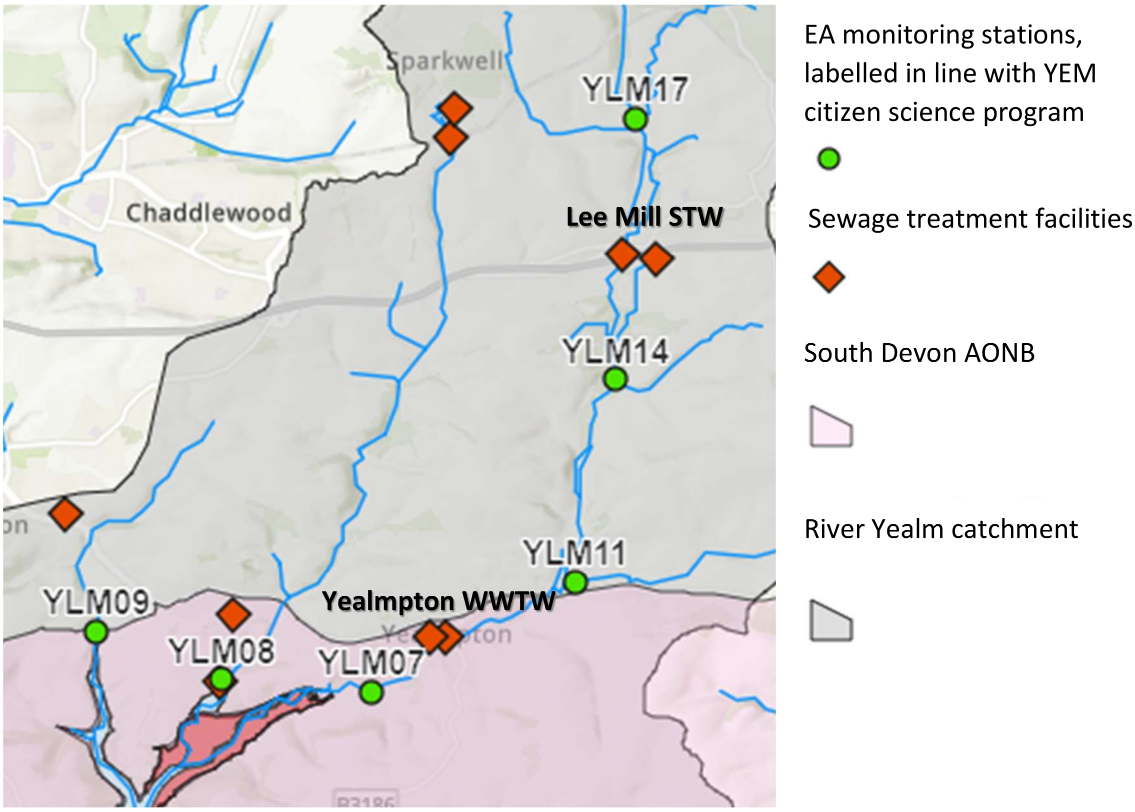


Figure 14: *Map of stations plotted according to the latitude and longitude of EA data. Red diamonds indicate sewage treatment facilities.*

Table 5: *Results from a series of Mann Whitney tests to determine differences in parameters either side of the Yealmpton WWTW and Lee Mill STW. Statistically significant results in bold are highlighted blue for increase and yellow for decrease.*

	YLM17	Lee Mill STW	YLM14	YLM11	Yealmpton WWTW	YLM07
Nitrate (mg/L)	1.20		**1.61**	**3.05**		**2.23**
n	809		508	684		174
Orthophosphate (mg/L)	0.031		**0.022**	**0.056**		0.049
n	931		628	806		147
Ammoniacal nitrogen (mg/L)	0.03	**0.86**	**0.03**	0.03	**7.80**	**0.032**
n	841	299	513	684	288	160
E.coli (no/100ml)	1598		**1440**	**692**		
n	680		419	601		
Enterococci (no/100ml)	575		**360**	**230**		
n	440		181	363		
Suspended solids (mg/L)	4.1	**14.6**	**3.0**	**4.5**	**31.0**	**3.9**
n	797	299	447	603	288	14
% oxygen saturation (%)	97.6		97.0	97.0	**58.9**	**96.4**
n	231		149	128	6	160
BOD 5-day (mg/L)	1.0	**5.0**	**1.2**	1.0	**11.0**	**1.1**
n	159	299	84	79	286	92

In both cases the concentrations of ammoniacal nitrogen, suspended solids and BOD 5-day increased significantly at the sewage treatment facilities then decreased significantly at the following station (Figure 15b and 16). In addition, the % oxygen saturation was significantly lower at the Yealmpton Waste Water Treatment Works, this is likely in response to increases in the other pollutants measured (Figure 15a).

The increase and subsequent decrease in the concentrations of ammoniacal nitrogen, suspended solids and BOD 5-day, and the associated changes in % oxygen saturation, indicate a rapid breakdown of pollutants such as ammoniacal nitrogen into nitrate (O'Neill, 1998). However, a significant increase in nitrate was observed at both YLM14 and YLM11, suggesting that there is an addition nitrate input between these two stations (Figure 17a).

At YLM07 nitrate significantly decreases indicating that Yealmpton WWTW is not a source of nitrate. Interestingly, increases in concentrations of ammoniacal nitrogen, suspended solids and BOD 5-day were greater at Yealmpton Waste Water Treatment Works when compared with Lee Mill Sewage Treatment Works. This suggests that perhaps nitrate is in fact not strongly associated with increases in ammoniacal nitrogen, suspended solids and BOD 5-day. In addition, orthophosphate concentrations also show a disconnect with these three parameters, increasing significantly between YLM14 and YLM11 rather than at either of the two sewage treatment facilities (Figure 17b).

The lack of sewage facilities between YLM14 and YLM11 suggest alternative pollutant sources for nitrate and orthophosphate. A brief investigation into the land use in the area indicates that the mostly likely source of nutrient pollution is agriculture. Both the sections of land between YLM14 and YLM11, and the length of the Long Brook tributary, which joins at YLM11, are surrounded by farmland. Neither section has an associated sewage treatment facility.

E.coli and *Enterococci* concentrations decreased significantly at YLM14 suggesting that the Lee Mill STW was not the source of bacteria to this system (Figure 18). Further significant decreases were observed between YLM14 and YLM11 suggesting that sources along the River Yealm are located further upstream, supporting the findings of the downstream investigation.

The comparison of stations before and after Yealmpton WWTW and Lee Mill STW did not highlight an association between sewage treatment and *E.coli* and *Enterococci* concentrations. However, this may not be the case with all sewage facilities.

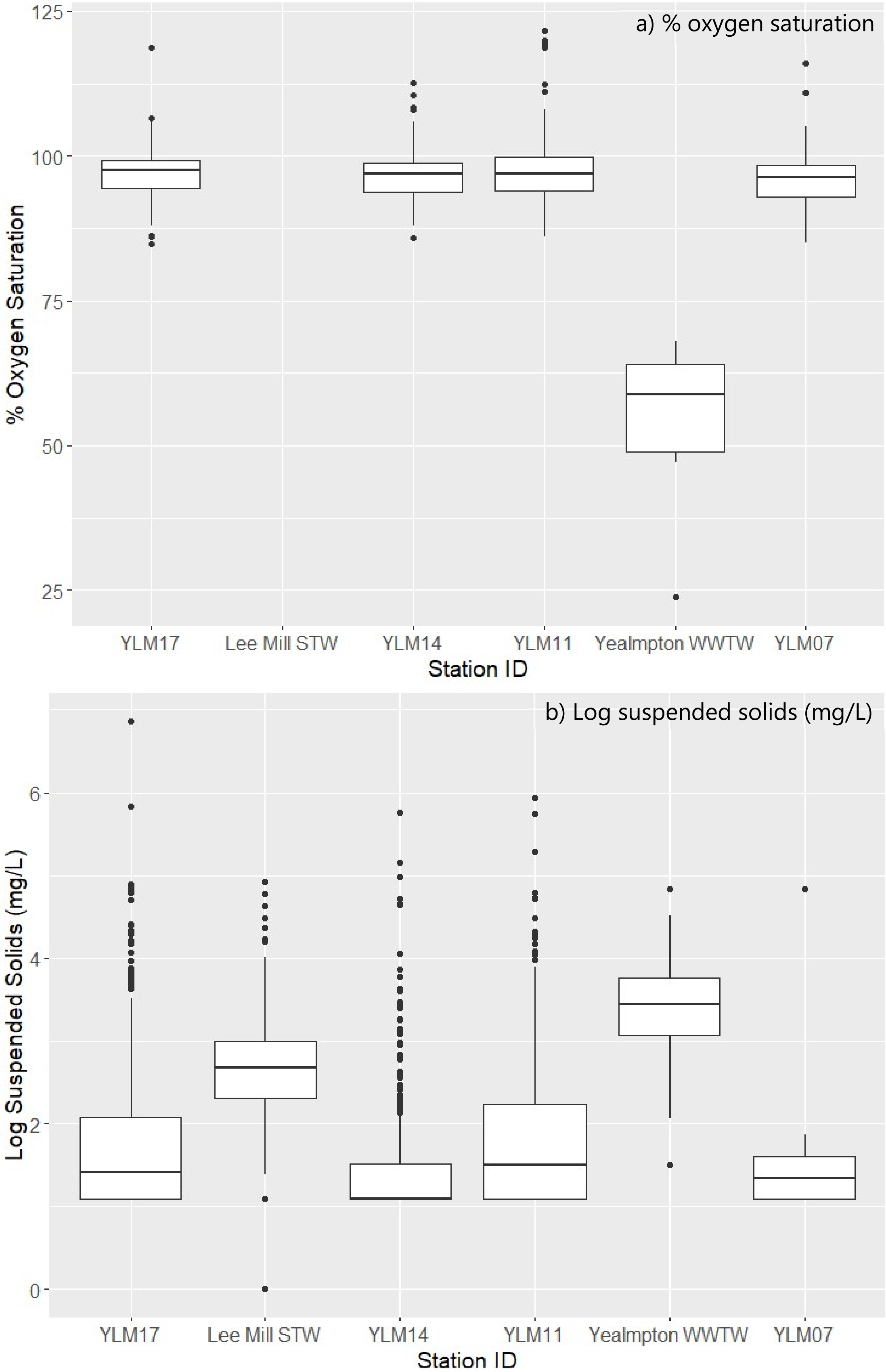


Figure 15: *Boxplots of EA monitoring data collected between 2000 and 2022 at stations YLM07, YLM11, YLM14, YLM17, and two addition sites, Yealmpton Waste Water Treatment Works and Lee Mill Sewage Treatment Works located adjacent to sewage treatment plants. a) % oxygen saturation b) Log suspended solids, data logged to better visualise patterns.*

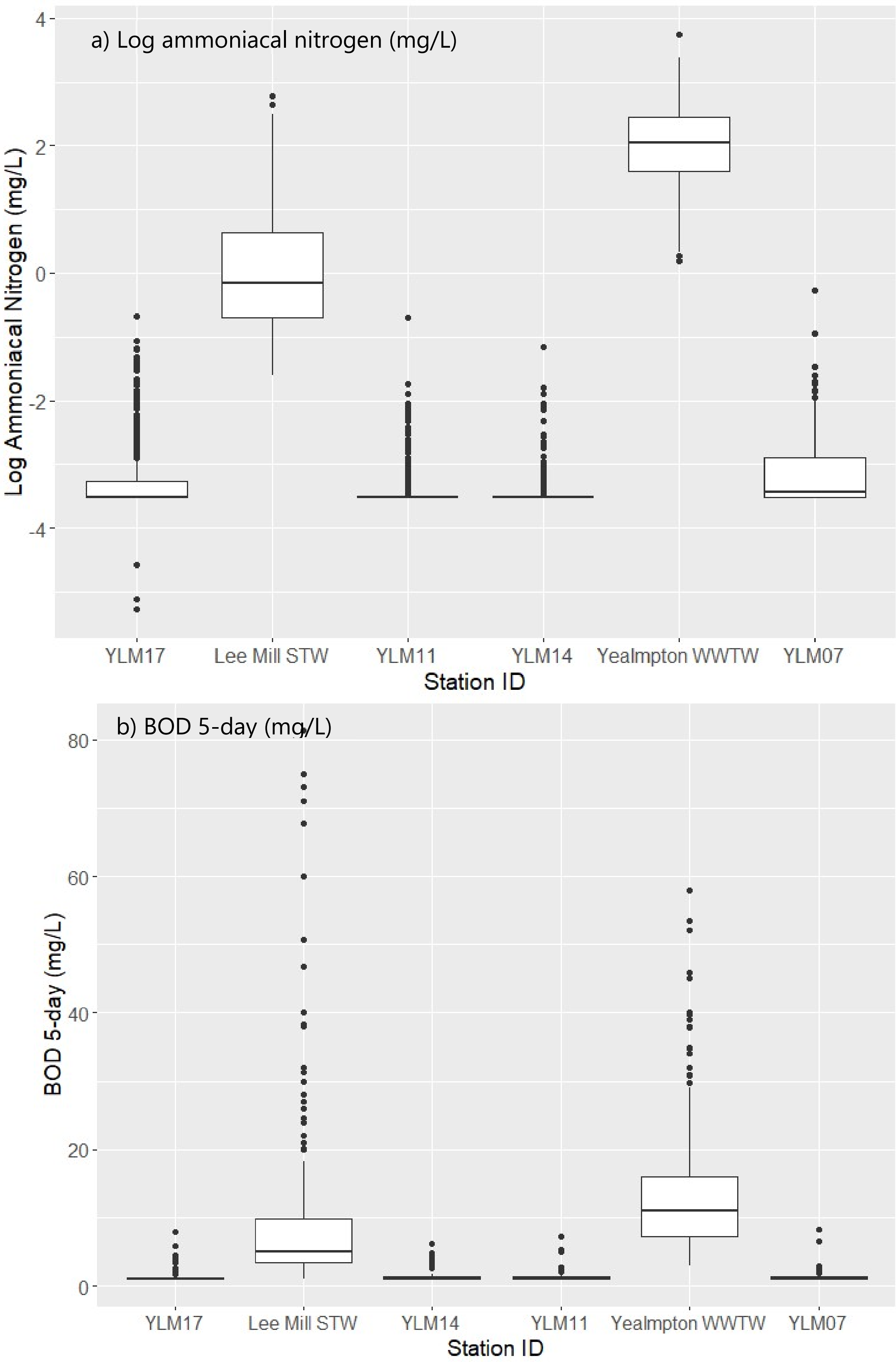


Figure 16: *Boxplots of EA monitoring data collected between 2000 and 2022 at sites YLM07, YLM11, YLM14, YLM17, and two addition sites, Yealmpton Waste Water Treatment Works and Lee Mill Sewage Treatment Works located adjacent to sewage treatment plants. a) Log ammoniacal nitrogen, data logged to better visualise patterns b) BOD 5-day.*

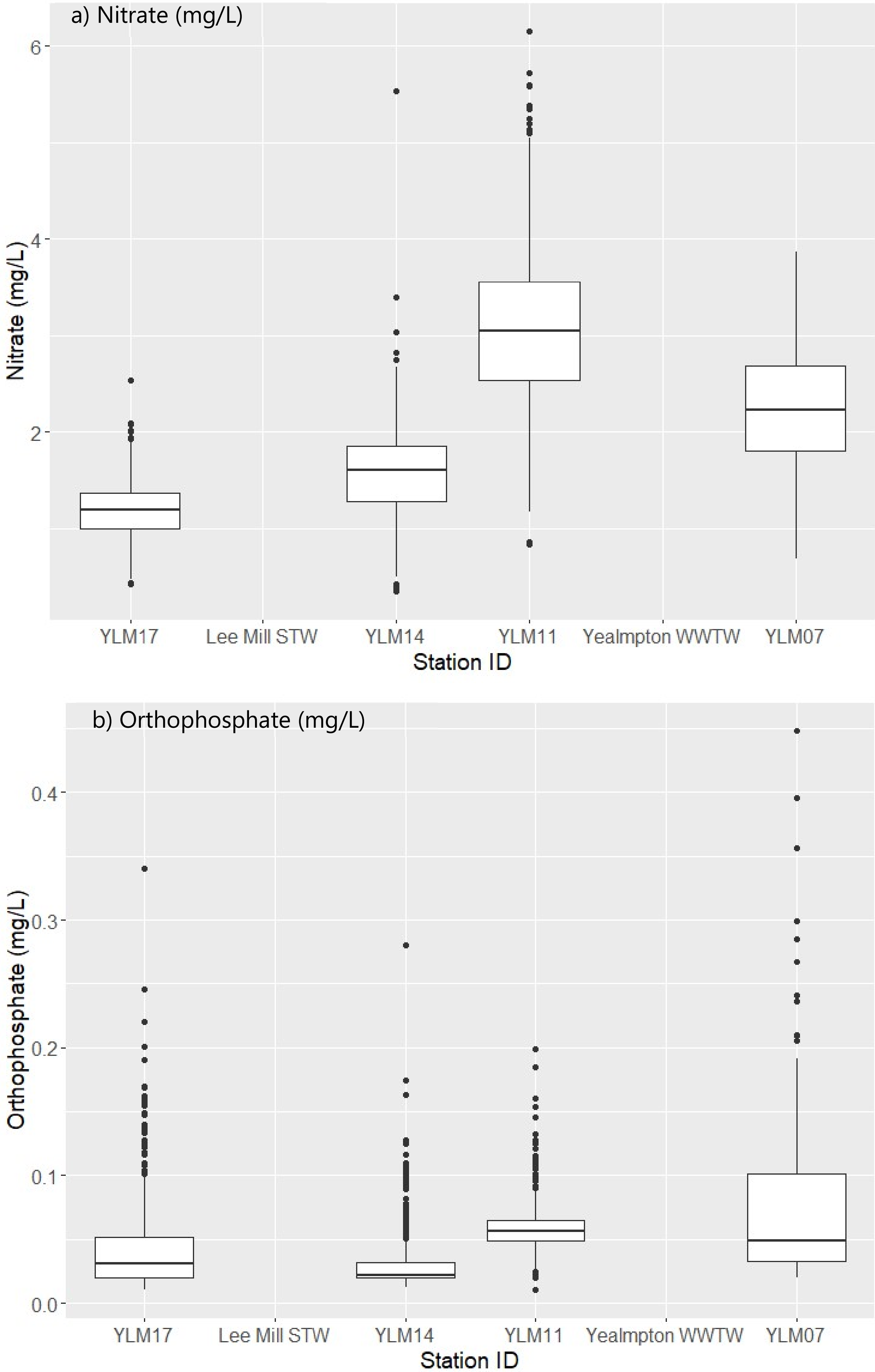


Figure 17: *Boxplots of EA monitoring data collected between 2000 and 2022 at stations YLM07, YLM11, YLM14, YLM17, and two addition sites, Yealmpton Waste Water Treatment Works and Lee Mill Sewage Treatment Works located adjacent to sewage treatment plants. a) Nitrate (mg/L) b) Orthophosphate (mg/L).*

