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Temporal Analysis of Ammoniacal Nitrogen and Chloride Concentrations on River Tees at Bran Sands (2012–2021)

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ABSTRACT

Bran Sands, situated within the Tees Estuary, has been significantly impacted by decades of industrial activity, including steel production, shipbuilding, and chemical manufacturing. Which have contributed to substantial changes in water quality and sediment composition due to the continuous discharge of millions of litres of industrial wastewater into the estuarine ecosystem. This study assesses long-term trends in key water quality parameters, such as ammoniacal nitrogen, pH, chemical oxygen demand (COD), and biochemical oxygen demand (BOD), in the Bran Sands, between 2012 and 2021. The analysis utilises descriptive statistics to summarise and interpret the pollution loads from the Bran Sands sewage treatment works, and time-series graphs to evaluate the effectiveness of wastewater treatment improvements over time. Results indicate significant reductions in pollution levels, with ammoniacal nitrogen, BOD, COD, and pH concentrations frequently exceeding compliance limits at the inlets, particularly at the Wilton Complex Main Effluent and Bran Sands inlets, but remaining within permissible thresholds at the outlets. Temperature and salinity at river Tees also maintained within acceptable limits. However, Chlorine was measured above compliance limits at both inlets and outlets monitored sites, with an inclining trend throughout the study period. Chlorine reacts with organic and inorganic compounds, forming persistent chlorinated by-products that affect freshwater and marine organisms. Chronic exposure to residual chlorine has been linked to growth inhibition, reproductive impairment, and mortality in fish and invertebrates. These findings warrant continuous monitoring and adaptive management to sustain water quality improvements and protect aquatic ecosystems.

INTRODUCTION

Background of the Study

Surface water, which covers approximately 70% of the Earth's surface, plays a crucial role in supporting life by providing drinking water, agricultural irrigation, and industrial applications (Baker et al., 2016). However, the effects of industrialisation and population growth have led to pollution of water sources and hence water pollution affecting aquatic life (Ahmed, 2016). Water pollution is a natural occurrence as well as a man-made phenomenon (Uddin et al., 2021). Natural factors affecting water quality include hydrological, climatic, topographical, and geological influences (Magesh et al., 2013; Mahmood, 2018). However, human activities such as industrial waste disposal, agricultural runoff, and sewage discharge contribute to the accumulation of pollutants such as heavy metals, nutrients, and organic contaminants, which can disrupt aquatic ecosystems and pose risks to human health (Sun et al., 2019; Azuma et al., 2019; Zhao et al., 2020).

Among the most important parameters of water quality is ammoniacal nitrogen (NH_4^+-N) which is toxic and contributes to water pollution (Ding et al., 2021). High levels of ammoniacal nitrogen in surface water are mainly due to industrial effluents, agricultural fertilisers and sewage discharge (USEPA, 1985). High concentrations of ammoniacal nitrogen can cause eutrophication, oxygen depletion, and fish mortality, thereby degrading water quality and aquatic biodiversity (Liu et al., 2014). Other essential water quality indicators include pH, temperature, turbidity, dissolved oxygen, biological oxygen demand (BOD), chemical oxygen demand (COD), heavy metals, chloride, sulfate, pesticides, and biological contaminants (Sivaranjani et al., 2015). When these parameters exceed regulatory limits, they pose significant environmental and health risks (World Health Organization, 2011; CCME, 2001).

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Given the increasing threats to water quality, continuous monitoring and assessment have become global priorities to ensure the sustainable management of water resources (Ly et al., 2014; Behmel et al., 2016; Mama et al., 2021). Over the past two decades, extensive research has been conducted on surface water quality, providing insights into pollution sources and ecosystem health (Drasovean & Murariu, 2021). However, long-term studies on water quality trends in industrialised estuarine environments remain limited. Literature on some of the spatio-temporal assessment of estuarine ecosystems includes Motru river estuary, Romania (Ionuş, 2010); Estuarine systems from South Africa (Russell, 2013); Estuary of Duliujian river, China (Sun, et al., 2019); Scheldt estuary, Belgium and Netherlands (Van Damme, et al., 2005); Zhangweinan river basin, china (Xu, et al., 2012); Ying river basin, china (Liu, et al., 2016); Tapi etsuary, west coast of India (Kumar, et al., 2009); Narmada estuary, Gujarat, India (Kumar, et al., 2015); Bay of Bengal, India (Vishnupriya, 2015).

Bran Sands is situated in the mouth of the River Tees in the Tees Estuary which is one of the most industrialised areas of the UK. This research seeks to address this research gap by providing an evaluation of Bran Sands in Tees Estuary from the year 2012 to 2021. The results will be useful in understanding the current state of water quality, and the efficacy of current legislation in an estuarine system that is impacted by human activities.

Problem Statement

Bran Sands is located in the Tees Estuary and has been subjected to industrialization for many years, including steel processing, ship construction, and chemical industries. These activities have led to significant impacts on water quality since billions of litres of industrial wastewater are discharged into the estuarine environment, which is a threat to aquatic life and human health (Barne et al., 1996; DEFRA, 2002; Khatoon et al., 2013; Tyagi et al., 2018; Khatri et al., 2017a,b).

Despite the enhancement of environmental standards and water management in the last three decades, Bran Sands is still at risk of suffering from historical pollution and current industrial effluents (Hunter, 2022). Therefore, there is a lack of long-term data on the key water quality parameters such as chloride and ammoniacal nitrogen which are important to determine the pollution status and health of the estuarine ecosystem (Seager et al., 1988; Eddy, 1999; McKenzie et al., 2003; Harding et al., 2019; Patel & Sahoo, 2022).

Lack of long-term monitoring particularly in relation to trends in water quality has limited understanding of pollutant persistence and the efficacy of measures put in place (Nelson, 2003). However, there is no extensive research that has been done to analyze the historical trends of these pollutants at Bran Sands. This study seeks to fill these gaps by analyzing historical water quality data, determine the sources of pollution and assess the level of compliance with the environmental standards. The results will be useful in enhancing the quality of water in estuaries and help in the formulation of future conservation measures.

Research Aim and Objectives

The overarching aim of this dissertation is to assess the temporal variations of water quality in the Bran Sands, Tees estuary between 2012 and 2021.

The specific objectives of this research are:

- To identify and evaluate the common water quality indicators contributing to the pollution of Tees estuary at Bran Sands
- To assess the long-term trends of the water-quality indicators at Bran sands
- To check whether the water quality is in compliance with the environmental standards limits
- To investigate the potential environmental and ecological impacts of variations over time.
- To provide recommendations for sustainable water quality management and pollution mitigation in the Bran Sands estuary.

Significance of the Study

Water quality evaluation is important for human and ecological health especially in industrialised estuarine systems (Ouyang, 2005; Lodder, et al., 2010). Ammoniacal-nitrogen and chloride are the most significant anthropogenic pollutants affecting water supply safety, aquatic life, and ecosystem stability. The analysis of these pollutants is important in understanding the sources of contamination and impacts on the environment especially as water sources decrease and industries increase (Olubukola et al., 2021).

It is therefore important to identify the main human and natural sources of these pollutants and develop appropriate measures to address them in order to minimize potential adverse health effects (Olubukola, et al., 2021). Furthermore, data acquired through water quality evaluation provide empirical evidence to support environmental and health decision-making. Consequently, the results of this study will assist environmental agencies, regulators, and companies by offering high-resolution water quality data that can improve monitoring programs, conservation efforts, and pollution control techniques in Bran Sands and the wider Tees Estuary.

Structure of the Dissertation

This dissertation is organised into six chapters:

- Chapter 1: Introduction – Provides an overview of the research background, problem statement, objectives, significance, and study structure.
- Chapter 2: Literature Review – Examines previous research on estuarine pollution, including the common water quality indicators, and the sources of pollution
- Chapter 3: Methodology – Outlines the research design, data sources, and analytical methods used in the study.
- Chapter 4: Results and Discussion – Presents and interprets the findings in relation to existing literature, including trends in pollutant concentrations, water quality assessment, and potential environmental impact.
- Chapter 5: Conclusion and Recommendations – Summarises the key findings, suggests policy and management interventions, and identifies areas for future research.

LITERATURE REVIEW

Introduction

Numerous studies have been conducted to assess and monitor surface water quality; however, evaluating water quality using an extensive range of parameters can be both time-consuming and costly. To optimise water quality assessments, it is essential to identify key indicators that can effectively represent overall water quality while requiring minimal resources in terms of time and cost (Moeinzadeh et al., 2024).

This chapter, therefore, aims at identifying the important water quality parameters that are useful in evaluating estuarine habitats. It also presents a synthesis of literature on the classification of these parameters, their temporal and spatial variations, and their sources of pollution.

Water Quality Indicators

Numerous studies have employed various water quality indicators to assess surface water pollution. For example, Abed et al. (2019) evaluated the water quality of the Al-Gharraf River, a major tributary of the Tigris River in southern Iraq, using 25 physicochemical parameters. These included electrical conductivity, total solids, total dissolved solids, suspended solids, turbidity, total hardness, alkalinity, pH, temperature, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), chloride (Cl^-), fluoride (F^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), silica (SiO_2), ammonia (NH_3), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), iron (Fe^{2+}), and aluminium (Al^{3+}).

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Similarly, Gupta et al. (2017) analysed the water quality of the Narmada River in India using three different WQI models: the Weighted Arithmetic WQI, the National Sanitation Foundation WQI, and the Canadian Council of Ministers of the Environment WQI. Their assessment focused on eight key parameters: pH, turbidity, temperature, DO, BOD, total dissolved solids, phosphate (PO_4^{3-}), and nitrate-nitrogen (NO_3-N). Yadav and Khandegar (2019) conducted a study on the Yamuna River in Delhi, evaluating pollution levels through physicochemical indicators such as pH, temperature, DO, total dissolved solids, salinity, and conductivity.

In another comparative study, Ghani et al. (2018) examined the Malaysian WQI, which is based on six core water quality parameters—pH, BOD, COD, NH_3-N, DO, and total suspended solids (TSS). They contrasted this index with multiple biotic indices, including the biomonitoring working party, family biotic index, average score per taxon, and the singapore biotic index.

However, estuarine environments present unique challenges due to their dynamic nature, with fluctuating salinity, pH, temperature, and oxygen levels, as well as the presence of pollutants such as ammoniacal nitrogen (NH_3-N) and chloride (Cl^-) (Eddy, 2005). In all, there is at least a total of 69 water quality indicators are available for selection (see Figure 2.1), with their choice being influenced by several key factors. These include: (a) the natural properties of the water being assessed, (b) the intended use of the water, (c) the environmental significance of a given water quality indicator and (d) the required level of quality and purity (Bartram & Ballance, 1996; Uddin et al., 2021; Boyacioglu, 2010).

Classification of Water Quality Parameters Based on Natural Properties

The 69 water quality indicators are categorized into three groups: physical, chemical, and biological. Physical and chemical parameters are more useful for the initial assessment of water quality, while biological parameters provide a more comprehensive assessment of the environment (Uddin et al., 2021; Drasovean & Murariu, 2021). As shown in Figure 2.1, six indicators are used to measure biological qualities, ten for physical qualities and fifty-three for chemical qualities of surface water. This classification makes it easy to evaluate the quality of surface water depending on certain factors.

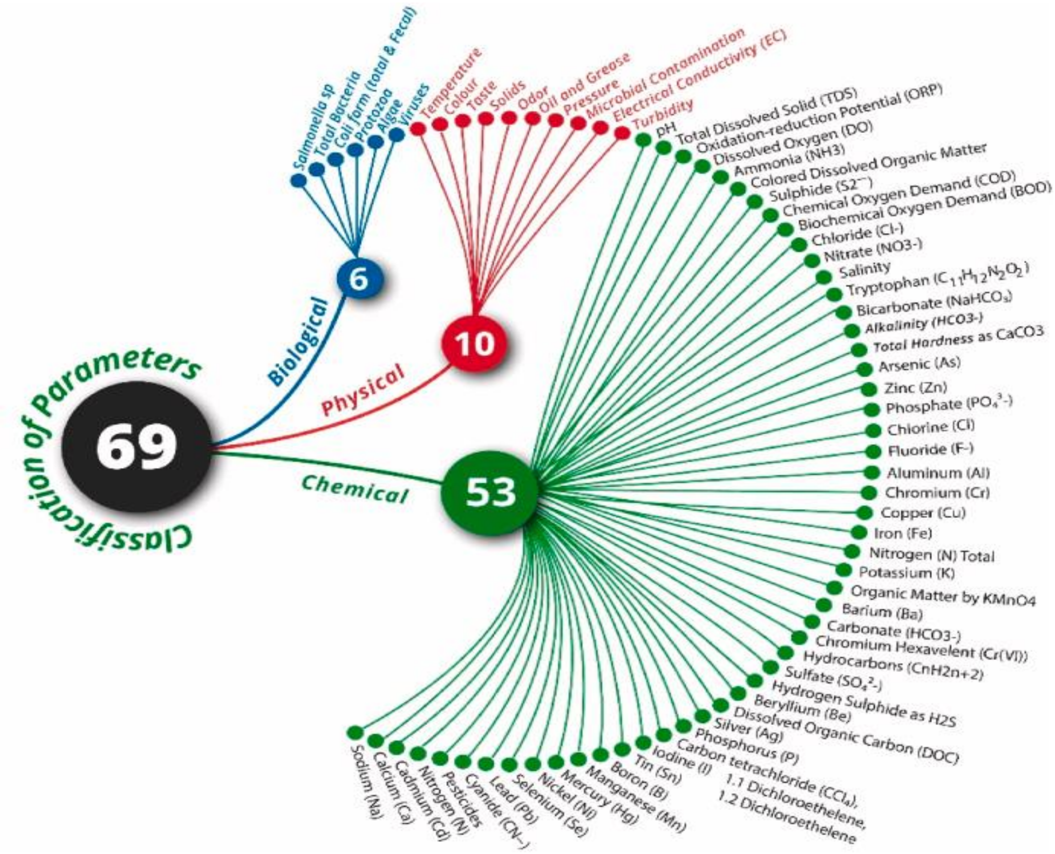

Figure 2.1 Taxonomy of 69 water quality indicators and their natural parameters *(Syeed, et al., 2023).*

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Physical Parameters

Physical parameters are essential in determining the observable characteristics of water, including its appearance and sensory properties. These parameters consist of ten distinct parameters that can be measured without altering the chemical composition of the substance (Gorde & Jadhav, 2013a; Hussen et al., 2018).

Temperature is a critical physical parameter, influencing various properties of water, including solubility, viscosity, odours, and chemical reactions (Omer, 2019). it is essential for aquatic life, as even moderate fluctuations can significantly impact bacteria, algae, invertebrates, and fish (Gurpal et al., 2013; Ranjeeta et al., 2011). Natural variations in water temperature occur both daily and seasonally, with many aquatic organisms exhibiting narrow temperature tolerances. While some species can buffer against atmospheric temperature extremes, higher water temperatures reduce dissolved oxygen levels, leading to an increase in BOD and COD. However, once a critical temperature threshold is exceeded, aquatic organisms die, resulting in a sharp decline in BOD values (Verma & Singh, 2013).

Taste and odour are other key indicators of physical parameters indicating water potability, often arising from organic or inorganic contaminants (Lin et al., 2018; Omer, 2019).

Chemical Parameters

Water interacts with various chemical substances, altering its molecular composition and forming new compounds (Chormey et al., 2018). This review identifies 53 chemical indicators, including pH, DO, alkalinity, BOD, Cl^-, inorganic toxic substances, copper (Cu), nitrogen (N_2), F^-, Fe, manganese (Mn), and zinc (Zn) being among the most significant (Omer, 2019).

pH is a critical chemical parameter measuring the acidity or alkalinity of water, with values below 7 indicating acidity, 7 representing neutral water, and values above 7 indicating alkalinity (Xu, 2014; Arora, 2017). Extreme pH levels can suggest industrial or chemical pollution, which may be harmful to aquatic organisms (Omer, 2019).

Nitrogen (N_2) is a key nutrient for aquatic organisms such as fish and microorganisms, and exists in four forms: organic nitrogen, ammonia nitrogen (NH_3-N), nitrite nitrogen (NO_2^-), and nitrate nitrogen (NO_3^-) (Xu, 2014). Among these, ammonia nitrogen is particularly hazardous due to its high toxicity and prevalence in surface waters (Sarda & Sadgir, 2015). Elevated concentrations of ammonia nitrogen are indicators of sewage contamination, while excessive nitrate levels promote algal blooms, degrading water quality (Tchobanoglus et al., 2003). The U.S. Environmental Protection Agency reported that ammonia concentrations between 0.5 to 23 mg/L are acutely toxic to nineteen invertebrate species, while levels ranging from 0.88 to 4.6 mg/L are lethal to 29 fish species (USEPA, 1985e).