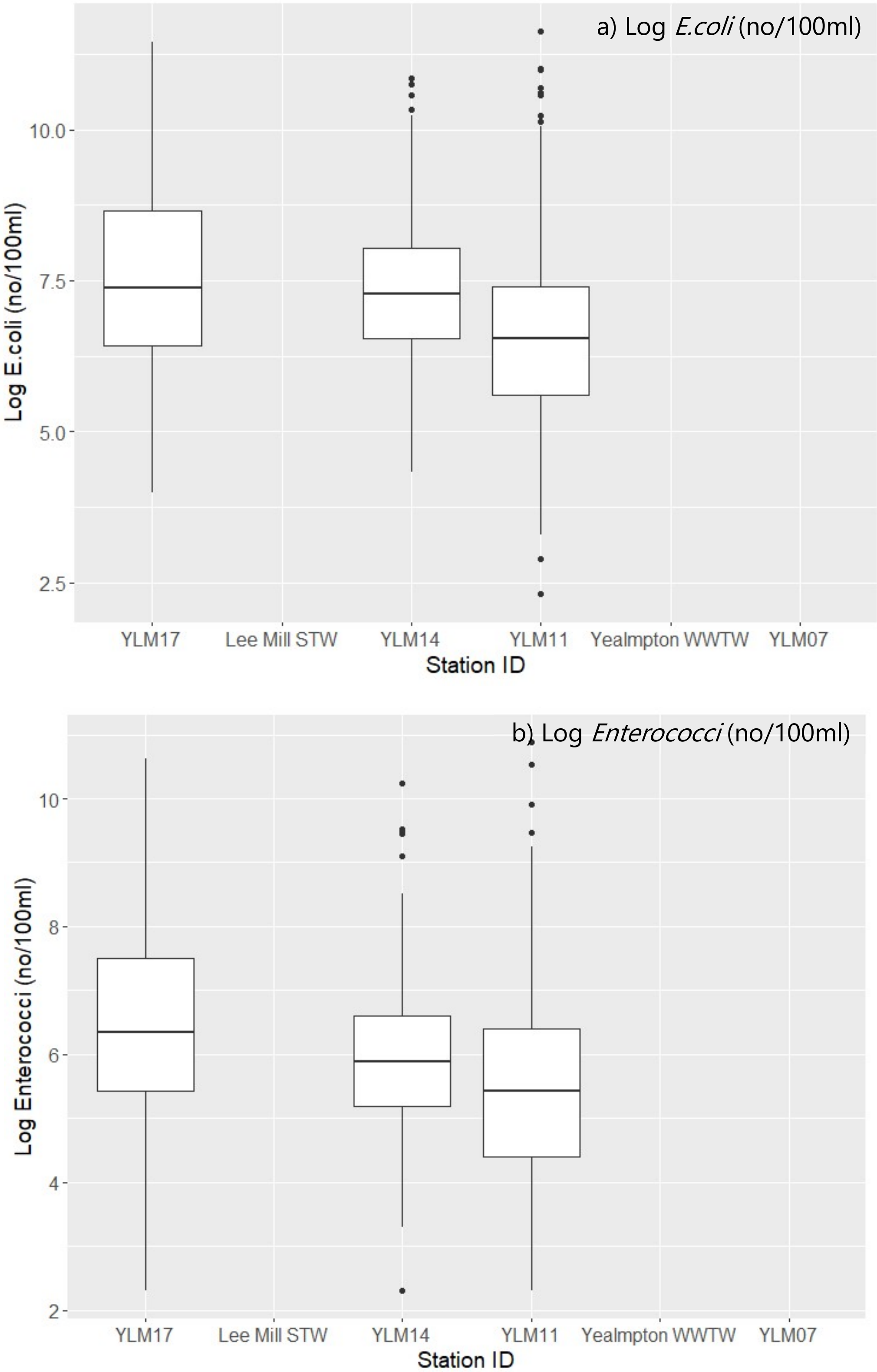


Figure 18: *Boxplots of EA monitoring data collected between 2000 and 2022 at stations YLM07, YLM11, YLM14, YLM17, and two addition sites, Yealmpton Waste Water Treatment Works and Lee Mill Sewage Treatment Works located adjacent to sewage treatment plants. a) Log E.coli (no/100ml) b) Log Enterococci (no/100ml), data logged to better visualise patterns.*

2.3.5 Multidimensional scaling – EA data

Multidimensional scaling creates clustering of data points to better visualise groupings and links between observations.

Figure 19 shows the monthly average of EA data at stations in 2012-2017. There is evidence of station specific clustering. Stations YLM11, YLM14 and YLM17 exhibit the strongest clustering indicating that these stations have the least month-month variation. Stations furthest upstream and downstream are the most variable.

Figure 20 shows clustering of variables from EA data taken at all stations averaged from 2012-2017. The clustering of variables allows links between them to be observed. This figure clearly shows a strong link between orthophosphate and nitrate concentrations as well as *E.coli*, *Enterococci* and suspended solids. Rainfall and ammoniacal nitrate measurements are not linked with other variables measured. Given the conclusions drawn from the sewage treatment study above the close links between orthophosphate and nitrate indicate that these variables are associated with agricultural, while *E.coli*, *Enterococci* may link more closely with sewage treatment.

A second set of MDS plots shows the clustering of variables from stations YLM08 and YLM25. This provides a comparison of the variables at the upstream and downstream ends of the catchment and gives clues as to the sources of pollution. At YLM08 the link between *E.coli*, *Enterococci* and suspended solids is strong, suggesting that sewage treatment may exert the greatest control at this point in the catchment. While at YLM25, orthophosphate, nitrate and suspended solids are closely clustered suggesting agriculture activity may have a stronger influence over water quality here. Ammoniacal nitrogen is also present in this cluster, suggesting that ammoniacal nitrogen is associated with both sewage treatment, and agricultural practices.

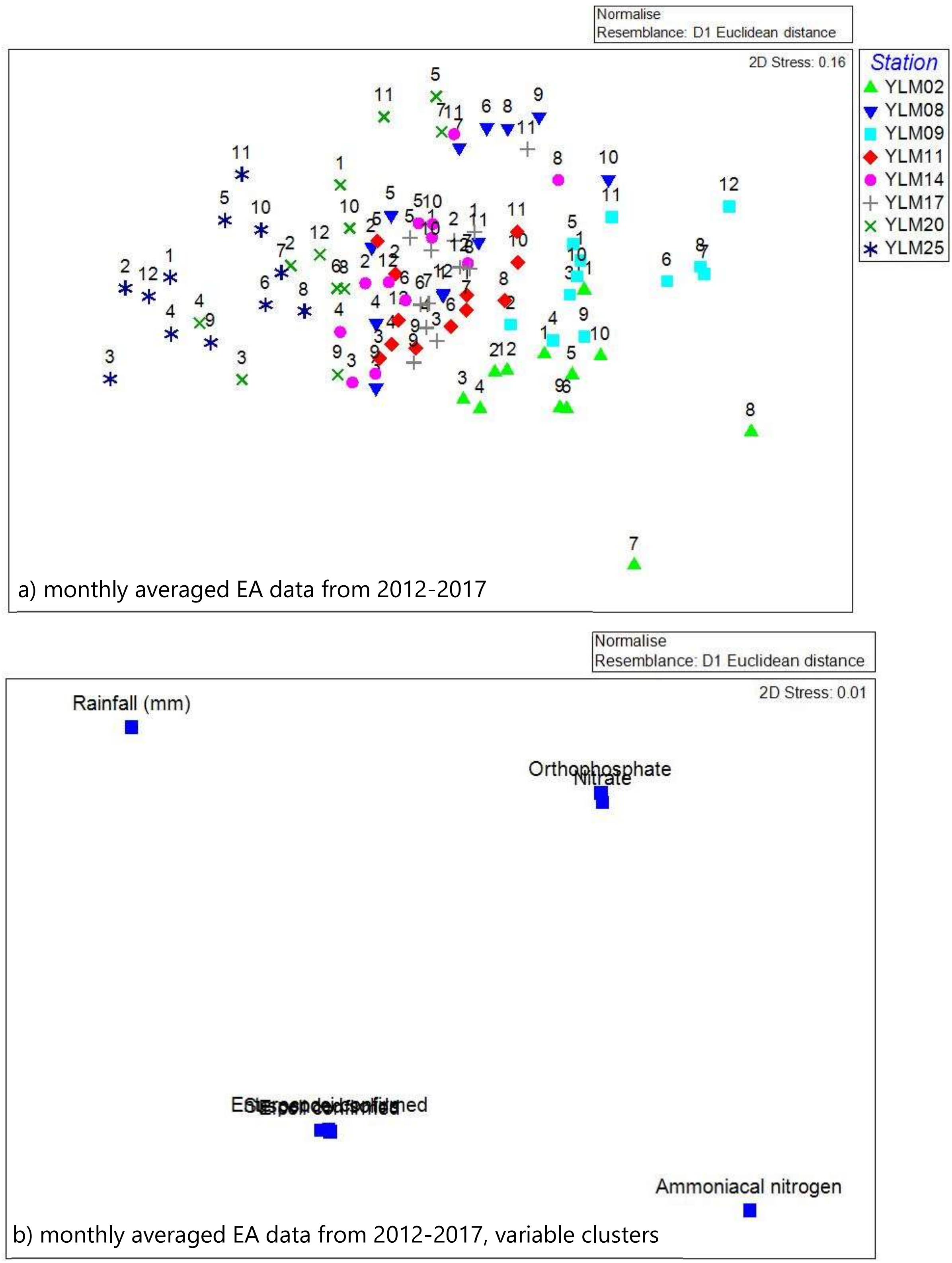
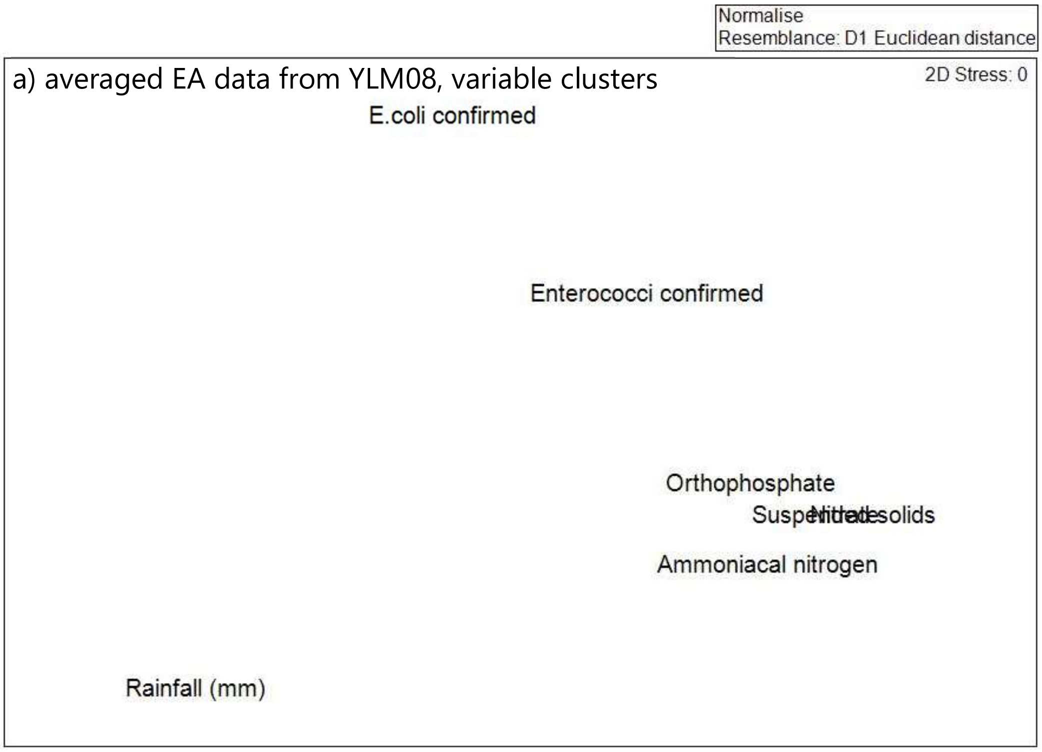


Figure 19: *MDS plots of a) the monthly averaged from each station using EA data from 2012-2017 and b) the variables from averaged EA data from all stations in 2012-2017.*



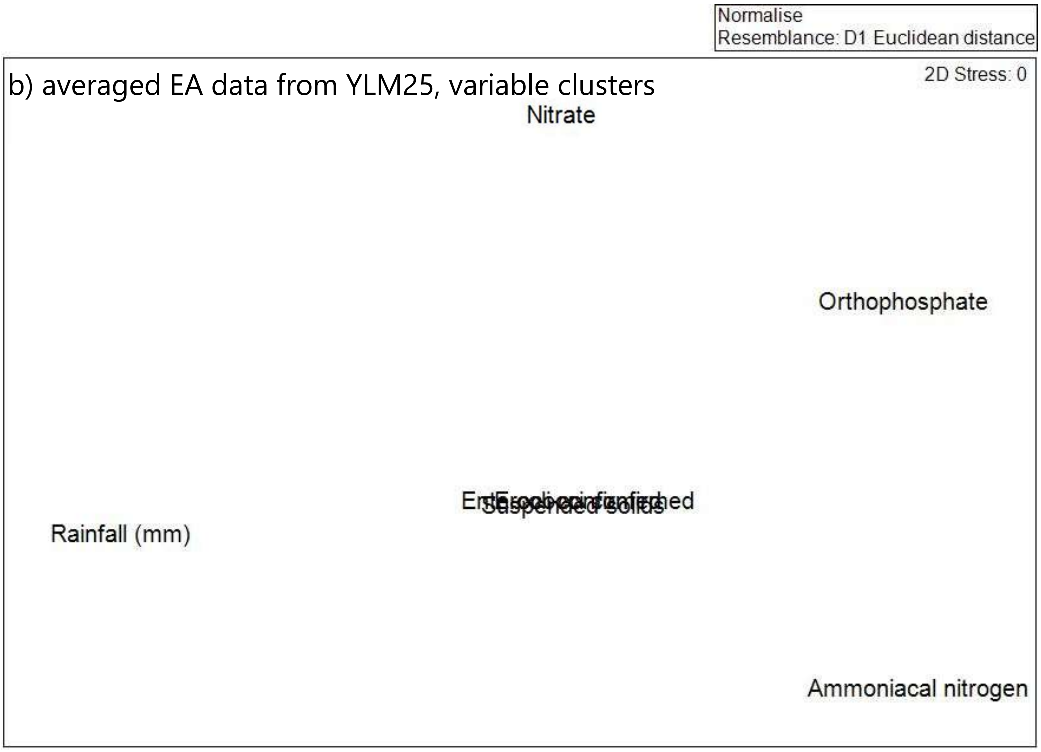


Figure 20: *MDS plots of a) the variables averaged from station YLM08 using EA data and b) the variables averaged from YLM25 using EA data.*

2.3.6 Metal and Chemical Analysis

An analysis of metal and chemical concentrations was completed, to ensure all pollutant types were represented in this investigation. The monitoring of metal and other chemical pollutants was inconsistent and measured over a short time period, 07/2011- 02/2012, and 2000-2014, respectively. For this reason, it cannot be used in observations of long-term change, however, remains a useful tool for commenting on pollutant types evident within the catchment.

Chemical analysis was conducted using measurements at station YLM07 only (Figure 21). Of the measurements taken, 89% did not exceed the detection limit of the instrumentation. However, both 1,2-dichloroethane and chloroform exceeded the detection limit in 2000-2001, reaching concentrations of 8.84 and 4.4 μg/L respectively before dropping significantly and remaining low for the remainder of the monitoring period.

It is possible that the presence of chloroform in the water column could be derived from the treatment of wastewater and chlorination of drinking water, this is consistent with the fact that YLM07 is located downstream of the Yealmpton WWTW. However, this WWTW continues to be active and therefore does not explain the subsequent drop in chloroform concentration. This suggests perhaps the peak could be indicative of a leak event, or a change in practice that reduced the concentration entering the river system.

1,2-dichloroethane peaked during the same period as chloroform. 1,2-dichloroethane in the water column could be derived from several sources, including plastics, rubber, dyes, lubricants and pesticides (Delaware Health and Social Services, 2013). Given the land-use within this catchment, it is likely that pesticide use is the cause of 1,2-dichloroethane pollution. Waste products from activities associated with the Lee Mill industrial estate further upstream could be another explanation, however, neither of these potential sources explain the short-term nature of this pollutant peak.

The Environment Agency data used begins in 01/2000 just as the peaks in chloroform and 1,2-dichloroethane were observed. Having access to observations of these chemicals pre-2000 may assist in determining the extent to which these pollutants were evident in the system in the past and may help identify potential inputs. Finally, there may have been change to the measurement techniques, this change in protocol may have altered the detection limit.

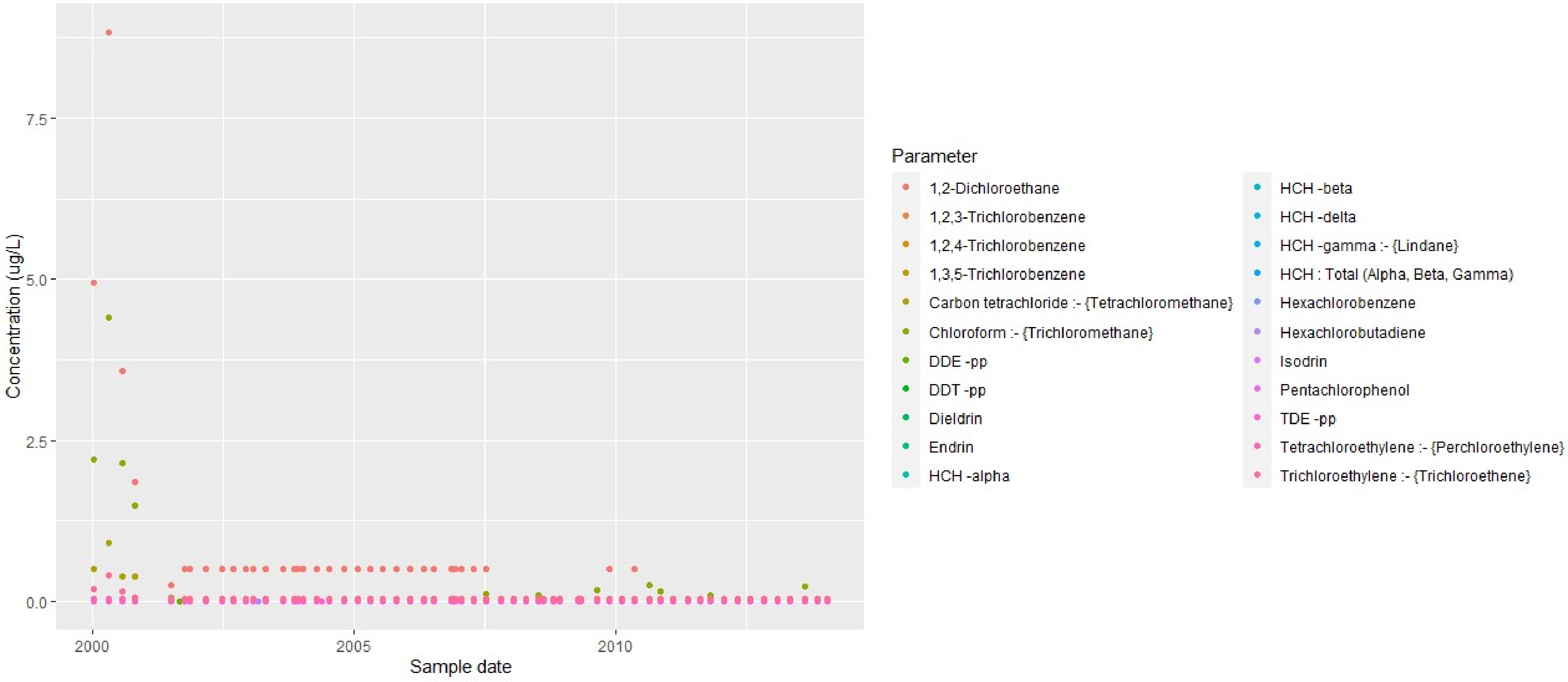


Figure 21: *Concentrations of chemicals taken by the EA at station YLM07, Puslinch Bridge.*

Metal concentrations were measured at four stations between 07/2011 and 02/2012. This six-month database provides information on the state of metal pollution in the water column at that point in time, but cannot be used to make assumptions about current or future metal pollutants. Many metals were measured over this time, most of which fell below the detection limit of the equipment used.

The following metals had concentrations greater than this limit, aluminium, calcium, copper, iron, magnesium, manganese, nickel, potassium, sodium, strontium and zinc.

Of these metals, calcium, magnesium, and strontium correlated with distance, increasing downstream. This is a natural process explained by the build-up of ions from rock, clay and soil breakdown as the water travels downstream (Oborne *et al.* 1980). The concentrations of these metals increased with increased salinity.

Several other metals exhibited low concentrations at YLM25, then increased at YLM20 before gradually decreasing again with distance downstream. Metals following this pattern were copper (Figure 22), iron, manganese, nickel. YLM20 is the point at which the River Piall joins the River Yealm. As such, this indicates a source of metal pollution between YLM25 and YLM20, and/or somewhere along the River Piall, this is likely the Lee Mill industrial site and associated China Clay works.

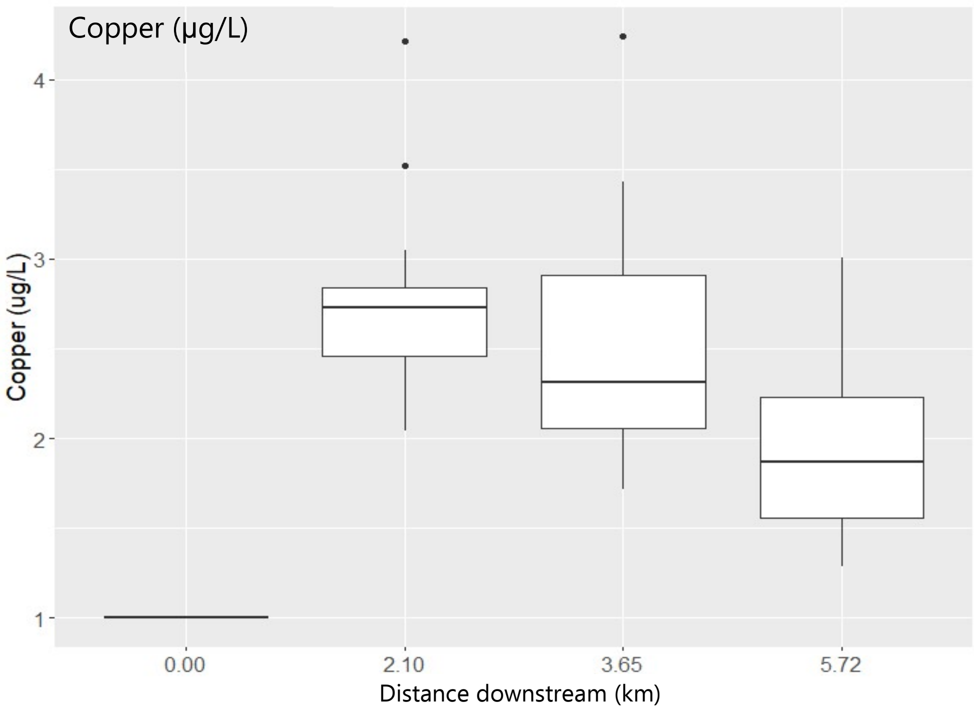


Figure 22: *Boxplots of copper concentrations taken by the EA at stations YLM25, YLM20, YLM17 and YLM14 between 07/2011 and 01/2012.*

2.4 Discussion

The data collected by the EA provides a picture of the state of the water in the catchment and how it has changed over time. The nine stations selected represent all tributaries entering the River Yealm to demonstrate spatial as well as temporal change. The monitoring activities of the EA, while extensive, were not consistent over time or space. Measurements taken at each station varied in terms of timeframe and parameters taken. As such, any observations of the state of the catchment must be caveated by the statement that future monitoring needs to occur on a better regulated and consistent manner to allow better comparisons to be made and to determine the success of changes to catchment management.

2.4.1 Temporal and Spatial Change in Nitrate

One of the main focuses of this section was the analysis of nitrate concentrations in the Yealm catchment. As discussed previously the monitoring and management of nitrates in UK rivers is high priority among management groups, stakeholders and governments as it is deemed one of the most influential pollutants to UK riverine systems (Maier *et al.* 2009; Tappin, *et al.* 2013). The introduction of the Nitrates Directive in 1991 paved the way for better monitoring and control of nitrate use in river catchments and has led to establishment of many Nitrate Vulnerable Zones, covering 70% of UK land area (DEFRA, 2009; Musacchio *et al.* 2019). The Yealm catchment, however, is not designated as an NVZ, and as such is not subject to the strict controls associated with these zones (Research Centre of European Commission, 2019).

The concentrations of nitrate and how they vary temporally and spatially is therefore an important consideration for groups such as the YEM group that may be considering new management strategies to improve the biodiversity of their catchment.

Nitrate concentrations measured by the EA demonstrate changes over time and space. The concentrations increase with distance downstream, indicating that sources of nitrate are evident along the length of the river. The highest concentrations of nitrate are found at the furthest downstream stations, namely, Newton Ferrers (YLM02), Puslinch Bridge (YLM07), Cofflete Creek (YLM09) and Silverbridge Lake (YLM08). This is likely the result of build-up from both diffuse and point sources of pollution and water moves downstream.

Nitrate concentrations varied temporally on seasonal and interannual scales. Concentrations decreased slightly in the summer months, increasing again in the autumn, though monthly differences were not statistically significant. Nitrate concentration was not significantly correlated with rainfall. A comparison of seasonal variation in the first and last five years of monitoring provided detail on changes to this pattern of variation. The summer low in 2018-2022 lasted longer than in 2005-2009 indicating a seasonal shift over time. In fact when comparing the monthly nitrate concentrations between 2005-2009 and 2018-2022 only the concentrations measured in August were significantly different. This could be an indicator of climate change as longer summers have caused a shift in seasonal timings (Hannaford, 2015; Watts *et al.* 2015). In addition, concentrations of nitrate were more variable in 2005-2009, reaching higher peaks than in 2018-2022. The stations with the greatest variability in both time periods were YLM07 and YLM09 suggesting that control of nitrate concentrations is less well-regulated in the areas around these stations. YLM08 also exhibited high variability in 2005-2009.

Nitrate concentrations measured in the first and last years of monitoring showed a significant decrease in concentration at seven of the nine stations measured. This could be the result of stricter regulations to reduce the amount of nitrate entering riverine systems. Since the start of this monitoring process the regulations on nitrate usage and release have tightened (European Commission, 2023). However, two of the stations monitored showed an increase in nitrate concentration indicating that, though controls appear to have improved overall, there are still areas that require extra attention when making future river management plans.

It was also clear from the annual variation comparison that stations further upstream remained more consistent over time, suggesting that it would be more beneficial for conservation and management effort to focus their attention on downstream areas whilst continuing to monitor inputs along the length of the river. The variation between stations must also be addressed with particular attention being given to the areas surrounding Cofflete Creek and Puslinch bridge.

The concentrations of nitrate overall remain below the threshold of the Nitrate Vulnerable Zone suggesting that the presence of nitrates in the water column are unlikely to have detrimental impacts on life within the catchment. However, greater control in highly variable areas should be considered to ensure this risk remains a low as possible.

2.4.2 Temporal and Spatial Change in Orthophosphate

As with nitrate, orthophosphate concentrations are also of great interest because of their association with wastewater treatment and agricultural activities (Uncles *et al.* 2002; Matějíček *et al.* 2003; Edwards and Withers, 2008; Neal *et al.* 2010; Tappin *et al.* 2013).

Orthophosphate concentrations similarly increase downstream, indicating an accumulation of phosphate compounds from sources located along the full length of the river. The sharpest increases in concentrations occurred at stations YLM20 and YLM11. These stations also mark the joining of the River Piall and Longbrook to the main Yealm river. Thus, suggesting that water entering from these tributaries carries a higher orthophosphate concentration from sources further upstream. Conversely, station YLM14 exhibited a decrease in orthophosphate concentration paired with a reduction in suspended solids. The joining of Brook Lake at this point suggests the waters of Brook Lake are of a higher quality, temporarily diluting the orthophosphate and suspended solids concentrations in the Yealm.

The orthophosphate concentration also exhibited some seasonal variation, with higher values being reported in summer and autumn months. Orthophosphate concentration was not significantly correlated with rainfall. Though, similarly to nitrate, the month-to-month differences were not statistically significant. The build-up of orthophosphate in the system was much more abrupt in 2018-2022 when compared to 2005-2009. Additionally, during the summer and autumn of 2018-2022 measurements exhibited greater variation than in 2005-2009. In all cases, variation increased where mean concentrations were higher. In fact, when comparing measurements taken in 2005-2009 and 2018-2022, there were significant increases observed in spring and summer months. In both time periods measurements taken at Newton Ferrers (YLM02) and Puslinch Bridge (YLM07) had the most variability, indicating orthophosphate control was least effective in these areas. Interestingly, the furthest upstream station at Cornwood (YLM25) also exhibited high variability during the 2018-2022 period.

It appears that orthophosphate concentration may be controlled by both sewage treatment and agricultural activity. A catchment wide downstream increase suggests a diffuse source such as agriculture, while several large peaks located at individual stations suggests point sources from sewage treatment facilities, including Newton Ferrers STW and Yealmpton WWTW.

Conversely to nitrate, the concentrations of orthophosphate in the first and last year of monitoring, do not exhibit an overall decrease. In fact, concentrations remained mostly consistent, but exhibited significant increases at Newton Ferrers (YLM02) and Cofflete Creek (YLM09) since 2007. The increase in concentration at these stations indicates a new source of orthophosphate to the system in 2007. Both stations YLM02 and YLM09 are the only stations along their tributary making it difficult to pinpoint the exact position of these inputs.

To gain a better understanding of the orthophosphate concentrations and thus produce effective management strategies, focus needs to be drawn to these highly variable, high concentration regions; in this case, Newton Ferrers, Puslinch Bridge and Cofflete Creek. Phosphate concentrations generally must be closely monitored. Further increases and unexpected peaks are evidence of new sources that must be managed carefully to reduce potential damage to the riverine system.

2.4.3 Spatial Change in *E.coli* and *Enterococci*

The concentrations of *E.coli* and *Enterococci* show little temporal variation, they exhibit no clear seasonal pattern and their interannual changes, exhibit both increases and decreases at different points along the river.

They do, however, exhibit clear spatial variation. Concentrations of both *E.coli* and *Enterococci* increased steadily to Marks Bridge (YLM17) before decreasing further downstream. This indicates that sources of both bacteria are located upstream of this point, cumulating in a peak in concentration at Marks Bridge. When looking at the catchment as a whole, a second peak at Cofflete Creek is also evident.

In addition, *E.coli* and *Enterococci* concentrations are alarmingly high. In fact 48.8% of *E.coli* and 18.1% of *Enterococci* concentrations are higher than that of bathing standard which lies at 900 no/100ml and 580 no/100ml, respectively. The fact that these values are so high indicates a real need to target their regulation when planning future catchment management strategies.

A focus on controlling concentrations of these bacteria is vital for the improved management of the entire catchment. Though peaks fall most consistently at Marks Bridge (YLM17) and Cofflete Creek (YLM09) there is evidence of both *E.coli* and *Enterococci* peaks at all stations indicating a real lack of control of these bacteria.

2.4.4 Sewage Treatment Facilities

To better determine the impact of potential pollutants in the Yealm catchment, the sources must first be identified. The three most common land use types in the Yealm include agricultural land, industrial use and small towns. The towns along the Yealm are relatively small and rural and are likely to have little impact on the water quality in the river systems. Conversely, the agricultural land is very likely to impact the water quality, however as it covers a large area and will therefore need to be managed as a diffuse source of pollution. This section of the investigation, therefore, focuses on the industrial land use, namely, sewage treatment facilities. The Yealm catchment, though small, hosts several sewage treatment facilities, however, only two were selected for this investigation, the reason for this selection is highlighted in Section 2.3.4.

At both sewage treatment facilities concentrations of ammoniacal nitrogen, suspended solids and BOD 5-day increased in the water adjacent to it before decreasing by the time the water reached the next station. In addition, the % oxygen saturation was severely reduced alongside the sewage treatment facilities. This indicates that the presence of ammoniacal nitrogen and high suspended solid concentrations can have adverse impacts on the water chemistry and microorganism assemblage. A subsequent reduction in oxygen saturation could lead to a loss of biodiversity and shift in populations, in the immediate area.

Nitrate, orthophosphate, *E.coli* and *Enterococci* concentrations were compared at stations either side of these sewage treatment facilities.

Nitrate and orthophosphate concentrations. Nitrate concentrations increased in downstream of Lee Mill STW but decreased following Yealmpton WWTW. In addition, nitrate concentrations increased between YLM14 and YLM11, a stretch of river on which there are no sewage treatment facilities. Orthophosphate followed much the same pattern.

The lack of sewage facilities between YLM14 and YLM11 suggest alternative pollutant sources for nitrate and orthophosphate. A brief investigation into the land use in the area indicates that the mostly likely source of nutrient pollution is agriculture. Both the sections of land between YLM14 and YLM11, and the length of the Long Brook tributary, which joins at YLM11, are surrounded by farmland. Neither section has an associated sewage treatment facility. Therefore, suggesting that nitrate and orthophosphate inputs are associated with agriculture.

E.coli and *Enterococci* concentrations decrease between YLM17 and YLM11 suggesting that the Lee Mill STW and Yealmpton WWTW are not sources of these bacteria. However, when considering trends across the entire catchment it is clear that *E.coli* and *Enterococci* concentrations, peak at YLM02, YLM09 and YLM17, each of which is downstream of a sewage treatment facility. As such, sewage cannot be ruled out as a source of these bacteria.

2.4.5 Source regions within the catchment

Throughout this investigation, several areas have been highlighted as potential source areas of pollutants.

Cofflete Creek, Newton Stream and Long Brook show evidence of nitrate, orthophosphate along their lengths. Cofflete Creek and Newton Stream also have high *E.coli* and *Enterococci* concentrations. In addition, both stations are located at downstream at the entry points of the estuary.

The River Piall appears to be a source of metals as well as nitrate and orthophosphate, likely as a result of the activities conducted at Lee Mill industrial site and associated sewage treatment facility, the Lutton STW is also located along this river.

Each of these areas is a cause for concern in the catchment. Identifying and tackling the sources of pollution in these regions is vital for the improvement of management plans and the betterment of the water quality and biodiversity of the whole catchment.

Section 3.1 investigates the potential impact of the pollutants found within the catchment on the estuarine system and vital habitats within it.

Figure 23 summarised the change in nutrient pollution both over time and throughout the catchment. The build-up of both nitrate and orthophosphate is evident, as well as the high concentrations exhibited at Newton Stream (YLM02) and Cofflete Creek (YLM09). This further emphasises the need for understanding how these nutrients move through the estuary and what the potential impacts might be.