Acute ammonia toxicity in fish can cause hyperexcitability, loss of equilibrium, heightened cardiac output, increased respiratory rate, and elevated oxygen uptake. In extreme cases, it can lead to convulsions, coma, and death. Chronic exposure is associated with poor hatching rates, growth inhibition, developmental abnormalities, and damage to the kidneys, gills, and liver (USEPA, 1986).

DO is a direct indicator of water quality and a crucial parameter for assessing pollution levels (Xu, 2014). Aquatic organisms, including fish, bacteria, and microorganisms, rely on DO for survival. However, as organic matter decomposes, microorganisms consume DO, releasing carbon dioxide (CO_2) and reducing oxygen availability in the water (Xu, 2014; Tchobanoglus et al., 2003).

BOD measures the oxygen required to biologically decompose organic matter in water (Environmental Agency, 1999). Wastewater treatment plants, industrial effluents, and agricultural runoff contribute biodegradable organic waste, increasing BOD levels. Microorganisms metabolize organic matter, consuming large amounts of oxygen during the oxidation process (Nuruzzaman et al., 2018). Elevated BOD levels signal high microbial loads and substantial organic pollution. Acceptable BOD limits vary depending on disposal methods, with maximum values ranging from 10 mg/L for direct environmental discharge to 300 mg/L for sewer disposal (AOS Treatment Solutions, 2018).

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Classification Based on Intended Use

The evaluation of surface water quality should be tailored to its intended use, geographical location, and specific water type (Murariu et al., 2019). Consequently, potable water must be free from harmful chemicals and microorganisms that could pose risks to human health (Drasovean & Murariu, 2021). On the other hand, water for agricultural or irrigation purposes should not have high sodium ions, high nitrate levels or other impurities that may affect the fertility of the soil and crop production (Drasovean & Murariu, 2021; Bartram & Ballance, 1996).

Due to the versatility of water, the scientific community suggests that one should choose a unique set of parameters to determine the water's fitness for a specific use (Gorde & Jadhav, 2013b; Murariu et al., 2019). Figure 2.2 below illustrates this classification where each water quality parameter is assigned to a usage category depending on its relevance. For instance, pH is a crucial parameter across all categories, while coliform bacteria primarily impact the quality assessment of domestic and freshwater sources. The figure further outlines the number of parameters required for a comprehensive evaluation within each category. Fisheries require the assessment of 28 parameters; Agricultural water necessitates an evaluation of 30 parameters; Freshwater bodies used for human consumption involve 47 parameters; Domestic water quality is determined by 44 parameters; and Industrial water management relies on the assessment of 26 parameters.

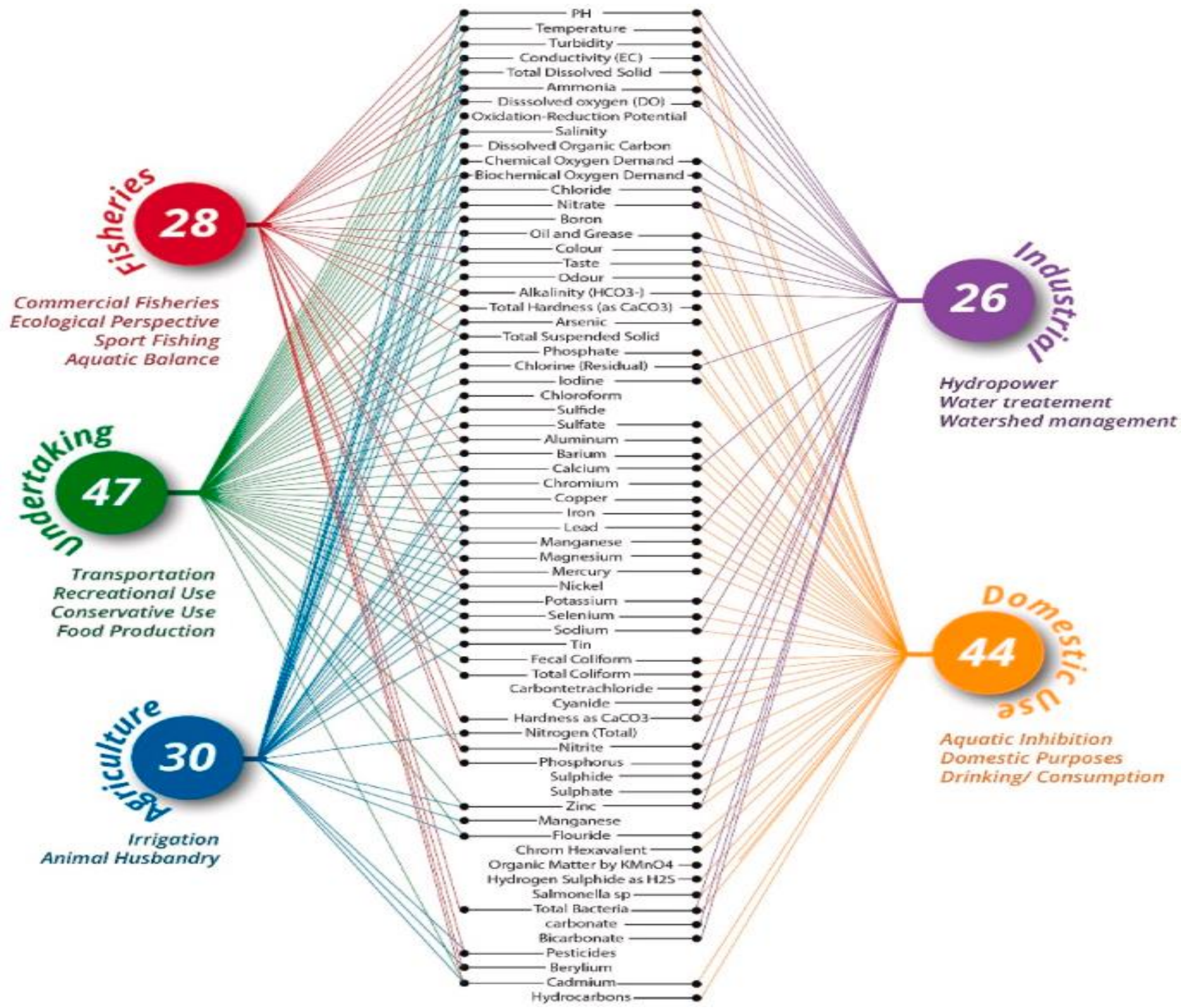

Figure 2.2 Classification of 69 factors by five basic surface water uses (Syeed et al., 2023)

However, in practical applications, most WQI models assess only a fundamental set of parameters. This core set typically includes temperature, pH, DO, COD BOD, and NH_3–N (Omer, 2019). The number of parameters considered in a given assessment generally ranges between 4 and 26, depending on the availability of data (Syeed et al., 2023).

Water Quality in English Rivers

The current status of English rivers falls below good ecological standards as only 14% meet the required criteria (UK Parliament, 2021). The water quality of English rivers is among the poorest in Europe (UK Parliament, 2021). Despite the UK government's best efforts, the Water Framework Directive, which mandates that all rivers attain excellent status by 2027, remains unmet.

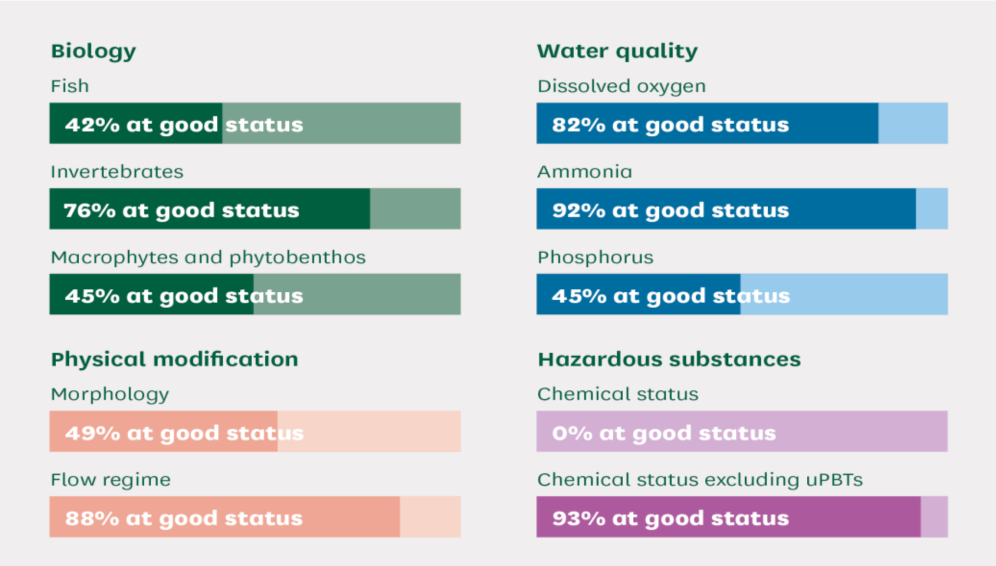

Figure 2.3 River water quality indicators for England (Environment Agency, 2025).

Water companies, the Government, and regulators claim that water quality in English rivers has improved since the 1990s (Bevan, J., 2020; Pow, 2021). While this statement holds true in certain aspects, as illustrated in Figure 2.3, overall progress can sometimes obscure fewer encouraging trends. For example, data from the Department for Environment, Food and Rural Affairs (DEFRA) indicates that efforts by the Environment Agency and water companies over the past two decades have resulted in a 67% reduction in phosphorus (P) and a 79% reduction in ammonia (NH_3) levels compared to 1995 (DEFRA, 2021). However, despite these improvements, ammonia above permissible limits remains the leading cause of water bodies failing to achieve good ecological status.

Bevan (2021) asserts that the water industry and the agricultural sector, the two primary pollutants in English rivers, have failed to adequately address the issue, leading to a halt in improvements in water quality. He did note that rivers are in better shape now than they were decades ago, but he stressed that improvement has stopped and water quality is still inadequate.

Sources of Pollution

Approximately 80% of marine and coastal water quality degradation worldwide is attributed to large-scale human activities (UNEP, 1995; Zann, 1995). Land-based activities—including urbanisation, industrial expansion, and agricultural development—can have profound negative impacts on marine and estuarine ecosystems. These activities introduce suspended sediments, excessive nutrients, pathogens, heavy metals, and various other pollutants into coastal waters, leading to environmental deterioration (UNEP, 1995; Zann, 1995).

Pollution from Sewage and Wastewater

Wastewaters are generated by many industries as a consequence of their operation and processing, is the second major contributor of pollution into surface waters in England and Wales nitrogen pollution, which accounts for approximately 25-30% of (Environment Agency, 2019; DEFRA, 2021). Organic matter decomposition produces ammonia as a byproduct which mainly stems from human waste. Wastewater treatment plants that do not finish their treatment process release effluents containing high levels of ammonia into rivers and estuaries (Edwards et al., 2024).

Annual nitrogen loads in UK estuaries vary regionally. The highest nitrogen concentrations are observed in the Mersey, Severn, Humber, Clyde, Solent, and the Thames estuaries, where agricultural runoff and industrial discharges are prominent. These estuaries drain catchments with high nitrate soils, many of which are designated as Nitrate Vulnerable Zones (NVZs) (Nedwell et al., 2002). In contrast, estuaries in West Wales and northern Scotland exhibit lower nitrogen loads due to their relatively infertile catchments and lower population densities.

The total land area of England amounts to 58% which falls under NVZ classification because of nitrogen pollution issues. The eutrophic areas make up 6% of the total land area which affects estuaries lakes and reservoirs (House of Commons Environmental Audit Committee, 2018). In accordance with the Nitrates Directive and the Urban Waste Water Treatment Directive, sixteen shallow tidal harbours and estuaries in Wales and England have been deemed eutrophic by the Environment Agency (2019). In England, the majority of monitored estuaries (93%) and coastal bodies of water (47%), according to the Environment Agency (2019), have nitrogen levels that are too high to be considered in "good ecological status" according to the Water Framework Directive (WFD).

Agricultural Land Use

Agricultural pollution from rural areas is the largest contributor (40%) to pollution in the surface water of England and Wales (DEFRA, 2021), accounting for approximately 50-60% of nitrogen Ammoniacal nitrogen serves as a primary ingredient in fertilisers. Surface runoff from agricultural lands transports excessive ammonia during rainfall events which causes water quality deterioration and eutrophication of nearby water bodies (Craswell, 2021). In some regions, nitrate concentrations in water draining from agricultural soils exceed 50 mg/L in over 35% of England.

Conclusion

This chapter has provided a comprehensive overview of key water quality indicators commonly used in the assessment of surface water receiving treated effluent discharges. Some of the indicators include pH, dissolved oxygen, chemical oxygen demand, biological oxygen demand, and ammoniacal nitrogen. Furthermore, the chapter also discussed the current status of surface water quality in England and the measures taken by the authorities.

The review showed that the concentration of major water pollutants in English rivers has reduced over the years since 1990, which is an indication of better management of water quality. Nevertheless, the concentrations above the MAC remain the key factors that hinder many water bodies from obtaining a good ecological status. This may be seen as a positive development in the general improvement of the quality of water in the river but the presence of these pollutants remains a problem to the environment.

The next chapter provides a step-by-step procedure of how water quality from Bran Sands effluents was assessed in terms of the pollutants and their effects.

METHODOLOGY

Introduction

This chapter aims at providing a general background on the analytical techniques that can be employed in the analysis of water quality parameters from Bran Sands effluents. The research uses both historical data analysis and statistical analysis to assess the trends and the possible effects on the environment of these parameters. This approach enhances the scientific credibility of the findings and conclusions on water quality in the estuary based on the collected data.

Study Area

Bran Sands, located in Middlesbrough, Cleveland, North Yorkshire, with coordinates 54°36'41"N and 1°07'23"W, is a remnant of the once extensive Tees Estuary that has undergone significant anthropogenic modifications over the past two centuries. Large-scale land reclamation for industrial development, particularly up to the 1970s, resulted in the loss of approximately 90% of the original intertidal habitat, which has contributed to environmental degradation (Environment Agency, 2023).

The River Tees extends across 160 kilometers from its source at Tees Head in the Cumbrian Pennines at 893 meters above sea level (Environmental Agency, 1999). The river begins its journey in Cow Green Reservoir after crossing moorlands before traveling east through Teesdale to reach Barnard Castle and then continues to Darlington. The river expands into a broad meandering path that stretches across an extensive plain with the Cleveland Hills and Durham Hills on both sides. The river terminates its journey by draining into Tees Bay which represents a shallow sea embankment. The upper course features hard rock formations and the estuarine lowlands contain clay, peat, alluvium, river gravels and blown sands. The sandy sediments of Tees Bay form its base while dunes exist on its surface.

Historically, wastewater management in Teesside involved direct sewage disposal into the estuary. However, the EU Urban Waste Water Treatment Directive prohibited sewage sludge dumping at sea (New Civil Engineer, 1999). Northumbrian Water Ltd. (NWL) responded by launching the Tees Estuary Environmental Scheme (TEES) at Bran Sands. The plan called for NWL to treat its sewage treatment effluent a second time before discharging it. Major Teesside industrial companies were also compelled to lessen the amount of pollutants they released into the estuary (Environment Agency, 1999). The TEES initiative involved the construction of pumping infrastructure at Portrack, Cargo Fleet, and Eston sewage treatment plants, facilitating the transfer of municipal sewage via dedicated pipelines to the Effluent Treatment Works (ETW) at Bran Sands (New Civil Engineer, 1999).

The Bran Sands ETW treats domestic sewage and biodegradable industrial waste from surrounding facilities. A regional sludge treatment centre was established at Bran Sands to process both indigenous and external sludges from multiple Northumbrian Water treatment works. The facility produces dried sludge granules and pellets, which are repurposed for agricultural applications and the cement industry (Mason & Coverdale, 2007). Treated effluents are discharged into Dabholm Gut following septicity treatment and disinfection.