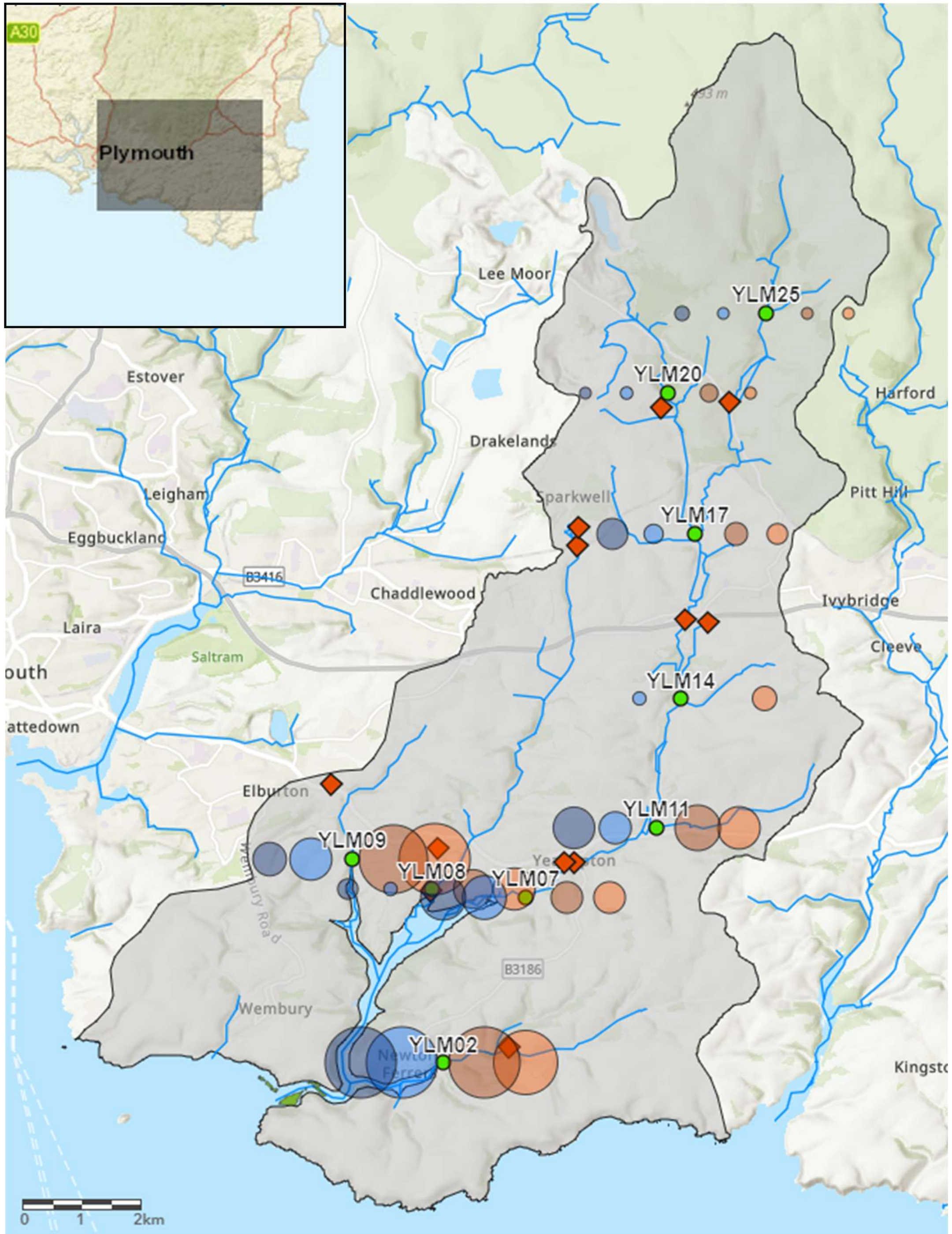


Figure 23: *A summary of the change in nitrate and orthophosphate over time and with distance downstream, highlighting the accumulation at estuary entry sites.*

3.1 Estuary Field Study

3.1.1 Objectives

The EA monitoring data gathered did not have consistent measurements of estuarine parameters, meaning conclusions drawn about the catchment could not be extended to the estuary. As such, a field study was conducted on estuarine waters to determine the transport and distribution of pollutants through the estuary and their impact on the health of the seagrass beds. Samples collected in the field were analysed for nutrient and chlorophyll concentration and several other basic parameters including temperature and turbidity.

3.1.2 Justification

The EA data investigation highlighted the pollutant types within the catchment and what concentrations of such pollutants were entering the estuary. The two most important pollutants in the Yealm catchment are nitrate and phosphate, as both tend to increase with distance downstream, reaching a peak at these estuarine entry points.

This section of the project determined the current concentrations of these nutrients within estuarine waters, as well as investigating additional parameters including chlorophyll concentrations, turbidity and salinity. It also allows observations of the transport of nutrients through the estuary.

Investigating the potential impact of river derived nutrients in the estuary is important when considering catchment wide management plans (Nnane *et al.* 2011; Haidvogl, 2018). Various unique estuarine habitats are found in the Yealm estuary, most notably, several seagrass beds (Yealm Estuary to Moor, 2022). These seagrass ecosystems are incredibly important for marine life and water quality as well as providing numerous ecosystems services (Duarte, 2000; Waycott *et al.* 2009).

3.2 Methods

Boat surveys were arranged in April, May and June to collect water samples and measure basic parameters including salinity, temperature, turbidity at seven sites along the estuary. Water samples were subsequently analysed for nutrient and chlorophyll concentration.

3.2.1 Boat Surveys

Samples were collected at seven sites within the Yealm estuary to determine the changes in nutrient concentration, chlorophyll and physical parameters with distance downstream (Figure 24). Sites were selected to provide a representative picture of the estuary while also targeting seagrass bed locations as recorded by Natural England (Natural England, 2023). This enabled a comparison of pollutant concentration entering the estuary to the concentrations in the water column above these seagrass beds.

A YSI probe was used to take measurements of temperature, dissolved oxygen, % oxygen saturation, conductivity, pH, turbidity, and salinity. Measurements were taken at the surface and at depth (1m above the seabed).

At each site samples were collected at surface and depth for nutrient and chlorophyll analysis. Samples used for nutrients (100ml) were syringe filtered at sea (45μm GF filters) and immediately frozen on return to the lab, while those used for chlorophyll (2 litre samples) were vacuum filtered in the lab (0.7 μmGF) and the filters frozen for later analysis.

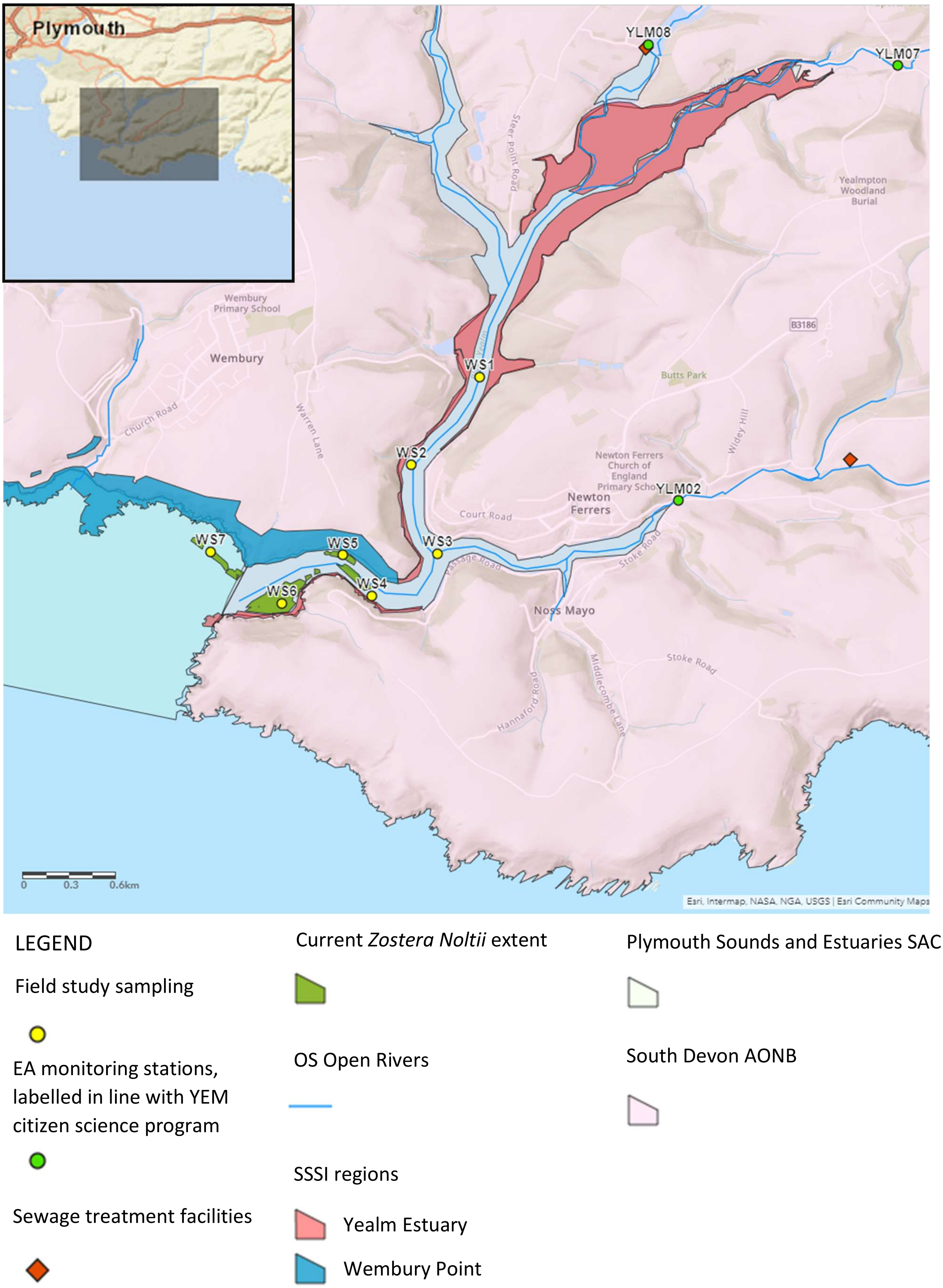


Figure 24: *Map of water sampling sites measured on 18/04/2023, 18/05/2023 and 26/06/2023. Current seagrass extent (Zostera sp.) recorded by Natural England overlaid (update 06/06/2023).*

3.2.2 Nutrient Analysis

Nutrient concentrations were measured using a Skalar automated nutrient analyser. Before analysis, a set of combined standards were made. A HACH test was conducted to determine whether elemental nitrogen and phosphorous concentrations in samples fall within the measurement range of the Skalar.

Samples were placed into the autosampler (Figure 25). The metal sampling probe aspirates a portion of the contents for a given time period. The sampling probe goes into a wash solution before moving onto the next sample. A peristaltic pump brings samples into the chemical module. The flow of reagents is determined by the diameter of the plastic tubing, and the distance between and speed of rollers.

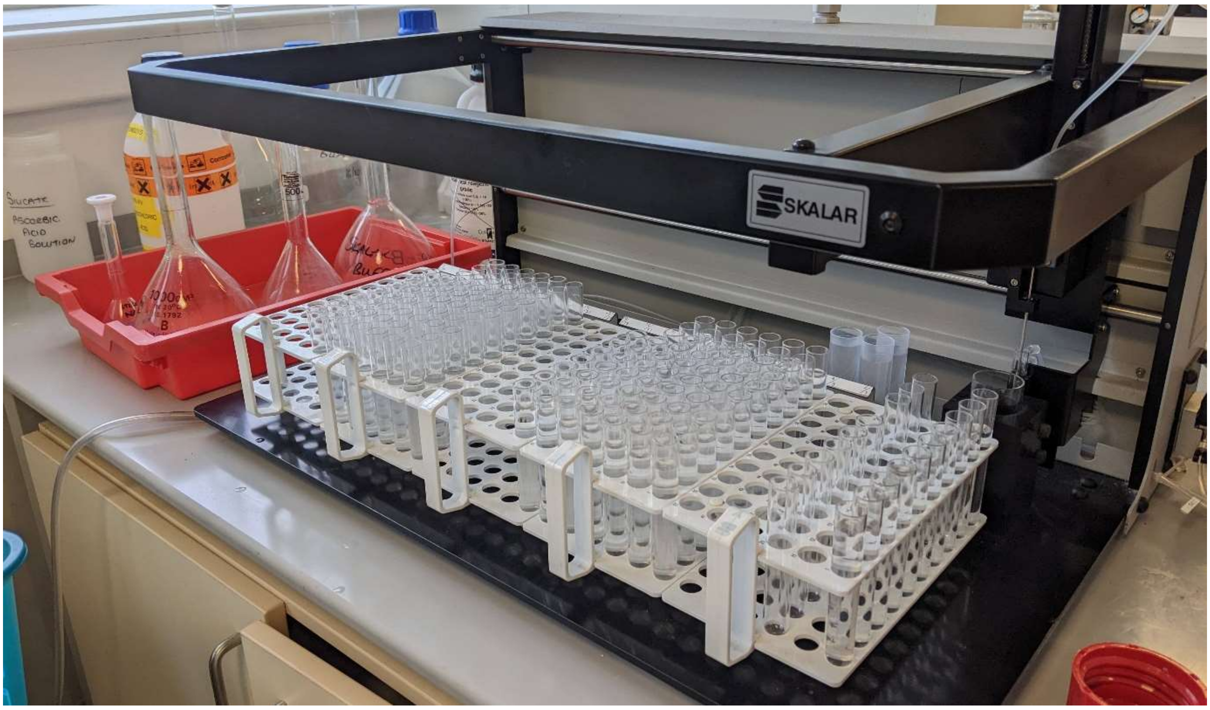


Figure 25: *Autosampler and sampling probe.*

The chemical module brings together samples and reagents, allowing the following reactions occur (Figure 26).

- Nitrate detection uses the Greiss reaction in which nitrate is reduced to nitrite using a copperised-cadmium column. The nitrite is then determined by diazotizing with sulphanilamide which couples with N-1-Naphylethylene diamine dihydrochloride to create a pink azo dye (Moorcroft *et al.* 2001).

- Phosphate detection uses the reaction of P with ammonium molybdate and antimony-phosphomolybdate complex (Drummond and Maher, 1995; Baldwin, 1998). This is then reduced by ascorbic acid forming a blue complex.

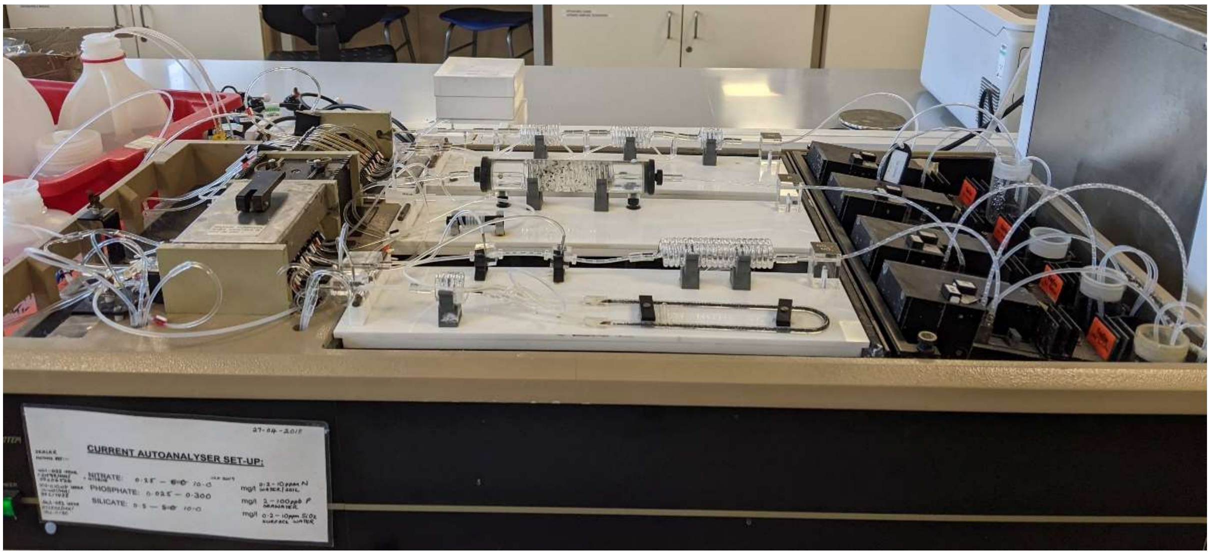


Figure 26: *Chemistry modules with nitrate/nitrate and phosphate lanes.*

The detection of nitrate and phosphate uses spectrophotometry at 540nm and 800nm, respectively (Moorcroft *et al.* 2001; Drummond and Maher, 1995). Concentrations are calculated using Beer-Lambert Law which states that the absorbance of a substance is directly proportional to its concentration. A calibration curve of absorbance was calculated using the set of combined standard solutions. Calibration curves calculated during this Skalar run are plotted in Appendix C.

From the calibration curve, concentrations of elemental N and P are automatically generated. Manual conversion of this into nitrate (NO_3) and phosphate (PO_4) was calculated.

3.2.3 Chlorophyll Analysis

Frozen filter papers were used to measure the chlorophyll concentrations of water samples collected in May and June.

Filters were defrosted before use. First, 1.6ml of 90% acetone and a small amount of silicon zirconia beads were added to filters before homogenising for 30 seconds on high using a Bullet Blender Storm 24 bead beater.

Residual beads and filter paper were filtered out (0.7µmGF) leaving only a solution of suspended chlorophyll. The absorbance of each sample was measured using JENWAY 7310 Spectrophotometer at following wavelengths: 480, 630, 645, 663 and 750nm.

Chlorophyll a, b and c concentrations were calculated using the following equations (Strickland and Parsons, 1972). E refers to the absorbance measured at each wavelength.

Chlorophyll a = 11.64*E663 - 2.16*E645 + 0.10*E630

Chlorophyll b = 20.97*E645 - 3.94*E663 - 3.66*E630

Chlorophyll c = 54.22*E630 - 14.81*E645 - 5.53*E663

Conversion to concentration µg/L was as follows:

Mg/L = Chlorophyll_x / Volume filtered

3.3 Results

3.3.1 YSI Probe Measurements

Measurements taken by the YSI probe describe the state of the water within the estuary. Many of the parameters measured follow seasonal trends including temperature, % oxygen saturation and/or were influenced by tidal cycles such as salinity.

Turbidity decreased from April to June and with distance downstream (Figure 27a). The turbidity was lower at the surface than at depth.

Salinity increased with distance downstream, and from May to June (Figure 27b). Most likely related to water temperature and tidal cycle.

3.3.2 Nutrient Analysis

Nutrient concentrations were measured in triplicate using the Skalar, the results were averaged and plotted against distance downstream (Figure 28).

Nitrate concentrations decreased month-to-month and were most variable in April and May. Concentrations decreased downstream in both surface and bottom waters in April, and surface waters in May. Nitrate and salinity had a strong negative correlation. Salinity increased both downstream and from April to June, nitrate decreased in both circumstances.

Phosphate concentrations were less than 0.1mg/L in all water samples except those collected at depth on 18/04/2023. These water samples had concentrations exceeding 0.2mg/L at sites 2-7. Phosphate concentrations exhibited a weaker negative correlation with salinity.

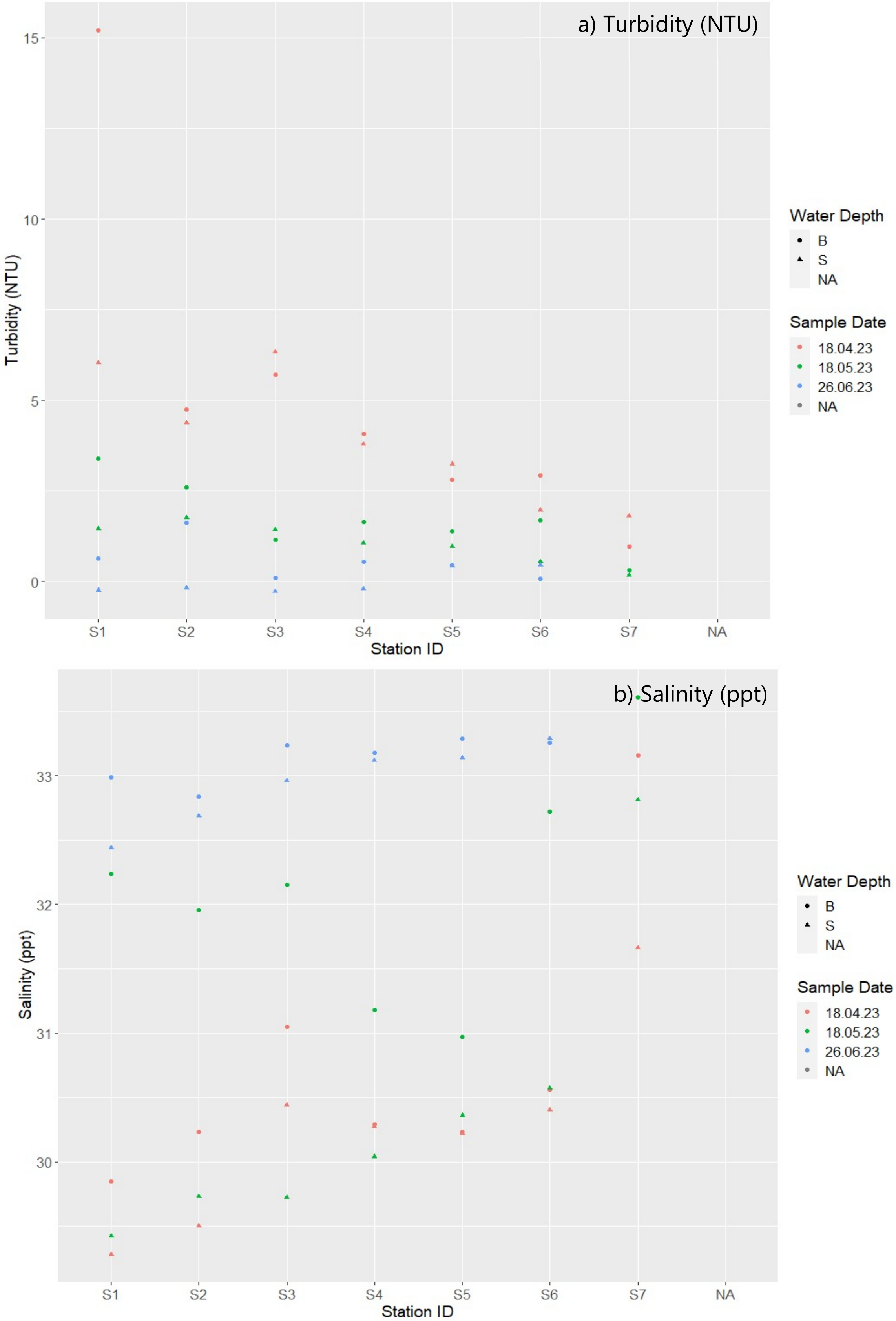
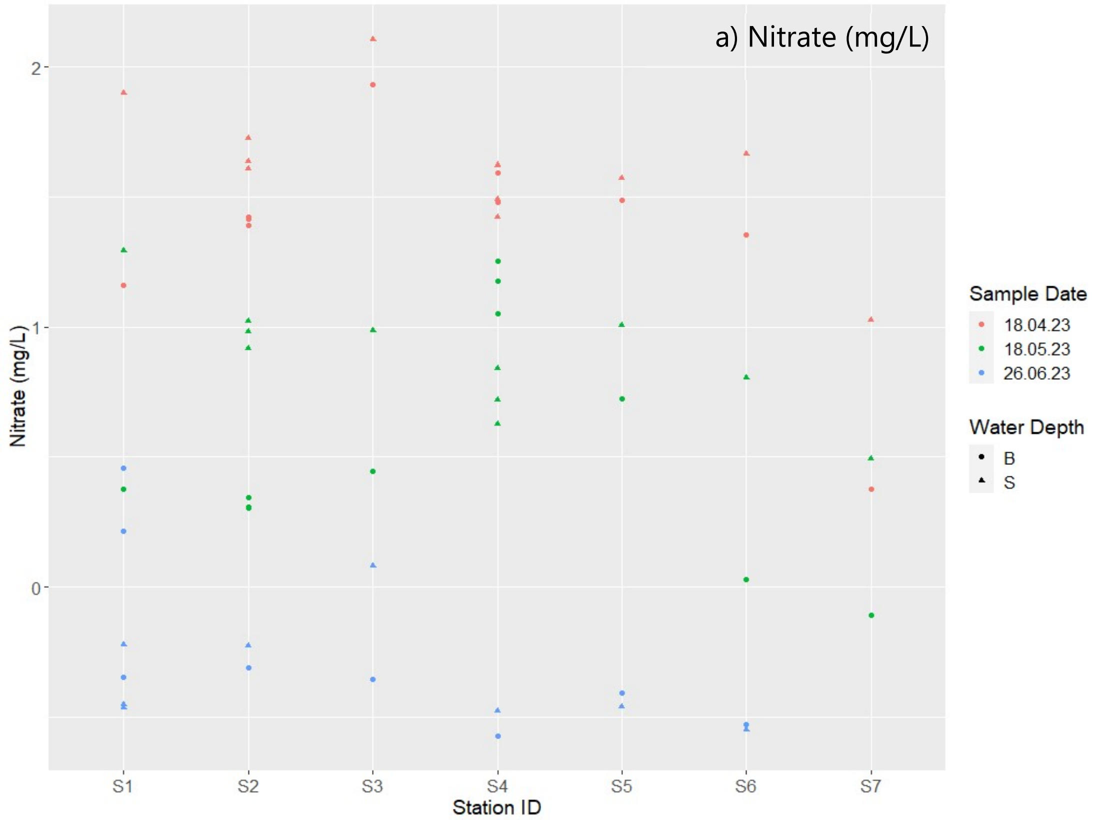


Figure 27: *Scatterplots of a) Turbidity (NTU) and b) Salinity (ppt) using data collected on 18/04/2023, 18/05/2023 and 26/06/2023 using a YSI probe at the surface and at depth.*



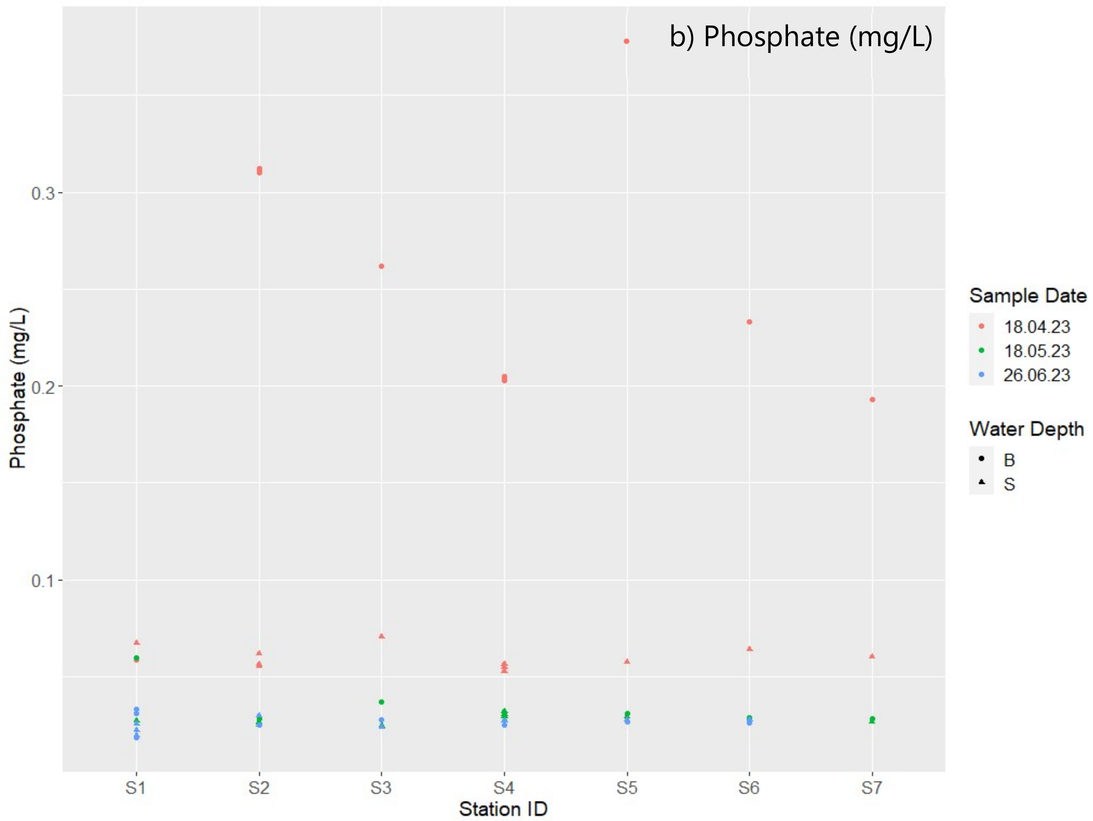
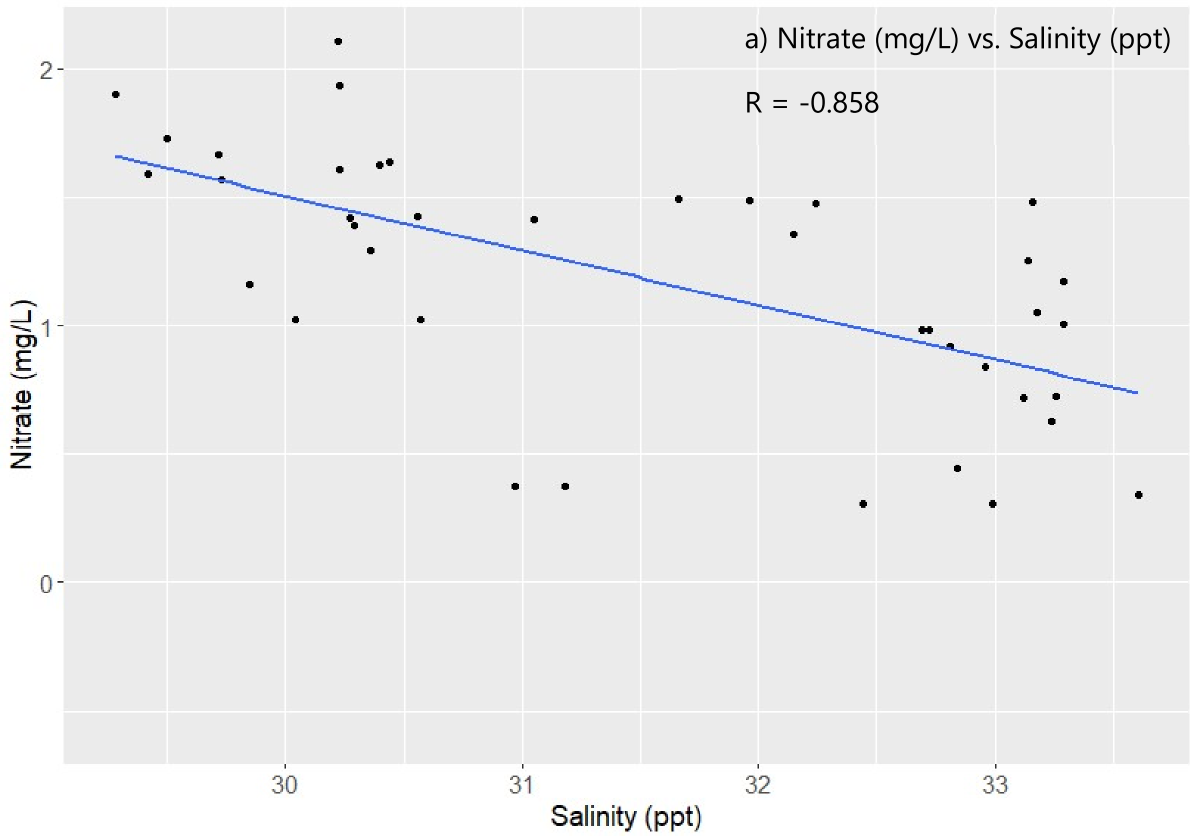


Figure 28: *Scatterplots of a) Nitrate (mg/L) and b) Phosphate (mg/L) using water samples collected on 18/04/2023, 18/05/2023 and 26/06/2023 at the surface and at depth, analysis was undertaken using Skalar automated nutrient analyser.*

3.3.3 Comparison of EA and field work data

Only one of the four estuary entry sites has been measured so far in 2023 by the EA. Data was collected at YLM02 in March and June, the closest date to one of our field study days being 22/06/2023. The nitrate and orthophosphate concentrations recorded by the EA on this day were 4.39 mg/L and 0.18mg/L, respectively. The highest concentrations measured from water samples collected during field work on 26/06/2023 were 0.081 mg/L of nitrate and 0.028 mg/L of phosphate.

Both samples were taken approximately 2 hours after high tide, discrepancies may be explained by increased volume and mixing in estuarine waters, diluting the nitrate and phosphate concentrations. The negative correlations with salinity exhibited by both nitrate and phosphate indicate that sources of both are river derived, meaning they will naturally decline when mixed with salt water and no new nitrate or phosphate is being added to the system. The correlation highlights this interaction (Figure 29). Higher concentrations on 22/06/2023 may also be explained by increased rainfall in the week leading up to this sampling when compared to the dry conditions recorded preceding sampling on 26/06/2023.



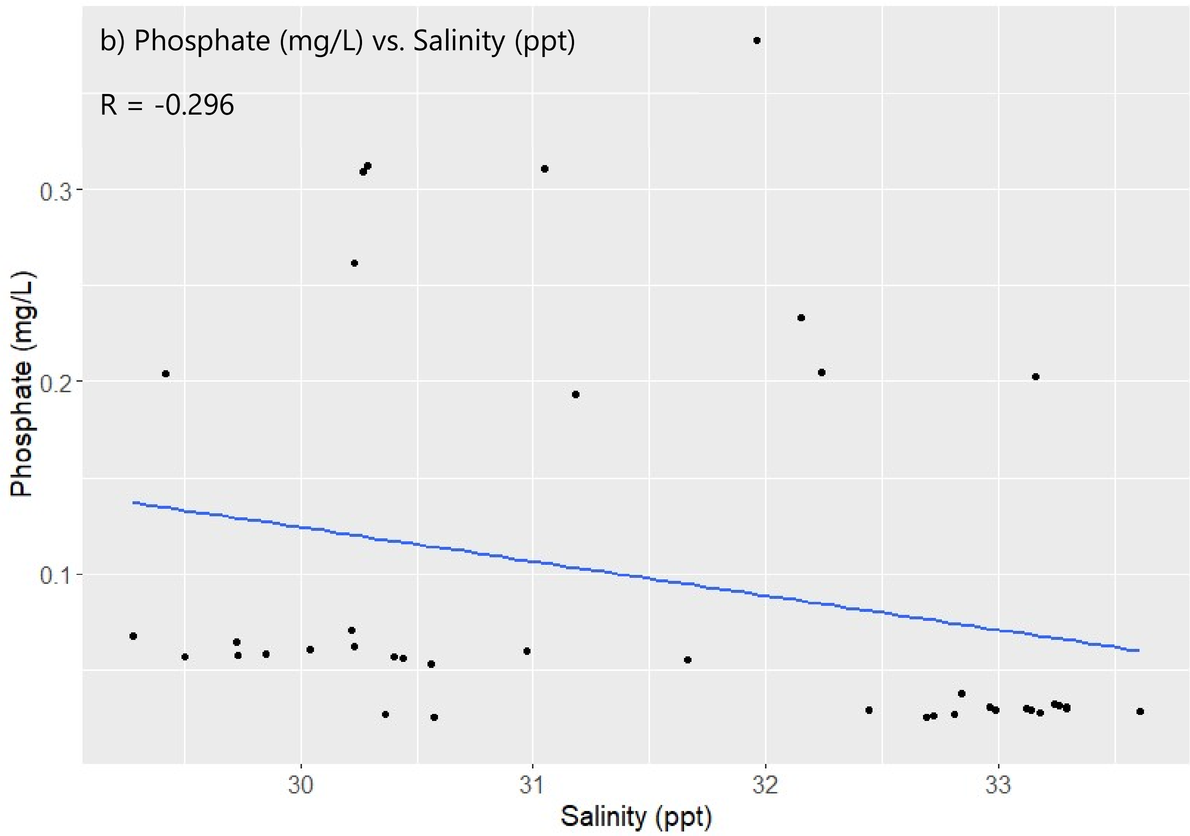


Figure 29: *Correlations of salinity and a) nitrate and b) phosphate from field data collected on 18/04/2023, 18/05/2023 and 26/06/2023.*

3.3.4 Chlorophyll Analysis

Chlorophyll absorbances were measured using spectrophotometry before being converted to concentration according to the amount of water filtered for each sample (Figures 30 and 31).

In May, concentrations peaked at depth at sites 2, 3 and 6 while it in June it peaked at 2, 3 and 6 in surface waters. The overall concentrations of chlorophyll remained consistent between the two sampling days. The change in depth of the chlorophyll peak is likely related to the time of day. Samples taken in June were later in the day suggesting this change is closely linked with diurnal migration.

The chlorophyll concentrations measured were compared to those measured by Maier *et al.* (2009) in the Taw estuary. The Taw is a eutrophic estuary meaning a comparison of the two may provide insight into the potentially damaging impacts of high chlorophyll concentrations. In the Taw, concentrations peaked at 100µg/L while in the Yealm, the peak was 2.48, 2.60 and 8.55µg/L for chlorophyll a, b and c, respectively. Indicating that this estuary is not yet at risk of eutrophication driven by increased nutrient concentrations in the catchment.