Procedures for Water Quality Analysis

The procedure of water quality analysis used in this study was carried out in four steps as shown in Figure 3.1

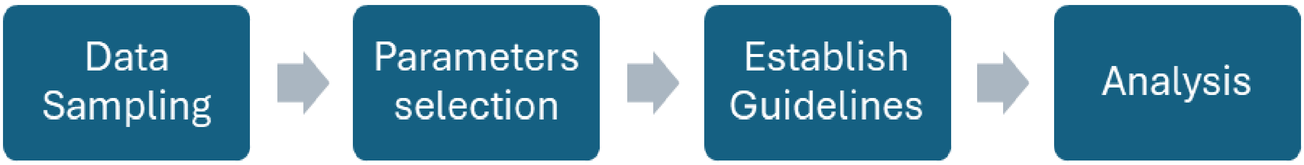

Figure 3.1 Steps for Water Quality Analysis

Data Collection and Sampling

Assessment of water quality in the Bran Sands was carried out at the following sampling site; River Tees at Dabholme Gut Confluence NE-45401356, Wilton Complex Main Effluent, NE-45400034 Bran Sands Stw Crude Inlet, NE-45401301; Bran Sands Phillips Petrolium Crude Inlt, NE-45401424, Bran Sands Treated Sewage, NE-45401254 and Bran Sands Outfall, NE-45400569 as illustrated in Figure 3.2.

The study obtained secondary data through electronic platforms from the national database accessible at https://environment.data.gov.uk/water-quality/view/landing. The UK water quality monitoring program includes Bran Sands as well as other important estuarine and coastal sites and is conducted by these agencies on a regular basis.

Figure 3.2 geographic representation of the Bran Sands, with sampling locations - the River Tees at Dabholme Gut confluence, Wilton Complex Main Effluent, Bran Sands Phillips Petrolium Crude Inlt, Bran Sands Stw Crude Inlet, and Bran Sands Treated Sewage, Bran Sands Outfall

Selection of the Water Quality Parameters

Water quality assessment model parameter selection requires careful attention because an excessive number of parameters can create the eclipsing problem which reduces the impact of essential indicators (Uddin et al., 2021; Gupta & Gupta, 2021). The selection process requires identifying key parameters that influence water quality assessment models between four and twenty-six parameters based on geographical location and physico-chemical properties and intended use of the water and environmental significance and data availability (Syeed et al., 2023).

Expert opinions play a significant role in parameter selection (Abbasi & Abbasi, 2012; Chidiac et al., 2023; Mogane et al., 2023). This method involves structured interviews or surveys with specialists, who determine the most appropriate set of parameters for evaluating a given water body (Abbasi & Abbasi, 2012; Hsu & Sandford, 2007; House, 1989). However, since this study relies on secondary data sources, parameter selection was informed by government and organizational reports rather than direct expert surveys.

The Tees Estuary serves various activities, including industrial effluent disposal, conservation, water abstraction, fishing, and recreation (Environmental Agency, 1999). Temperature changes are a major concern in the estuary, influenced by both local and global factors. Locally, the use of estuarine water for industrial cooling plays a significant role, forming thermal plumes that can adversely affect aquatic life, particularly migratory fish. Ensuring temperature stability is essential for maintaining indigenous species in Teesside.

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Effluents containing high organic content or specific inorganic pollutants significantly reduce oxygen levels in the estuary, especially during dry summer months when freshwater inflows are diminished and oxygen demand is higher. Industrial and sewage effluents from Bran Sands Outlets contribute to high BOD, COD, and ammonia nitrogen levels in the estuary (Environmental Agency, 1999). Ammonia, present in sewage effluent and riverine inputs, poses toxicity risks to fish, algae, and invertebrates. Elevated ammonia levels affect aquatic life in two primary ways: toxicity to aquatic organisms, which may lead to species loss, and oxygen depletion due to nitrification.

Estuarine pH levels typically range from 7.0 to 7.5 in fresher sections and between 8.0 and 8.6 in more saline areas (USEPA, 2006). pH is a critical factor for aquatic life in the estuary, as even small fluctuations can impact species survival. Species like salmon and sea trout present in the estuary struggle to survive if pH falls below 5.0 or exceeds 9.0 (Environmental Agency, 1999).

Salinity and Chloride levels in the Tees Estuary fluctuate due to tidal movements and seasonal changes (Garcés-Vargas et al., 2020). In the open ocean, salinity remains relatively constant at approximately 35,000 mg/L (NOAA, n.d.), but estuarine salinity is influenced by freshwater inflows and evaporation rates. In spring, increased river flow from the River Tees (due to snowmelt and rainfall) lowers salinity while significantly increasing chloride concentrations (Rivett et al., 2016). Discharges from Bran Sands sewage treatment further contribute to estuarine chlorine variations (Singh et al., 2023; Naidoo & Olaniran, 2014).

Water Quality Guidelines

Water quality guidelines provide statements and numerical values to describe water quality, based on expected usage (Olubukola, et al., 2021). The Environment Agency often uses the maximum limit for water treatment works discharge effluent in surface water, a concentration no sample must exceed, also known as upper tier or absolute limits. Table 3.1 presents the maximum compliance limit for the water quality parameters.

Table 3. 1 maximum compliance limits

Parameter	EA	EPDA	Citation
Ammoniacal Nitrogen	10 mg/L		(Environmental Agency, 2019)
BOD	50 mg/L		(Environmental Agency, 2019)
pH		9	(EPDA, 2020)
Temperature	35^0C		
Salinity	< 35ppt		
Chlorine	250 mg/L		(Environmental Agency, 2018)
COD	250 mg/L		(Environmental Agency, 2019)

Data Analysis

Water quality measurements in natural environments often exhibit high variability, necessitating the use of descriptive statistics to summarise and interpret the data effectively. The mean, commonly referred to as the average, is the most frequently used measure of central tendency. To calculate the annual arithmetic mean values, the Regression on Order Statistics method is applied, which provides unbiased estimates of arithmetic means and their confidence intervals, particularly when some recorded values are below the analytical detection limit (Lee & Helsel, 2005; Millard, 2013).

The results of the statistical analysis are presented in the form of time series diagrams, which show the annual arithmetic mean values of the water quality parameters and their 95% confidence intervals. These time-series analyses are useful in the formulation of policy decisions for regulatory agencies since they provide insights into the management of water and the formulation of valid conclusions on the quality of water (Drasovean et al., 2019; Nguyen & Huynh, 2022).

All the statistical analyses were performed using Microsoft Excel (2024 version) and IBM-SPSS 16.0 software for data processing and analysis.

Limitations of the Study

The study employs secondary data, which can cause problems in terms of frequency, precision, and completeness of measurements. Lack of data in some years may lead to problems in long-term trends and therefore can bias the assessment of changes in water quality.

The choice of water quality parameters is based on the recorded data and not on the assessment of all possible pollutants that may affect the water quality in the Tees Estuary; this means that some pollutants that may greatly affect the water quality dynamics may not be included in the analysis.

The confidence intervals for annual mean concentrations are approximate for two reasons: the data have been aggregated without regard to the correlation between multiple measurements taken at the same sampling sites and seasonal and incomplete data have not been taken into consideration.

Conclusion

This chapter has explained the research design that was used in the study in a detailed manner. The study uses secondary data collected from both local and national agencies to provide a sound analysis of the water quality trends. Also, the opinions of the experts were included to determine the most appropriate water quality parameters that would be relevant to the study area to make the assessment more meaningful. To analyse the collected data, descriptive statistical methods were used and the results presented by time series graphs to show the trends and fluctuations in the study period appropriately. These graphical representations will give long-term trends of the water quality parameters of interest. The next chapter will present and discuss the findings of the study, offering detailed interpretations of the observed trends and their relation with established standards

RESULT AND DISCUSSION

Trend of Water Quality Parameters

This chapter presents the long-term time series graphs for ammonia, COD, BOD, pH, Chlorine, Salinity, and Temperature, and salinity. The data indicates annual arithmetic means and 95% confidence intervals together with monthly median variations for each calendar year

Ammoniacal Nitrogen

Wilton Complex Main Effluent

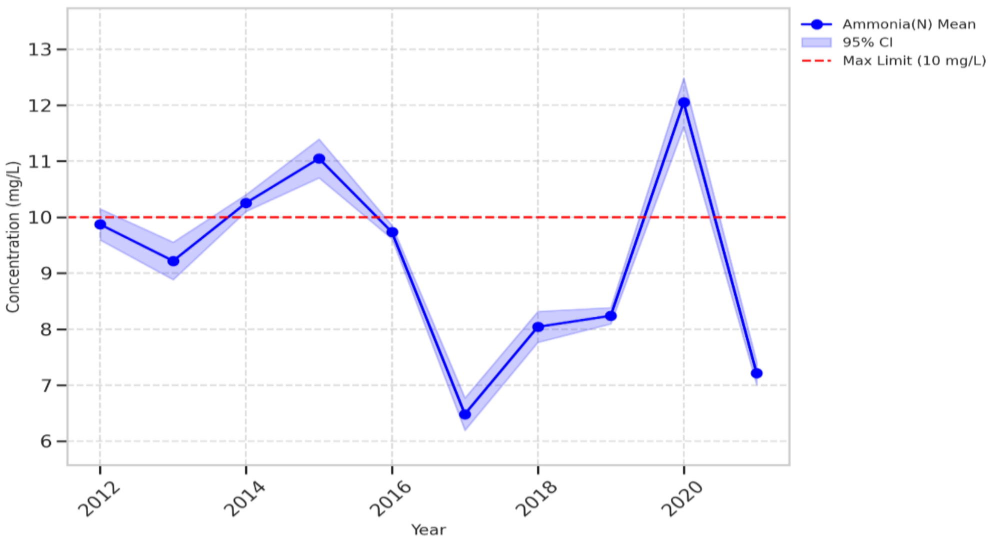

Figure 4.1 the annual mean level (with 95% confidence interval) of Ammoniacal Nitrogen at Wilton Complex Main Effluent from 2012 to 2021

As shown in figure 4.1, the concentration of ammoniacal nitrogen at the Wilton Complex Main Effluent fluctuated throughout the study period. In 2012, it started at 9.8 mg/L. Between 2013 and 2015, ammonia levels increased from 9.2 to 11.1 mg/L, exceeding the compliance limit of 10 mg/L. From 2015 to 2017, a significant decline was recorded, reaching 6.49 mg/L. However, the downward trend was short-lived, as ammonia levels resumed, peaking at 12.05 mg/L in 2020. Three years (2014, 2015, and 2020) exceeded the maximum compliance limit, indicating persistent challenges in ammonia control.

Bran Sands Inlets

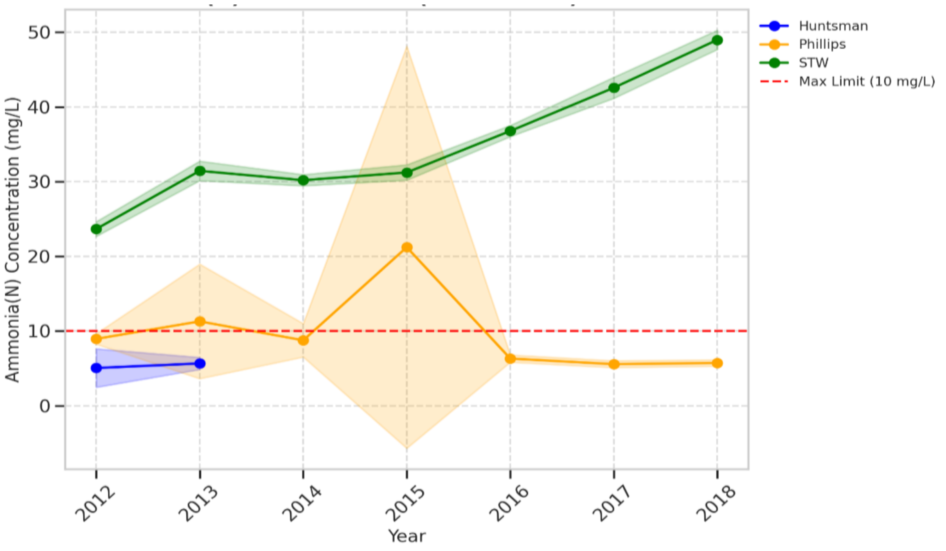

Figure 4.2 the annual mean level (with 95% confidence interval) of Ammoniacal Nitrogen at Bran Sands Phillips Petroleum Crude Inlt Bran Sands Huntsman Crude Inlet and Bran Sands Stw Crude Inlet from 2012 t0 2021

As shown in figure 4.3, the ammoniacal concentrations at Bran Sands inlets varied significantly across three monitored sites over the study period. The STW site consistently recorded the highest concentrations, increasing from 25 mg/L in 2012 to nearly 50 mg/L in 2018, exceeding the compliance limit. The Phillips site's concentrations often hovered near the limit, with some annual means exceeding it (2013 and 2015). The Huntsman site recorded values below the compliance limit, despite only 2 years of data available.

Bran Sands Outlets

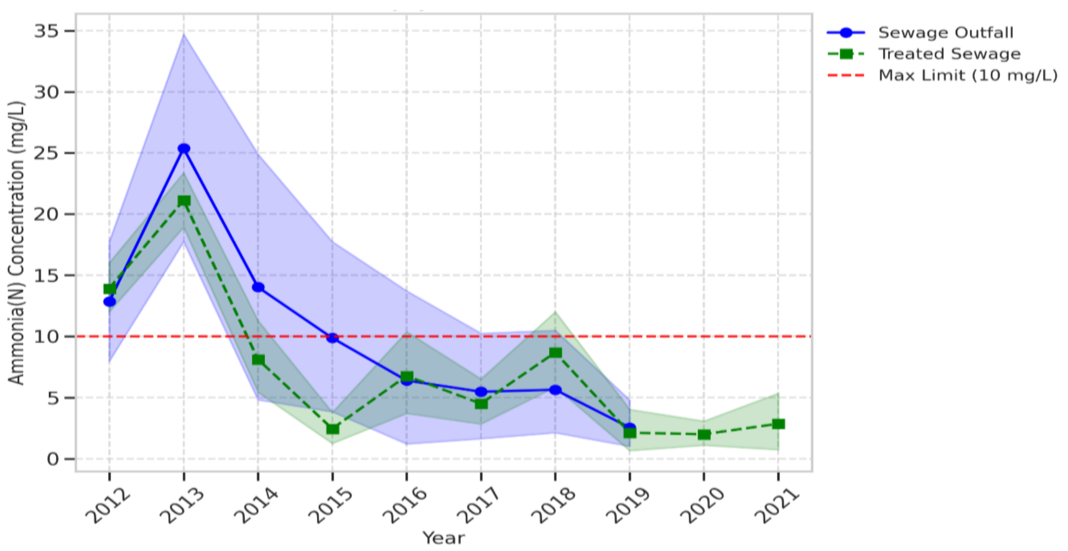

Figure 4.3 the annual mean level (with 95% confidence interval) of Ammoniacal Nitrogen in Bran Sand Outfall and Bran Sands Treated Sewage from 2012 to 2021

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As shown in figure 4.3, the concentration of Ammoniacal Nitrogen in Bran Sands Outlets showed a declining trend across the monitored sites over the last decade. Concentrations were highest in 2013 at approximately 22.19 mg/L, in treated sewage and 25. 37 mg/L in sewage outfall. However, from 2014 onwards, a marked decline in ammonia levels was observed, with both sites falling below the maximum compliance limit by 2015. Both sites show a general improvement in recent years, with levels remaining below the limit. This downward trend suggests enhancements in wastewater treatment practices, possibly through technological upgrades or stricter enforcement of regulatory measures.