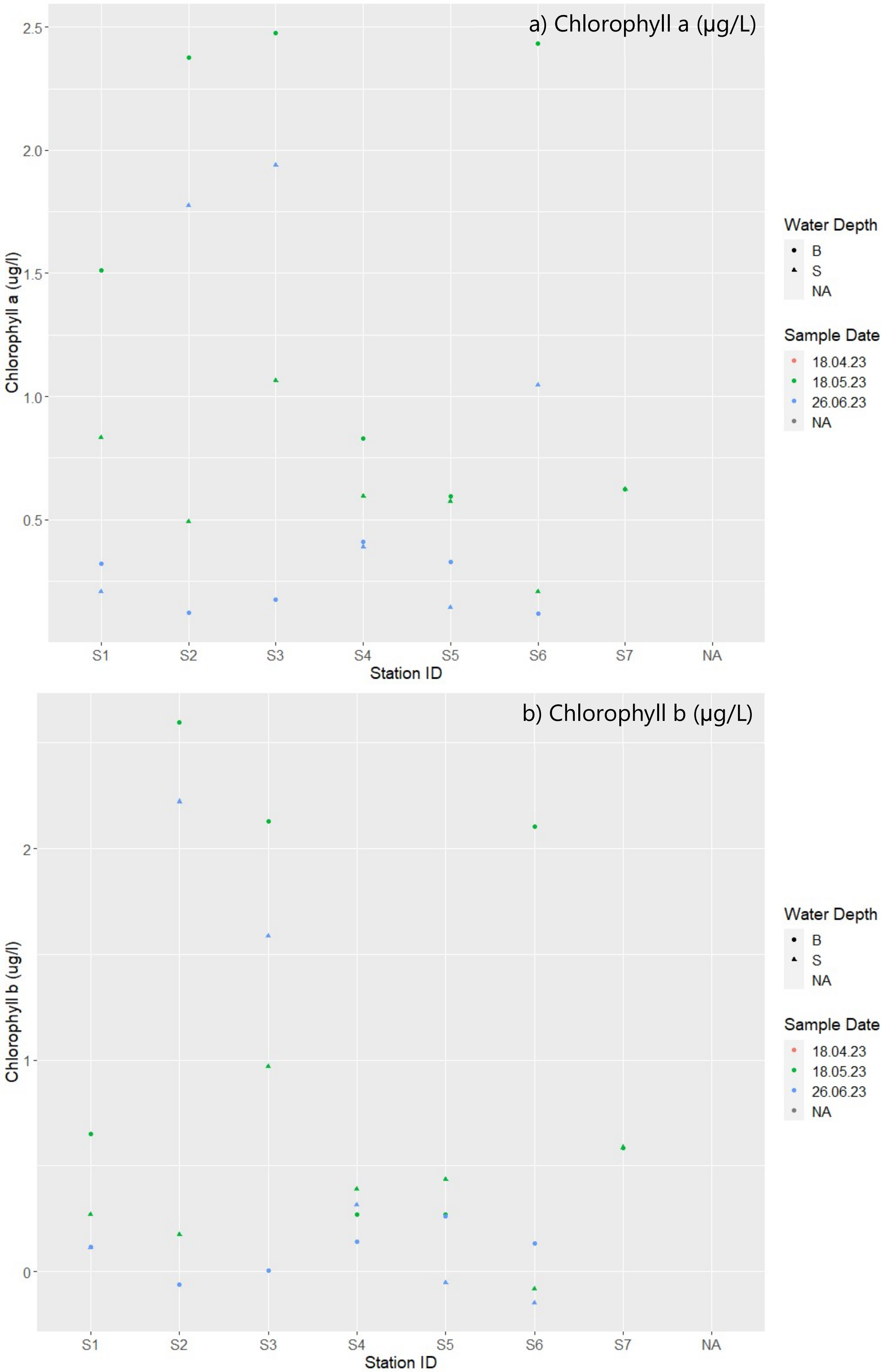


Figure 30: *Concentrations of a) chlorophyll a (µg/L), b) chlorophyll b (µg/L) measured from water samples collected in the Yealm estuary at sites 1-7 on 18/05/2023 and 26/06/2023 at the surface and at depth using a JENWAY 7310 Spectrophotometer.*

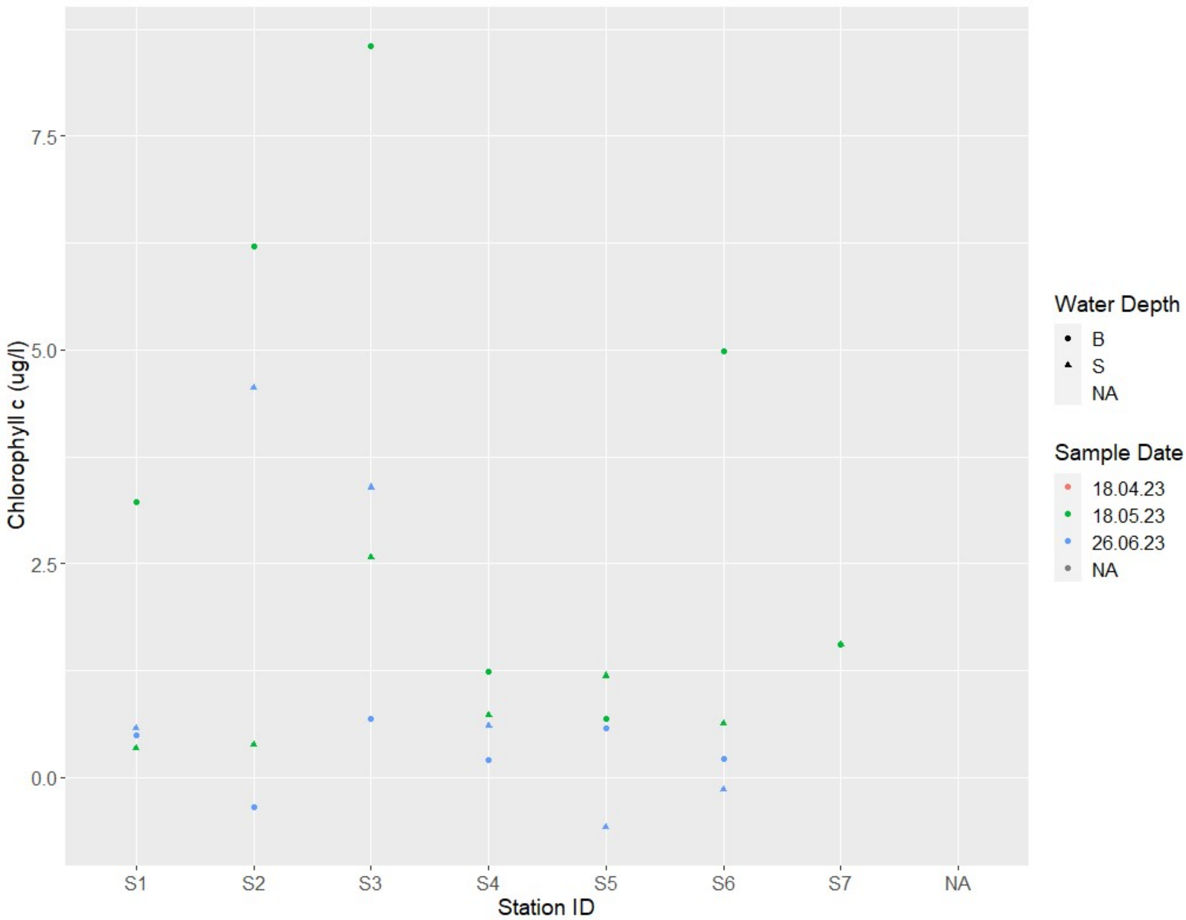


Figure 31: *Concentrations of chlorophyll c (µg/L) measured from water samples collected in the Yealm estuary at sites 1-7 on 18/05/2023 and 26/06/2023 at the surface and at depth using a JENWAY 7310 Spectrophotometer.*

3.3.5 Multidimensional Scaling

Using PRIMER 6 the field data was collated and an MDS plot created. Data were first plotted as a draftsman's plot to determine their distribution before being normalised to account for differences in units measured.

For the MDS plot, measurements were directly compared, meaning only parameters measured on all three sampling days could be included. These parameters were temperature, % oxygen saturation, dissolved oxygen conductivity, salinity, turbidity, depth, nitrate and phosphate; chlorophyll a-c and pH were excluded. The distance matrix was calculated using Euclidean distances before generating the MDS plot.

The MDS plot shows a clear distinction between measurements taken from surface and bottom waters (Figure 32). It also highlights a change in variability of measurements over time. Data points taken on 18/04/2023 were less well grouped, therefore indicating a great variability in the measurements taken on this day when compared to those taken on 18/05/2023 and 26/06/2023 which show a greater degree of clustering.

The clear clustering of data points further highlights the differences between monitoring dates and water depth. It is likely that changes of this nature driven by both seasonal variability including weather and tidal cycle.

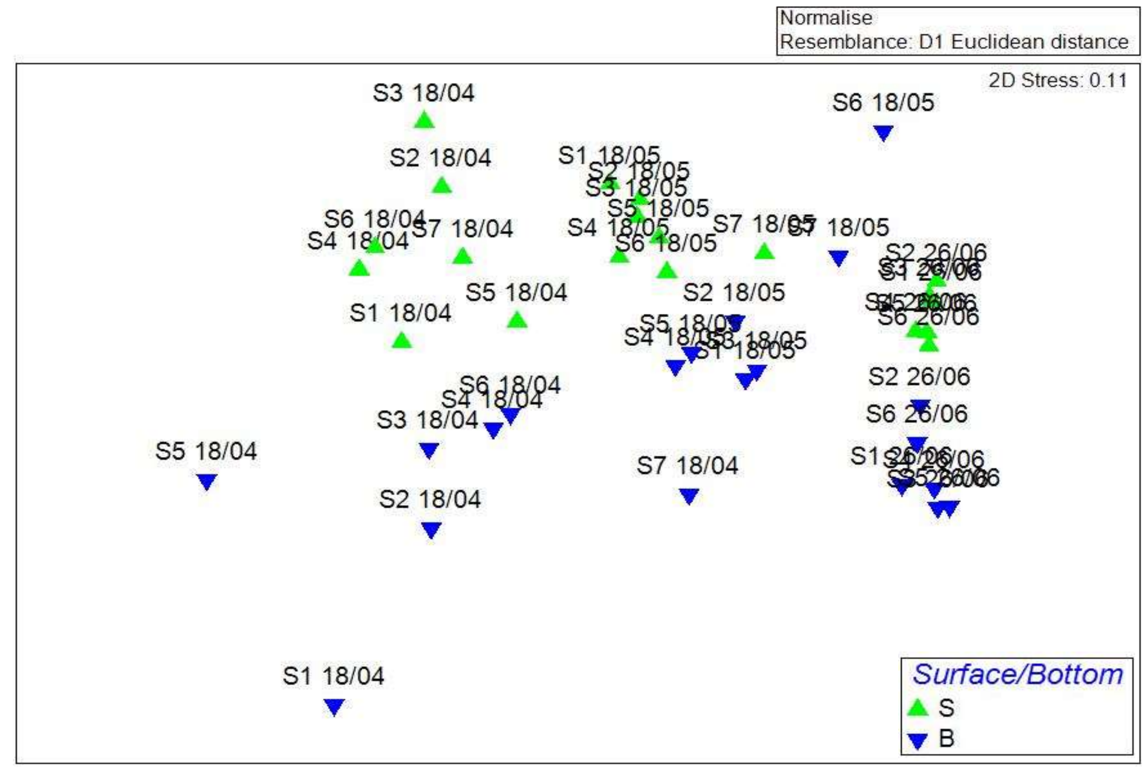


Figure 32: *MDS plot of data collected on 18/04/2023, 18/05/2023 and 26/06/2023, excluding pH and chlorophyll measurements.*

3.4 Discussion

The transport of nutrients through the Yealm estuary was investigated as a way of determining potential threats to the estuarine environment from riverine sources. The habitats of particular interest being the seagrass beds located in the lower part of the estuary.

3.4.1 Changes in Nutrient Pollution

Sample collection was carried out in April, May and June on the ebb tide. All physical parameters measured were strongly influenced by month-to-month changes in weather and/or tidal cycling.

To determine the transport of nutrients through the estuary, it was important to compare measurements taken on the day of sampling to those measured at estuarine entry sites monitored by the EA. Concentrations taken in the estuary were significantly lower than those measured at YLM02, the discrepancy between these two results can be explained by several factors. Firstly, increased volume; YLM02 is located in the Newton Ferrers creek which has a much smaller volume than that of the estuary, diluting the nutrient concentrations. Secondly, the high mixing rates and a short residence time in the Yealm estuary may disperse nutrients entering from the river systems quickly, causing their influence to be much less pronounced (Uncles *et al.* 2002). Thirdly, most of the nutrients entering from the riverine system will be used by marine organisms including phytoplankton (Kamjunke *et al.* 2023). Finally, the higher concentrations observed on 22/06/2023 may have been the result of high rainfall in the days leading up to it, conversely, before sampling on the 26/06/2023, very little rain had been recorded.

Nitrate concentrations decreased from April to June, in line with seasonal fluctuations observed in the EA data investigation. In addition, patterns of downstream variability changed over time. Concentrations decreased downstream at the surface and at depth in April, and at the surface in May. Water samples taken in June, and at depth in May showed a much greater homogeneity than was seen in April. Nitrate concentrations were strongly correlated with salinity. This indicates that the main driver for change of nitrate concentrations is the mixing of freshwater and saline waters in the estuary. From this investigation it is unclear whether the decrease in nitrate concentration associated with increased salinity was caused by dilution, dispersal or use by marine organisms. It is likely that all three play a role.

Phosphate concentrations showed little variability over each sampling day and the majority of samples remained below 0.1mg/L. However, in deep water samples taken in April, concentrations exceeded 0.2mg/L. This indicated that there was an input of phosphate into deeper waters on this date. This is likely a saltwater input as saline waters are denser and reside at depth as the tide moves in and out. However, this is a well-mixed estuary with a short residence time, so high concentrations of phosphate would also be expected in surface waters. Another explanation could be an increase in sediment disturbance. Phosphate tends to adsorb to suspended particles such as clays and muds which settle out in the sedimentation process (Meng *et al.* 2014). Resuspension of sediments at depth may have temporarily increased the concentration of dissolved phosphate in the water column (Wu *et al.* 2020; Monte *et al.* 2023).

3.4.2 Changes to Chlorophyll Concentration

Chlorophyll concentrations were taken in May and June only. They exhibited a shift in peak concentration from deeper waters in May to shallower waters in June. This indicates a shift in phytoplankton to shallower waters which may be explained by diel vertical movement as the June survey was conducted later in the day and/or by seasonal vertical migration patterns. Concentrations in May and June were relatively similar suggesting there was no evidence of month-to-month variation.

In addition, concentrations of chlorophyll appear to be well below the concentrations found in eutrophic estuaries including the Taw (100μg/L) (Tett, 1987; Maier *et al.* 2009. In its current state the estuary is not at risk of eutrophication, and thus habitats such as seagrass beds are unlikely to suffer the associated changes to light and nutrient availability and smothering by filamentous algae.

4.1 Synthesis

4.1.1 How does the state of the catchment impact the estuary

When investigating the pollution in the Yealm catchment it is important to consider the potential impact on the estuarine system. The EA monitoring data gathered did not have consistent measurements of estuarine parameters, meaning conclusions drawn about the catchment could not be extended to the estuary. As such, a field study was conducted on estuarine waters to determine the transport and distribution of pollutants through the estuary.

Overall conclusions about the state of the catchment and its potential impact on the estuary can be divided into two parts; what is coming down the estuary; and where is it coming from.

A discussion of temporal and spatial change in pollutants is provided in Section 2.4. To summarise, the following statements can be made. Firstly, nitrate control has improved over time, though continues to exhibit a downstream build-up. Secondly, phosphate concentrations have become more variable and reach high peaks in all areas of the catchment. Finally, *E.coli* and *Enterococci* concentrations, though exhibiting more control in later years, consistently exceed the safe bathing standards limit. These findings indicate that better control is required all round to manage the pollutants entering the riverine system and travelling downstream to the estuary.

In terms of sources of pollutants and areas of concern, there are several locations worth discussing. The first is the Newton stream. Samples taken in this area exhibit high concentrations of all pollutants measured, high variation in concentration is also evident, indicating a lack of pollutant control in this region. The same can be said for Cofflete Creek which consistently provides evidence of high pollutant peaks and little control over time. Both Newton Stream and Cofflete Creek have sewage treatment facilities upstream of the monitoring sites. The third location of interest is between YLM20 and YLM17, this area exhibits peaks in both *E.coli* and *Enterococci*, most likely from the Lutton STW. The area of river between YLM14 and YLM11 is an area of input for both nitrate and phosphate. The lack of sewage infrastructure on this stretch suggests that agriculture is the most influential input here, the joining of Long Brook also brings agriculture derived nitrate and phosphate. Finally, there are several point sources of pollutants that should be carefully monitored; the Lee Mill industrial site and the 11 sewage treatment facilities scattered throughout the catchment.

Given the current state of the catchment, the pollutant types evident in the water and the pollutant sources identified, it is important to determine the potential impacts on the estuarine environment.

The Yealm estuary is protected under several designations including the Plymouth Sound and Estuaries SAC, the South Devon AONB and the Yealm estuary and Wembury Point SSSI regions (Yealm Estuary to Moor, 2022; Natural England 2023). These designations have been appointed for several reasons including but not limited to the presence of several seagrass beds in the estuary (Yealm Estuary to Moor, 2022). The Yealm also has a history of oyster and mussel farming, though the high concentrations of *E.coli* in the water column mean constant monitoring is required and classifications to be regularly checked (Wilson, 1941; Cefas, 2010; Yealm Estuary to Moor, 2022). The Yealm estuary is a very short section of water, important for many recreational activities including boating and fishing (Yealm Estuary to Moor, 2022), and the popular Wembury Beach at its far end has been granted bathing water status (Yealm Estuary to Moor, 2022).

As such, the health and water quality of this estuary should be closely monitored and managed to ensure it continues to provide high quality habitat, and a clean and safe area for recreation. The pollutant levels in the Yealm catchment may be a threat to the estuary, particular as many of the pollutants measured accumulate downstream and reach peak concentrations at the point at which tributaries enter the estuarine system.

The seagrass beds are of particular concern as they provide a great deal of benefits not only to the organisms living within them, but also to the health of the estuary as a whole, and to the communities surrounding them. Seagrasses provide food and shelter to important species, they promote sedimentation and seabed stabilisation, and they filter water, improving the water quality of the surrounding area (Short and Wyllie-Echeverria, 1996; Diekmann *et al.* 2010; Curiel *et al.* 2021; Potouroglou *et al.* 2021). In addition, seagrass beds provide coastal protection through the reduction of wave energy, and act as nurseries for commercial fish species (Waycott *et al.* 2009; Paul and Amos, 2011; Curiel *et al.* 2021; The Plymouth Sound and Estuaries SAC, 2021). They also provide services in carbon capture and storage, storing up to

140 Mg C ha^{-1} (Nelleman *et al.* 2009; Fourqurean *et al.* 2012; Cullen-Unsworth and Unsworth, 2013; Duarte *et al.* 2013; Blue Carbon Initiative, 2023).

Understanding and monitoring the impact of river derived pollutants is therefore vital to the successful management of estuarine and seagrass environments. The two main pollutant types entering the estuarine system from the Yealm catchment are nutrients in the form of nitrate and phosphate, and bacteria, in particular *E.coli* and *Enterococci*.

Nutrient concentrations entering the estuary have the potential to trigger eutrophic events (Musacchio *et al.* 2019). Such events alter the water chemistry causing phytoplankton and algal blooms (Davison and Hughes, 1998; van Katwijk *et al.* 2009; Calleja *et al.* 2017; Curiel *et al.* 2021). These organisms then compete with macroalgal and seagrass assemblages, rapidly taking up nutrients, increasing turbidity, reducing light availability and in some cases, smothering slower growing species (van Katwijk *et al.* 2009; Calleja *et al.* 2017; Curiel *et al.* 2021). This change in species assemblage can trigger a positive feedback loop from which these slow growing species are unable to recover (van der Heide *et al.* 2007). Additionally, a loss of seagrass and macroalgal habitat will likely lead to a shift in population dynamics, reducing the available space, shelter and food provided for species normally living in these habitats. Including important commercial fish species, protected species including the long-snouted seahorses (Waycott *et al.* 2009; Unsworth *et al.* 2018; The Plymouth Sound and Estuaries SAC, 2021).

E.coli and *Enterococci* concentration are potentially damaging to filter feeding organisms, including those farmed and sold as food (Campos *et al.* 2013). The sediments in many estuarine systems holds a high concentration of E.coli and other bacteria over long periods of time (Wyness *et al.* 2019). These bacterial colonies pose little threat while contained within sediments, however when resuspended or eroded can lead to high suspended concentrations which are then able to travel, spreading into other environments including seagrass beds and shellfish beds (Wyness *et al.* 2019). Many of these bacteria are then able to make their way into the human food chain impacting both the shellfish industry and NHS (Campos *et al.* 2013; Hassard *et al.* 2016; Wyness *et al.* 2019).

When comparing the concentrations of nitrate and phosphate measured by the EA at Newton Ferrers and the data collected in the field, there is a significant difference. The concentrations measured in the river water were much higher than that of the estuary. The measurements taken also indicate that both nitrate and phosphate concentrations are negatively correlated with salinity. As such, it can be assumed that nitrate and phosphate concentrations in river water decrease in estuarine water for the following reasons. The first being dilution; the volume of water in Newton Stream is much less than that of the estuary, and as nitrate is typically derived from riverine water the concentration decreased when mixed with sea water. The second reason is use by marine organisms, namely phytoplankton (Kamjunke *et al.* 2023). The nitrate and phosphate entering the estuary are bioavailable, meaning they can be quickly absorbed and used in photosynthesis and growth (Asmala *et al.* 2013; Woodland *et al.* 2015). High concentrations of phytoplankton will rapidly decrease the amount of dissolved nutrients (Woodland, *et al.* 2015; Kamjunke *et al.* 2023). Finally, the Yealm estuary has a relatively short residence time (1.5 days) (Uncles *et al.* 2002). This means that nutrients entering the system are quickly washed through, limiting build-up and keeping concentrations low.

E.coli and *Enterococci* measurements were not taken on field study days and cannot be compared between the river and estuary. However, the high peaks and lack of control of these bacteria indicate that focus should be drawn to their management regardless of their potential estuarine impacts.

In its current state, the potential impact of nutrient pollution entering the estuary from the Yealm catchment is not significant. At the concentrations measured, there is little risk of eutrophic events. However, high concentrations of phosphate measured in May indicate that more attention is required to manage phosphate concentrations entering both the riverine and estuary systems. In addition, continuous monitoring of both nitrate and phosphate should be prioritised to determine the change estuarine concentrations in relation to seasonal variation, and in response to peaks in pollutants further upstream.

Chlorophyll concentrations measured un the estuary reflect this conclusion. Thresholds set by Tett (1987) and reinforced by findings by Maier *et al.* (2009) state that chlorophyll concentrations of 100µg/L are indicative of eutrophic events. The highest chlorophyll a concentration measured in the Yealm estuary was 2.45µg/L. As such, though there are risks to the estuary in terms of pollutant spikes and point sources. The high residence time (1.5 days) allows nutrient pollution to be quickly washed out of the estuary, reducing the time for phytoplankton blooms to build-up.

4.1.2 Does the current state of the estuary impact the seagrass?

In the Section 4.1.1, it was concluded that eutrophic events were unlikely to occur in the Yealm estuary given the current nitrate and phosphate concentrations observed and the response of phytoplankton in the water column.

However, monitoring of the seagrass beds is still a vital part of the management of this estuary system and should be considered going forward. Data collected by Tim Scott and team provide insight into the changes in seagrass coverage and canopy height in the Yealm estuary from in 2021-2022 (Figures 33 and 34). The following maps indicate that both canopy height and coverage have increased significantly between these two years of monitoring. This monitoring program is set to continue indefinitely to provide a clear picture of how the seagrass beds of the Yealm estuary change year on year and what the potential causes of this change may be. For instance, the increase in the coverage and canopy height observed between 2021 and 2022 was likely caused by the hot sunny weather experienced in the summer of 2022 (Met Office, 2023). This weather combined with a lack of summer storm activity (Met Office, 2023) provided the perfect conditions for seagrasses to grow and thrive. Monitoring activities went ahead in the 2023 season, however data has not yet been processed.

Continual monitoring of this kind will enable interannual change of seagrass coverage to be observed, which, coupled with monitoring of estuarine water quality would provide a better understanding of the dynamics of seagrass growth in the estuary. Nitrate and phosphate peaks, as well as measurements of chlorophyll concentrations would allow for the observation of the influence of nutrient pollution on the seagrass beds. It may also allow for predictions of future eutrophic events and their potential impact on the estuary system.

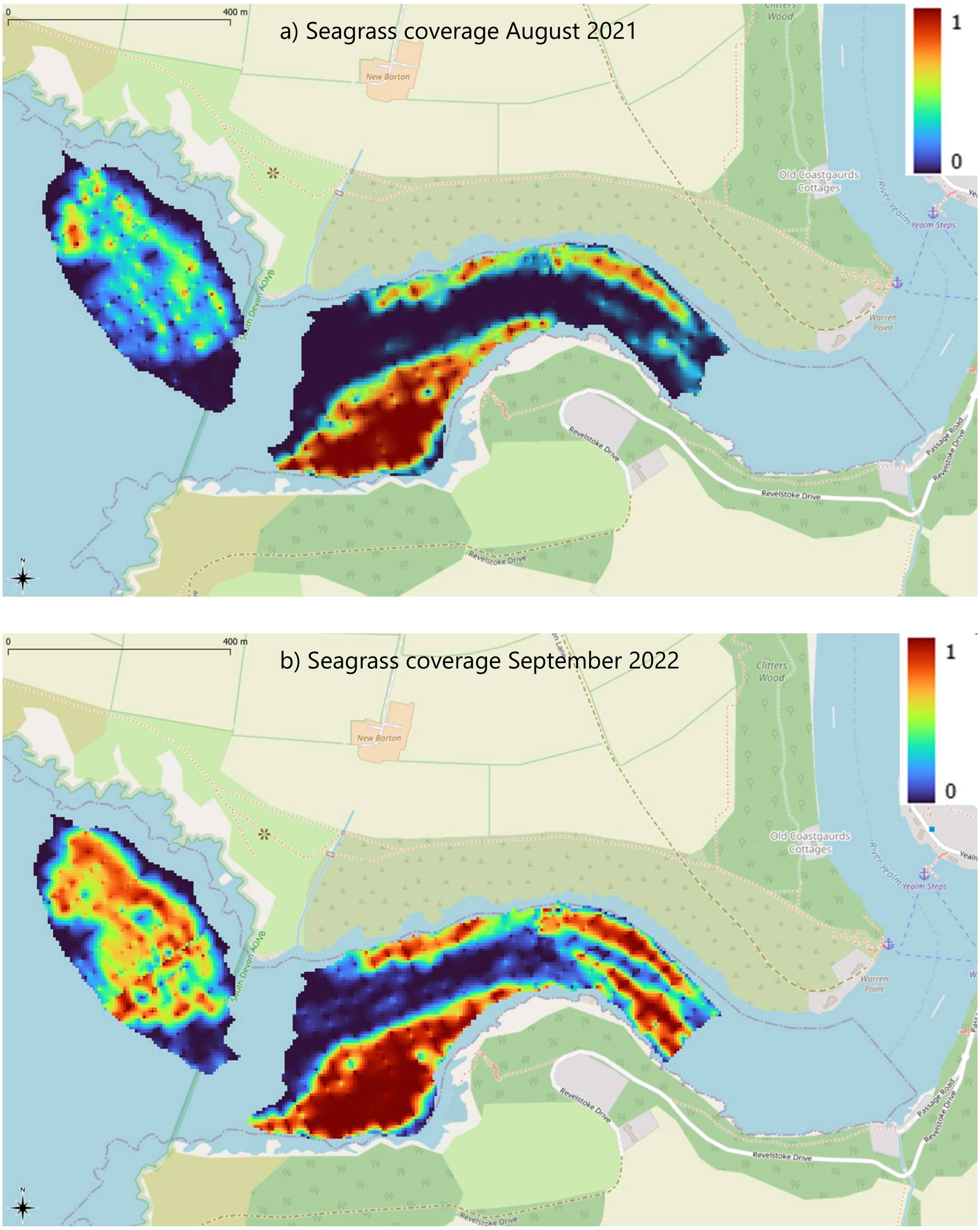


Figure 33: *Seagrass coverage measured using a Valeport echosounder on USV in a) August 2021 and b) September 2022. Data collected by Tim Scott and team.*

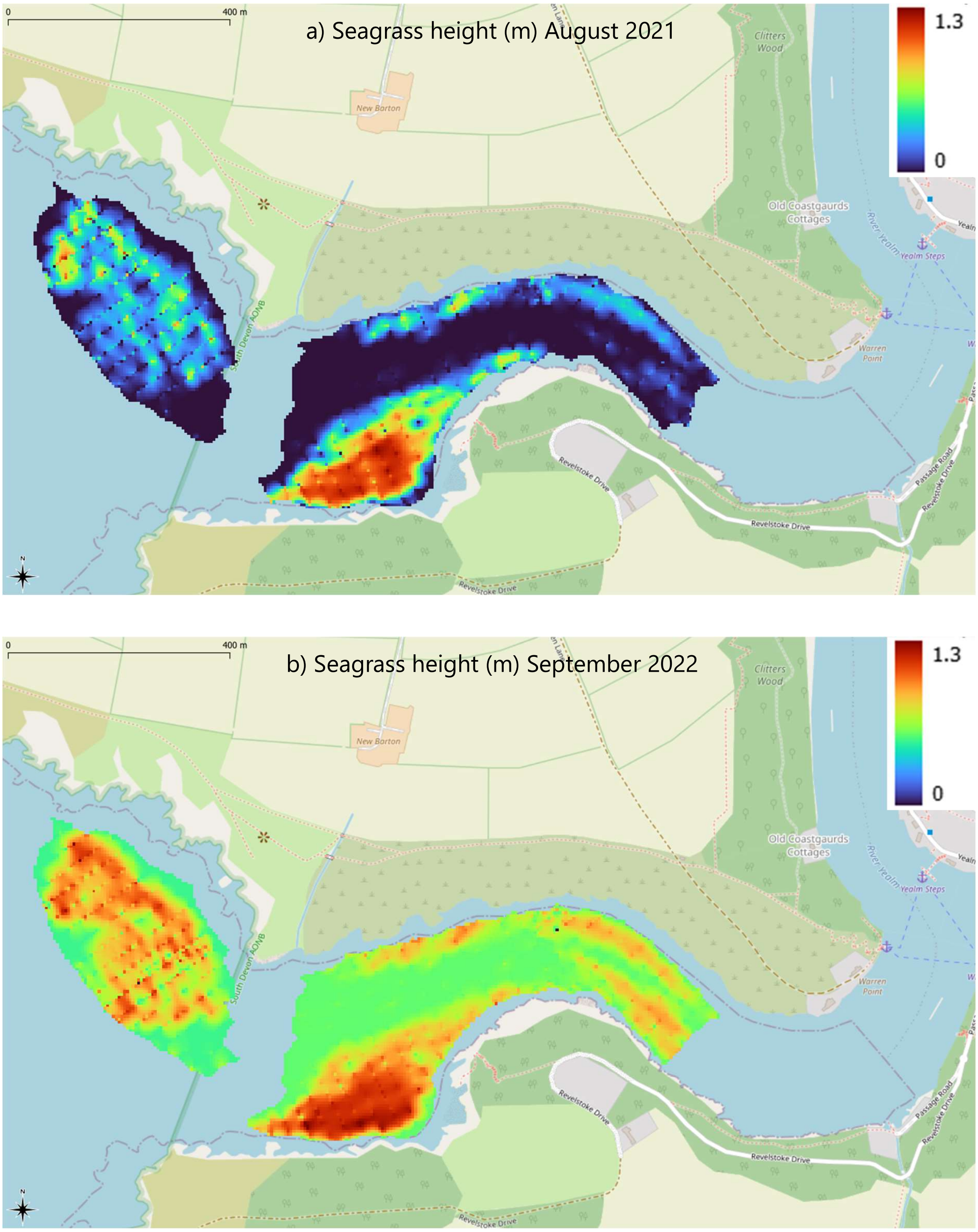


Figure 34: *Seagrass height (m) measured using a Valeport echosounder on USV in a) August 2021 and b) September 2022. Data collected by Tim Scott and team.*

4.1.3 Recommendations for the YEM group and management of the Yealm catchment

Part of the justification from this project was to ensure all data and findings are made available to the YEM group to further their research and work towards improving biodiversity in the Yealm catchment.

As such, the following suggestions to the YEM group can be made.

- Expand data collected by the citizen science project to include potential areas of input such as sewage treatment facilities, Lee Mill industrial site, Newton Stream, Cofflete Creek and Long Brook.
- Continue monitoring estuarine water quality, particular in the days surrounding peaks in nitrate, phosphate and suspended solids.
- Continue to work with and support groups that are working to reduce overall nitrate and phosphate release, including government policy changes.
- Support the continued monitoring of the Yealm estuary seagrass in the hope of generating a clear picture of changes over time.
- Continue to restore riparian habitats including woodland and grassland to help reduce run-off, particular in areas of agricultural land use and areas adjacent to towns.

4.1.4 Future work to be undertaken

The final statement of this project is that much more work needs to be done. This investigation has barely scraped the surface of determining the condition of the Yealm catchment and what the potential threats are. Developing a baseline dataset from which to compare future states is an enormous task, this project has focused on the chemical side, with an emphasis on nutrient and bacterial threats. There are numerous other investigations to be undertaken to fully understand the catchment and develop an effective and sustainable management plan.

Future investigations of the Yealm catchment could focus on additional factors such as an in-depth analysis of metal and chemical pollution, particularly those that have been highlighted by the WFD. Another potential study pathway would be to investigate the aquatic biodiversity, a study such as this could focus on the Electrofishing data combined with kick sampling to determine the impact of pollutants on both the vertebrate and invertebrate assemblage. An additional and highly important area of study would be to collect targeted water quality data at sewage treatment facilities, particularly after periods of heavy rain to gain better insight into release events.

In addition, those who undertake work such as this must ensure that long-term datasets are maintained and expanded for both riverine and estuary systems into the future. Catchment studies should also conduct monitoring on all tributaries as even the smallest stream can be a major source of pollution.

5.1 Conclusion

To conclude this investigation the hypotheses stated in Section 1.2 will be addressed.

> **H1:** Concentrations of pollutants increase significantly downstream.
>
> **H2:** Concentrations of pollutants are significantly different in the first and last year of monitoring by the Environment Agency.
>
> **H3:** Pollutant concentrations increase at the sites of sewage treatment facilities.
>
> **H4:** There is a significant seasonal variation in all pollutants analysed.
>
> **H5:** Concentrations of pollutants at estuarine entry points reflect those in the water column at seagrass beds.
>
> **H6:** The health of seagrass beds is impacted by high concentrations of pollutant input from the Yealm catchment.

Hypotheses one to four pertain to the state of water in the catchment as measured by the EA from 2000-2022. None of these hypotheses listed can be answered in a straight forward manner, most are both true and false. For instance, only nitrate and orthophosphate increased downstream, while all other parameters were much more variable. The same of true for hypotheses two, only nitrate showed an overall significant difference between the first and last five years of monitoring. In terms of sewage treatment facilities, neither nitrate, orthophosphate, *E.coli* or *Enterococci* varied consistently in relation to sewage treatment facilities. While ammoniacal nitrogen, suspended solids, oxygen saturation and BOD 5-day did. Finally, none of the parameters measured exhibited significant seasonal variability when compared month-to-month. Some showed a pattern of change but were not significant. The variability in the conclusions drawn only goes to highlight the need for more data and better, more consistent monitoring programs.

When investigating the state of the estuary in an attempt to answer hypotheses five and six we get a clearer picture. In both cases the hypotheses have been shown to be untrue. Nutrient pollution is rapidly diluted and dispelled by the higher volume and short residence time of the estuary. As such, the seagrass beds residing within the estuary are at low risk of eutrophication. However, this does not mean that they should be forgotten. The data collected on the estuary was taken on a very short time scale, more data needs to be collected to be able to fully answer these hypotheses.

Overall, the main conclusion to draw is that more and better quality data needs to be collected. Whether this is using citizen scientists, NGOs or governments groups does not matter. They key is that data are replicable, consistent, and thorough. To fully understand and manage the Yealm catchment the source areas, the estuary and all tributaries but be represented in data collection going forward.