BOD

Wilton Complex Main Effluent

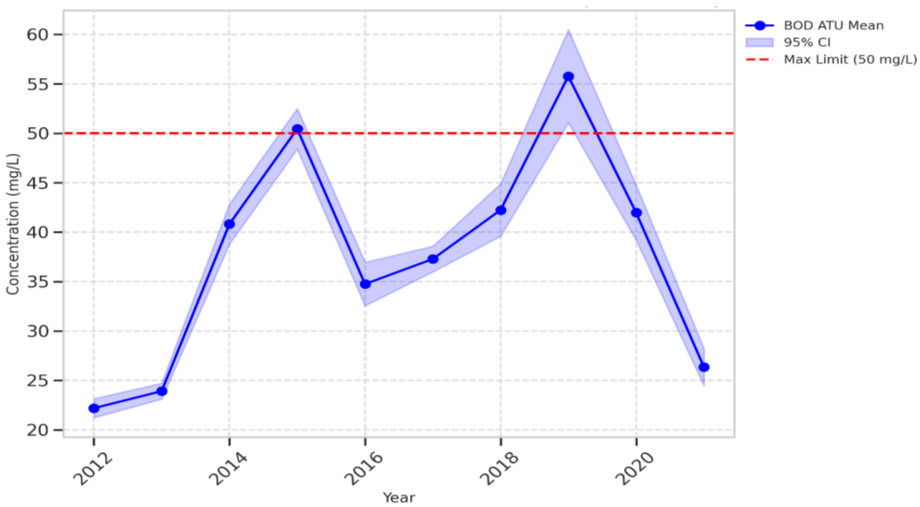

Figure 4.4 the annual mean level (with 95% confidence interval) of BOD at Wilton Complex Main Effluent from 2012 to 2021

As shown in figure 4.4, the concentration of BOD at the Wilton Complex Main Effluent indicate significant fluctuations over the study period. In 2012, it started at 22.21 mg/L, then increased to 50.12 mg/L in 2015. BOD levels declined to 34.71 mg/L in 2016, but then increased again from 2017 to 2019, reaching 55.78 mg/L in 2019. Regulatory compliance analysis shows that BOD concentrations exceeded the 50 mg/L threshold in two out of ten years (2015 and 2019)

Bran Sands Inlets

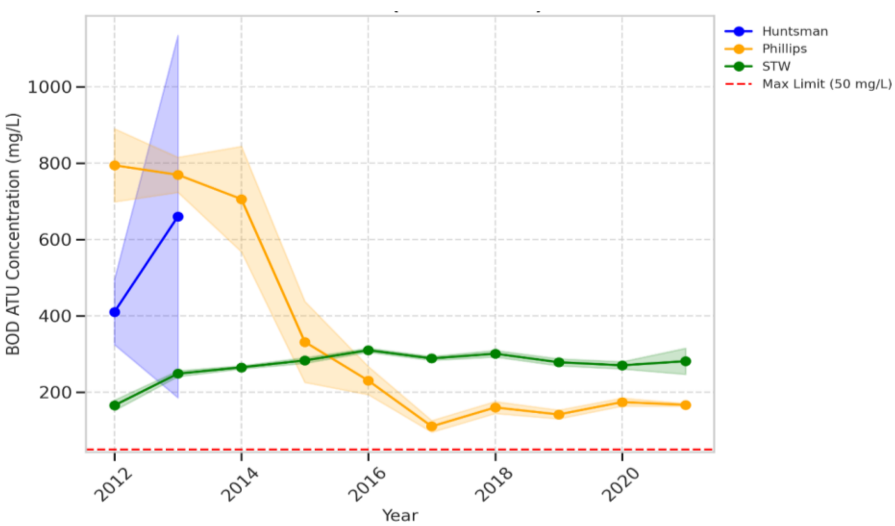

Figure 4.5 the annual mean level (with 95% confidence interval) of BOD at Bran Sands Phillips Petroleum Crude Inlt Bran Sands Huntsman Crude Inlet and Bran Sands Stw Crude Inlet from 2012 to 2021

As illustrated in Figure 4.5, BOD concentrations at the various Bran Sands inlets monitoring sites, were all significantly above the 50 mg/L maximum compliance limit over the study period. However, at the Phillips site a declining trend in BOD concentrations is evident, where levels dropped to 110.45 mg/L by 2017. The Huntsman site appears to be on an incline, although limited data is available to fully make up the trend. The STW site, also appears to be inclining, although with much less fluctuation compared to the other sites. The site began with a value of 165.5 mg/L in 2012, and ends with 281.12 mg/L in 2021

Bran Sands Outlets

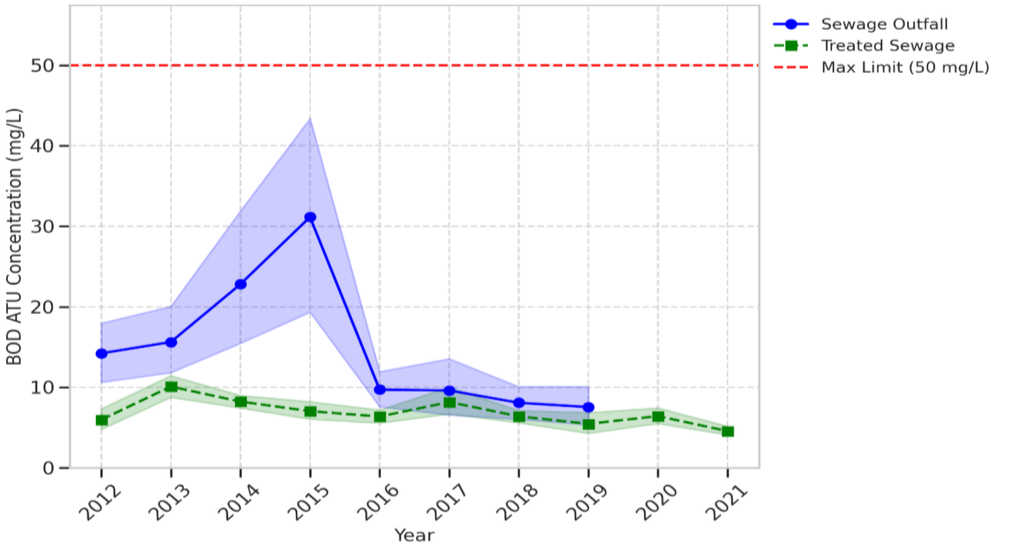

Figure 4.6 the annual mean level (with 95% confidence interval) of BOD at Bran Sand Outfall and Bran Sands Treated Sewage from 2012 to 2021

As shown in figure 4.6, BOD concentrations at Bran Sands outlets indicated a declining trend, with sewage outfall site reaching a peak in 2015 31.1 mg/L. After 2015, concentrations dropped to 9.71 mg/L by 2016, stabilizing around this level. Treated sewage site showed a stable trend, maintaining lower BOD levels compared to sewage outfall. Both sewage outfall and treated sewage remain below the regulatory maximum limit of 50 mg/L, demonstrating compliance with environmental standards.

COD

Bran Sand Inlets

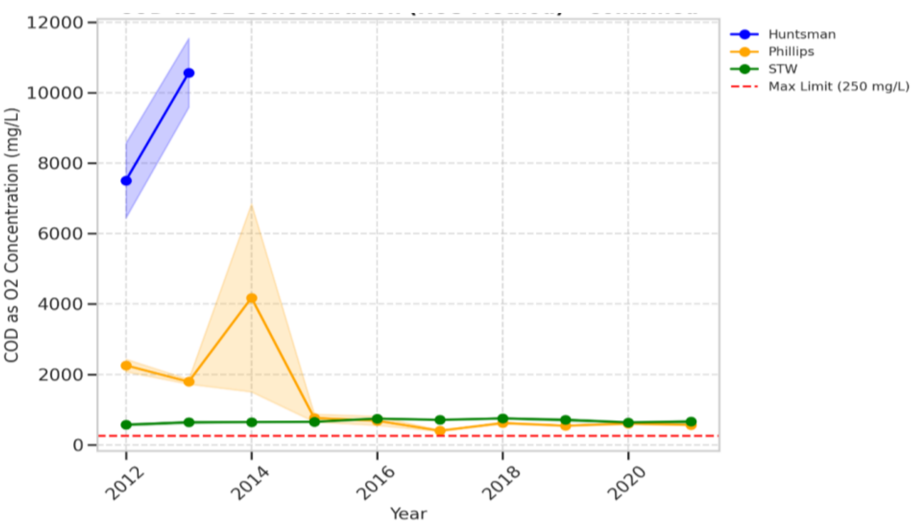

Figure 4. 7 the annual mean level (with 95% confidence interval) of COD at Bran Sands Phillips Petroleum Crude Inlt Bran Sands Huntsman Crude Inlet and Bran Sands Stw Crude Inlet from 2012 to 2021

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As illustrated in Figure 4.7, COD concentrations at the Bran Sands inlets across the monitored sites were significantly above the maximum compliance limit of 250 mg/L throughout the study period.