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Appendix a: Parameter Table

Table i: *Parameters measured by the Environment Agency at 9 stations throughout the Yealm catchment and the temporal scale of each.*

	YLM02	YLM07	YLM08	YLM09	YLM11	YLM14	YLM17	YLM20	YLM21
1,1,1-Trichloroethane		01/00 – 04/05							
1,2,3-Trichlorobenzene		01/00 – 01/14							
1,2,4-Trichlorobenzene		01/00 – 01/14							
1,2-Dichloroethane		01/00 – 01/14							
1,3,5-Trichlorobenzene		01/00 – 01/14							
Action Taken		01/00 – 12/00							
Active Aluminium: Dissolved						10/11 – 08/18			
Aldrin	05/04	01/00 – 01/14	05/04	05/04					
Alkalinity to pH 4.5 as CaCO3	01/13 – 02/19	03/00 – 12/21			03/00 – 12/03	03/00 – 04/17	03/00 – 02/17	12/13 – 11/22	03/00 – 11/22
Aluminium						07/11 – 08/18	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Aluminium, Dissolved						07/11 – 08/18	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Ammonia un-ionised as N	01/13 – 03/19	01/00 – 11/21	07/05 – 09/05	07/09 – 09/05	01/00 – 12/06	01/00 – 04/17	02/00 – 02/17	12/13 – 11/22	02/00 – 11/22
Ammoniacal Nitrogen as N	02/07 – 11/22	01/00 – 12/21	07/05 – 03/21	07/05 – 03/20	01/00 – 03/20	01/00 – 04/17	01/00 – 11/22	01/09 – 11/22	01/00 – 11/22
Arsenic, Dissolved	05/04	05/04	05/04	05/04					
Bacteroides CF128 primer	03/06	03/06	03/06	03/06					

Bacteroides HF183 primer	03/06 – 08/10	03/06	03/06 – 12/09	03/06 – 01/11					
Bacteroidetes Marker: All	09/07 – 08/10		09/07 – 12/09	09/07 – 01/11					
Bacteroidetes Marker: Ruminant	09/07 – 08/10		09/07 – 12/09	09/07 – 01/11					
Barium						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Barium, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
BOD: 5 Day ATU		01/00 – 12/06	07/05 – 09/05	07/05 – 09/05	01/00 – 12/06	01/00 – 12/06	01/00 – 09/13		01/00 – 12/06
Boron						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Boron, Dissolved	02/07 – 01/10		02/07 – 01/10	01/07 – 01/10	01/07 – 01/10	01/07 – 02/12	01/07 – 02/12	01/09 – 02/12	01/07 – 02/12
Cadmium		01/00 – 01/14				07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Cadmium, Dissolved	05/04	05/04	05/04	05/04	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Calcium		01/00 – 12/03			01/00 – 12/03	01/00 – 02/12	01/00 – 02/12	07/11 – 02/12	01/00 – 02/12
Calcium, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Carbon tetrachloride :- {Tetrachloromethane}		01/00 – 01/14							
Carbon, Organic, Dissolved as C :- {DOC}						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Chloroform :- {Trichloromethane}		01/00 – 01/14							
Chromium						12/11 – 02/12	12/11 – 02/12	12/11 – 02/12	12/11 – 02/12
Chromium, Dissolved	05/04	05/04	05/04	05/04		12/11 – 02/12	12/11 – 02/12	12/11 – 02/12	12/11 – 20/12

Coliforms, Faecal: Confirmed	05/04 – 01/14	05/04 – 03/06	05/04 – 01/14	05/04 – 01/14	01/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/09 – 04/13	01/07 – 01/14
Coliforms, Faecal: Presumptive: MF	05/02 – 01/14	05/02 – 03/06	05/02 – 01/14	05/02 – 01/14	01/07 – 01/14	06/05 – 01/14	06/05 – 01/14	01/09 – 04/13	01/07 – 01/14
Coliforms, Total: Confirmed: MF	02/07 – 01/14		02/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/09 – 04/13	01/07 – 01/14
Coliforms, Total: Presumptive: MF	05/02 – 01/14	05/02 – 09/05	05/02 – 01/14	05/02 – 01/14	01/07 – 01/14	06/05 – 01/14	06/05 – 01/14	01/09 – 04/13	01/07 – 01/14
Colour, Filtered	05/04	05/04	05/04	05/04					
Conductivity at 20C	03/05 – 04/14	07/05 – 09/05	07/05 – 06/05		07/05 – 09/05	07/05 – 02/07			
Conductivity at 25 C	01/13 – 03/19	05/10 – 12/21				07/11 – 04/17	03/07 – 02/17	07/11 – 11/22	07/11 – 11/22
Copper						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Copper, Dissolved	05/04	01/00 – 12/06	05/04	05/04	01/00 – 01/05	01/00 – 02/12	01/00 – 11/13	07/11 – 02/12	01/00 – 02/12
DDE -op		01/00 – 10/04							
DDE -pp	05/04	01/00 – 01/14	05/04	05/04					
DDT: Sum of components	05/04	05/04 – 01/14	05/04	05/04					
DDT -op	05/04	05/04 – 01/14	05/04	05/04					
DDT -pp	05/04	01/00 – 01/14	05/04	05/04					
Dieldrin	05/04	01/00 – 01/14	05/04	05/04					
Drins: Total (Aldrin, Dieldrin, Endrin, Isodrin)	05/04	05/04 – 01/14	05/04	05/04					
Endrin	05/04	01/00 – 01/14	05/04	05/04					
Enterococci: Intestinal: Confirmed: MF	06/12 – 11/22		06/12 – 03/21	06/12 – 03/20	06/12 – 03/20	06/12 – 03/16	06/12 – 11/22	06/12 – 11/15	06/12 – 03/16

Enterococci: Intestinal: Presumptive: MF	06/12 – 11/22		06/12 – 03/21	06/12 – 03/20	06/12 – 03/20	06/12 – 03/16	06/12 – 11/22	06/12 – 11/15	06/12 – 03/16
Escherichia coli: Confirmed: MF	02/07 – 11/22		02/07 – 03/21	01/07 – 03/20	01/07 – 03/20	01/07 – 03/16	01/07 – 11/22	01/09 – 11/15	01/07 – 03/16
Escherichia coli : HH2 genetic marker	03/06	03/06	03/06	03/06					
Escherichia coli: Presumptive: MF	02/07 – 01/14		02/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/07 – 01/14	01/09 – 06/12	01/07 – 01/14
Hardness, Calcium		01/00 – 04/00			01/00 – 05/00	01/00 – 05/00	01/00 – 05/00		01/00 – 05/00
Hardness, Magnesium		01/00 – 04/00			01/00 – 05/00	01/00 – 05/00	01/00 – 05/00		
Hardness, Total as CaCO3		01/00 – 12/03			01/00 – 12/03	01/00 – 02/12	01/00 – 02/12	07/11 – 02/12	01/00 – 02/12
HCH: Total (Alpha, Beta, Gamma)	05/04	05/04 – 01/14	05/04	05/04					
HCH: Total Isomers (Alpha, Beta, Gamma, Delta, Epsilon)		04/00							
HCH -alpha	05/04	04/00 – 01/14	05/04	05/04					
HCH -beta	05/04	01/00 – 01/14	05/04	05/04					
HCH - delta	05/04	05/04	05/04	05/04					
HCH -gamma :- {Lindane}	05/04	01/00 – 01/14	05/04	05/04					
Hexachlorobenzene	05/04	01/00 – 01/14	05/04	05/04					
Hexachlorobutadiene	05/04	01/00 – 01/14	05/04	05/04					
Iron						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Iron, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12

Isodrin	05/04	01/00 – 01/14	05/04	05/04					
Lead						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Lead, Dissolved	05/04	05/04	05/04	05/04		07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Lithium						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Lithium, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Magnesium		01/00 – 12/03			01/00 – 12/03	01/00 – 02/12	01/00 – 02/12	07/11 – 02/12	01/00 – 02/12
Magnesium, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Manganese						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Manganese, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Mercury		01/00 – 01/14							
Mercury, Dissolved	05/04	05/04	05/04	05/04					
Microbial Source Tracking	09/07 – 08/10		09/07 – 12/09	11/07 – 01/11					
MST Filtration	09/07 – 01/11		09/07 – 01/11	09/07 – 04/11		03/08	03/08		
National Grid Reference: Whole: Field report	08/08		08/08	08/08	08/08 – 12/09	08/08	08/08		08/08
Nickel						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Nickel, Dissolved	05/04	05/04	05/04	05/04		07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Nitrate as N	02/07 – 11/22	01/00 – 12/21	02/07 – 03/21	01/07 – 03/20	01/00 – 03/20	01/00 – 04/17	01/00 – 11/22	01/09 – 11/22	01/00 – 11/22
Nitrite as N	02/07 – 11/22	01/00 – 12/21	02/07 – 03/21	01/07 – 03/20	01/00 – 03/20	01/00 – 04/17	01/00 – 11/22	01/09 – 11/22	01/00 – 11/22

Nitrogen, Kjeldahl as N	03/07 – 11/22		02/07 – 03/21	01/07 – 03/20	01/07 – 03/20	01/07 – 03/16	01/07 – 11/22	01/09 – 11/15	01/07 – 11/22
Nitrogen, Organic as N	03/07 – 11/22		02/07 – 03/21	01/07 – 03/20	01/07 – 03/20	01/07 – 03/16	01/07 – 11/22	01/09 – 11/15	01/07 – 11/22
Nitrogen, Total as N	02/07 – 11/22		02/07 – 03/21	01/07 – 03/20	01/07 – 03/20	01/07 – 03/16	01/07 – 11/22	01/09 – 11/15	01/07 – 11/22
Nitrogen, Total Inorganic: (Calculated)		01/00 – 07/06			01/00 – 07/06	01/00 – 07/06	01/00 – 07/06		01/00 – 07/06
Nitrogen, Total Oxidised as N	02/07 – 11/22	01/00 – 12/21	02/07 – 03/21	01/07 – 03/20	01/00 – 03/20	01/00 – 04/17	01/00 – 11/22	01/09 – 11/22	01/00 – 11/22
Orthophosphate, Filtered as P	02/07 – 01/10		02/07 – 01/10	01/07 – 01/10	01/07 – 01/10	01/07 – 01/10	01/07 – 01/10	01/09 – 01/10	01/07 – 01/10
Orthophosphate, reactive as P	02/07 – 11/22	01/00 – 12/21	02/07 – 03/21	01/07 – 03/20	01/00 – 03/20	01/00 – 04/17	01/00 – 11/22	01/09 – 11/22	01/00 – 11/22
Oxygen, Dissolved: (Laboratory) as O2									01/00
Oxygen, Dissolved as O2	05/04 – 03/19	01/00 – 12/21	05/04	05/04	01/00 – 12/06	01/00 – 04/17	02/00 – 02/17	12/13 – 11/22	02/00 – 11/22
Oxygen, Dissolved, % Saturation	05/04 – 03/19	01/00 – 12/21	05/04 – 12/07	05/04 – 12/07	01/00 – 12/07	01/00 – 04/17	02/00 – 02/17	12/13 – 11/22	01/00 – 11/22
Parathion-ethyl :- {Parathion}	05/04	05/04	05/04	05/04					
PCB - 028	05/04	05/04	05/04	05/04					
PCB - 052	05/04	05/04	05/04	05/04					
PCB - 101	05/04	05/04	05/04	05/04					
PCB - 118	05/04	05/04	05/04	05/04					
PCB - 138	05/04	05/04	05/04	05/04					
PCB - 153	05/04	05/04	05/04	05/04					
PCB - 180	05/04	05/04	05/04	05/04					
PCB: Total	05/04	05/04	05/04	05/04					
Pentachlorophenol		01/00 – 01/14							
pH	05/04 – 03/19	01/00 – 12/21	05/04 – 12/07	05/04 – 12/07	01/00 – 12/07	01/00 – 04/17	01/00 – 02/17	07/11 – 11/22	01/00 – 11/22

pH: In Situ						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Phage: F+ Coliphage	03/06	03/06	03/06	03/06					
Phage: F+ Type II/III Bacteriophage	03/06	03/06	03/06	03/06					
Phage: F+ Type IV Bacteriophage	03/06	03/06	03/06	03/06					
Phenolic Odour							03/05 – 11/13		
Phosphate :- {TIP}	02/07 – 11/22		02/07 – 03/21	01/07 – 03/20	01/07 – 03/20	01/07 – 03/16	01/07 – 11/22	01/09 – 11/15	01/07 – 11/22
Phosphorus, Total as P	02/07 – 11/22		02/07 – 03/21	01/07 – 03/20	01/07 – 03/20	01/07 – 03/16	01/07 – 11/22	01/09 – 11/15	01/07 – 11/22
Potassium		11/01 – 07-06				11/01 – 02/12	11/01 – 02/12	07/11 – 02/12	11/01 – 02/12
Potassium, Dissolved						12/11 – 02/12	12/11 – 02/12	12/11 – 02/12	12/11 – 02/12
Preparation: DNA	09/07 – 08/10		09/07 – 12/09	09/07 – 01/11					
Salinity: In Situ	05/04	05/04	05/04 – 03/06	05/04					
Silver, Dissolved	05/04	05/04	05/04	05/04					
Sodium						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Sodium, Dissolved						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Solids, non-volatile at 500 C		03/05 – 09/05	07/05 – 09/05	07/05 – 09/05		07/05 – 09/05	07/05 – 09/05		
Solids, Suspended at 105 C	05/04 – 11/22	05/04 – 09/05	05/04 – 03/21	05/04 – 03/20	01/07 – 03/20	02/00 – 03/16	02/00 – 11/22	01/09 – 11/15	01/07 – 11/22
Streptococci: Faecal: Confirmed: MF	02/07 – 06/12		02/07 – 06/12	01/07 – 06/12	01/07 – 06/12	01/07 – 06/12	01/07 - 06/12	01/09 – 06/12	01/07 – 06/12
Streptococci: Faecal: Presumptive: MF	05/02 – 06/12	05/02 – 09/05	05/02 – 06/12	05/02 – 06/12	01/07 – 06/12	06/05 – 06/12	06/05 – 06/12	01/09 – 06/12	01/07 – 06/12

Strontium						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Strontium, Filtered						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Sulphate as SO4						07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12
Sulphate, Dissolved as SO4						12/11 – 02/12	12/11 – 02/12	12/11 – 02/12	12/11 – 02/12
TDE -pp	05/04	01/00 – 01/14	05/04	05/04					
Temperature of Water	05/04 – 11/22	01/00 – 12/21	05/04 – 03/21	05/04 – 03/20	01/00 – 03/20	01/00 – 04/17	02/00 – 11/22	01/09 – 11/22	01/00 – 11/22
Tetrachloroethylene :- {Perchloroethylene}		01/00 – 01/14							
Trichlorobenzene: Total (123-, 124-, 135-)		07/05 – 01/14							
Trichloroethylene :- {Trichloroethene}		01/00 – 01/14							
Turbidity		03/05 – 04/14	07/05 – 09/05	07/05 – 09/05		07/05 – 12/12	07/05 – 12/12	07/11 – 07/12	07/11 – 12/12
Type of flow as description		07/00 – 12/06			01/00 – 12/06	01/00 – 12/06	01/00 – 07/08		01/00 – 12/06
Visible oil or grease, significant trace: Present/Not found (1/0)	05/04	05/04	05/04	05/04			03/05 – 11/13		
Weather: Precipitation		01/00 – 12/06			01/00 – 12/06	01/00 – 12/06	01/00 – 07/08		01/00 – 12/06
Weather: Temperature		03/05				11/02			
Zinc		01/00 – 12/06			01/00 – 01/05	01/00 – 02/12	01/00 – 11/13	07/11 – 02/12	01/00 – 02/12
Zinc, Dissolved	05/04	05/04	05/04	05/04		07/11 – 02/12	07/11 – 02/12	07/11 – 02/12	07/11 – 02/12

Appendix b: R code

Preparing data for plot

```
x<-(df$columnname)
y<-(df$columnname)
group<-(df$columnname)
```

Scatter plots with trend line

```
ggplot(df,aes(x=x,y=y,col=group))+geom_point()+geom_line(method=lm)
```

Boxplot

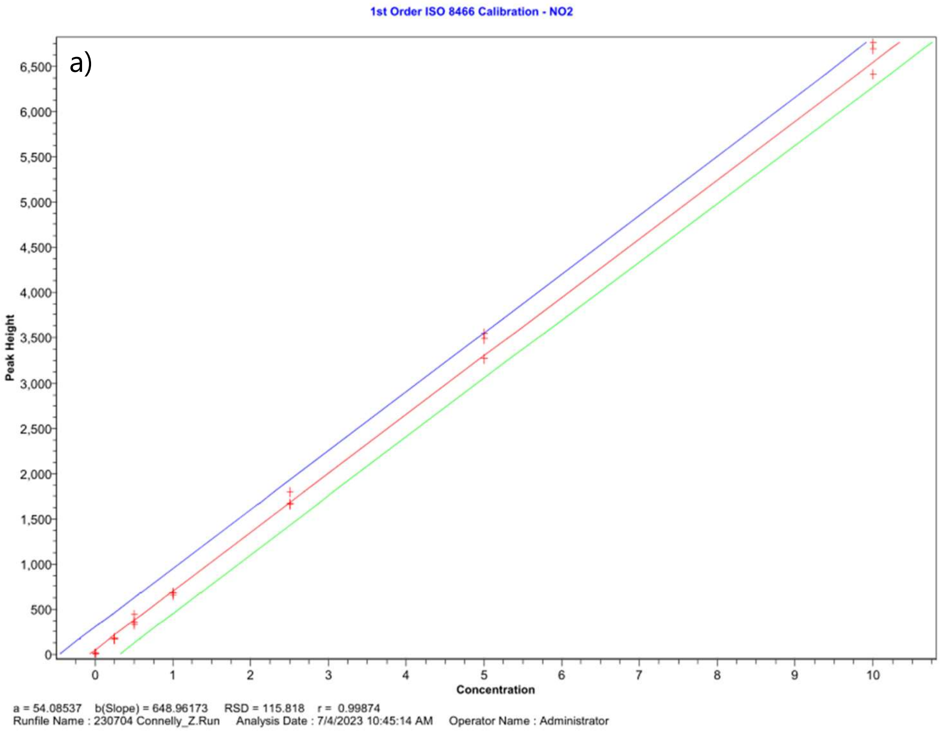
```
ggplot(df, aes(x=x, y=y))+geom_boxplot()
```

Scatter with standard error bars

```
ggplot(df, aes(x=x, y=y))+geom_point()+geom_errorbar(ymin=y-SE, ymax=y+SE, width=.2)
```

Appendix c: Skalar calibration curves

Calibration curves automatically generated by Skalar software used to calculate concentrations of elemental nitrate and phosphate.



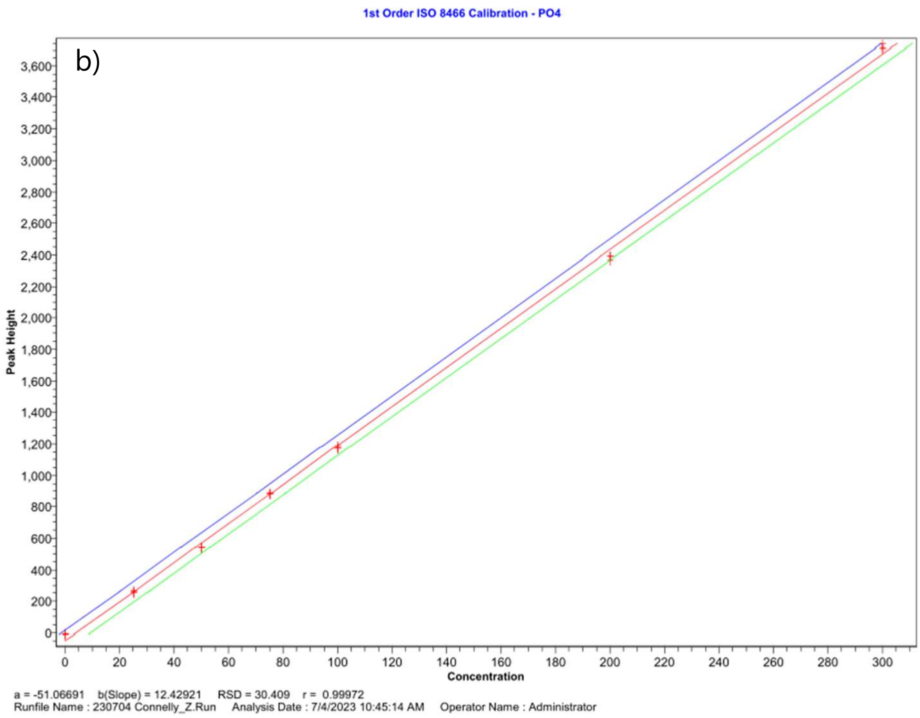


Figure i: *Calibration curves of a) nitrate and b) phosphate generated by Skalar software using combined standards.*