Bran Sand Outlets

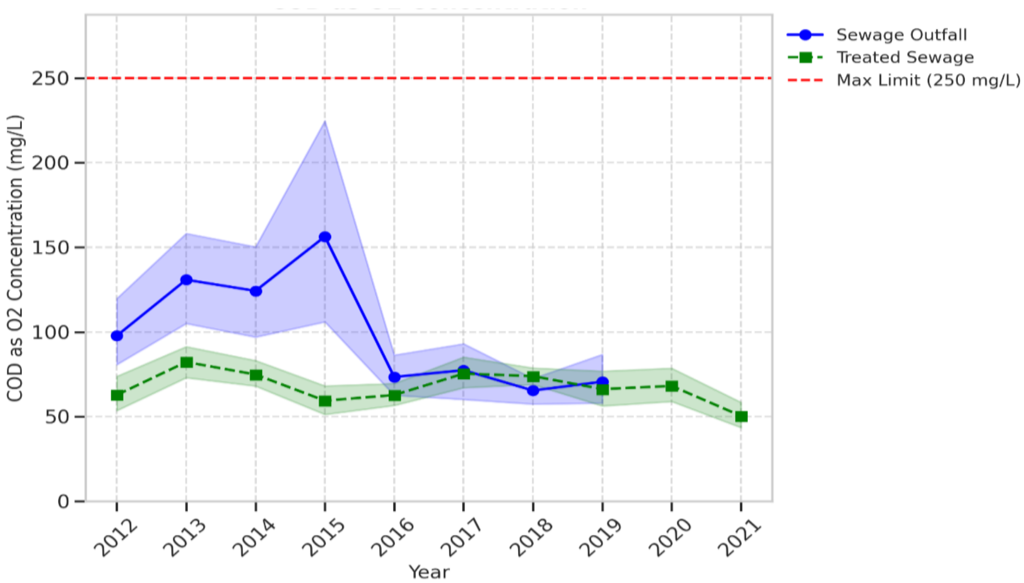

Figure 4. 8 the annual mean level (with 95% confidence interval) of COD at Bran Sand Outfall and Bran Sands Treated Sewage from 2012 to 2021

As shown in figure 4.8, COD concentrations at Bran Sands outlets declined across the monitored sites. The sewage outfall site experienced an increase from 2012 to 2015, peaking at 156.33 mg/L. Post-2015, the concentrations stabilized around 60-80 mg/L. Treated sewage sites consistently had lower COD concentrations, dropping from 82.25 mg/L in 2013 to 50.41 mg/L in 2021. Both sites remain below the regulatory limit, indicating effective wastewater treatment in Bran Sands in reducing organic and inorganic pollutants contributing to COD.

Chlorine

Bran Sand Inlets

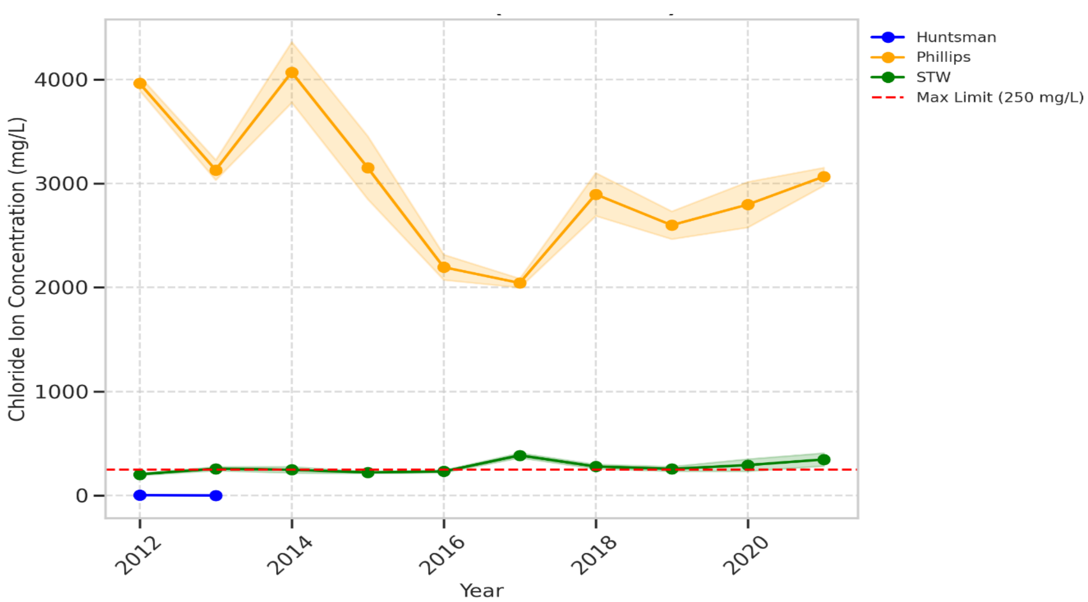

Figure 4.9 the annual mean level (with 95% confidence interval) of Chlorine at Bran Sands Phillips Petroleum Crude Inlt Bran Sands Huntsman Crude Inlet and Bran Sands Stw Crude Inlet from 2012 to 2021

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As shown in figure 4.9, chloride ion concentration at the Bran Sands inlets, revealed significant disparities across the monitored sites. Among the sites, the Phillips Petroleum dataset exhibits consistently elevated chloride concentrations, ranging between 2000 mg/L and 4000 mg/L, far exceeding the regulatory limit of 250 mg/L. In contrast, the STW dataset remains relatively stable, along the regulatory limit, although minor fluctuations occasionally result in slight exceedances such as in 2013, 2017, 2018, 2019, 2020, and 2021.

Bran Sand Outlets

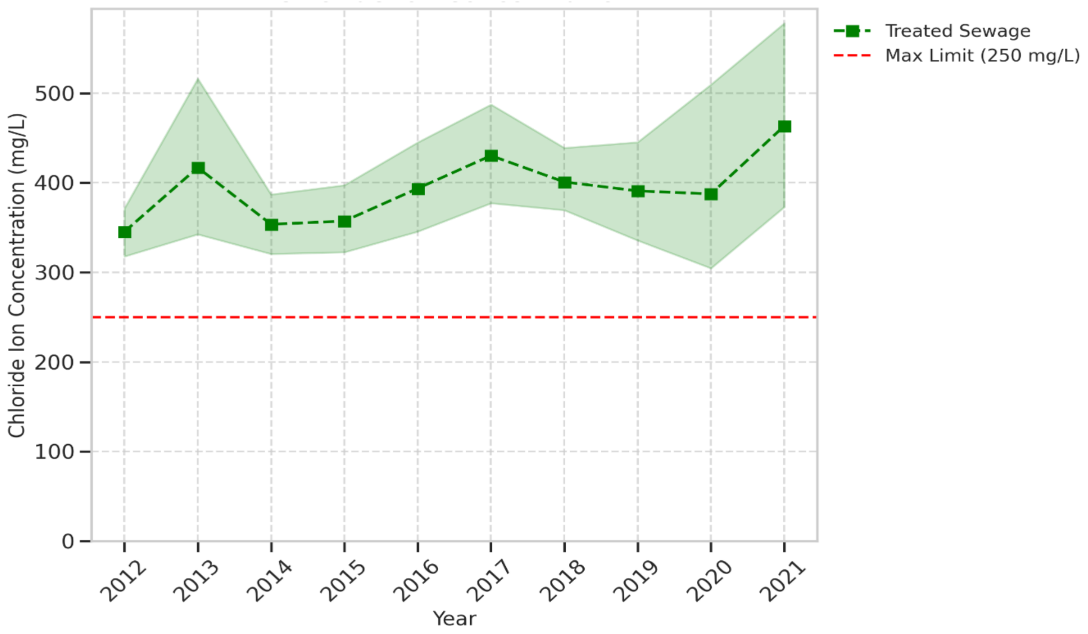

Figure 4.10 the annual mean level (with 95% confidence interval) of Chlorine in Bran Sand Outfall and Bran Sands Treated Sewage from 2012 to 2021

As shown in Figure 4.10, chloride concentrations at the Bran Sands outlets have been on an inclining trend, exceeding the maximum compliance limit throughout the study period.

pH

Wilton Complex Main Effluent

Figure 4.11 the annual mean level (with 95% confidence interval) of *BOD* at Wilton Complex Main Effluent from 2012 to 2021

As illustrated in Figure 4.11, the pH levels at the Wilton Complex Main Effluent consistently exceeded the maximum compliance limit in eight out of ten years. In 2012, the pH started at 9.3, then declined until 2014, reaching 8.9. From 2014 to 2015, a sharp increase was observed, peaking at 9.55. Between 2016 and 2020, pH values remained above the compliance limit, but in 2021, a steep decline brought the pH level significantly below the compliance limit.

Bran Sands Inlets

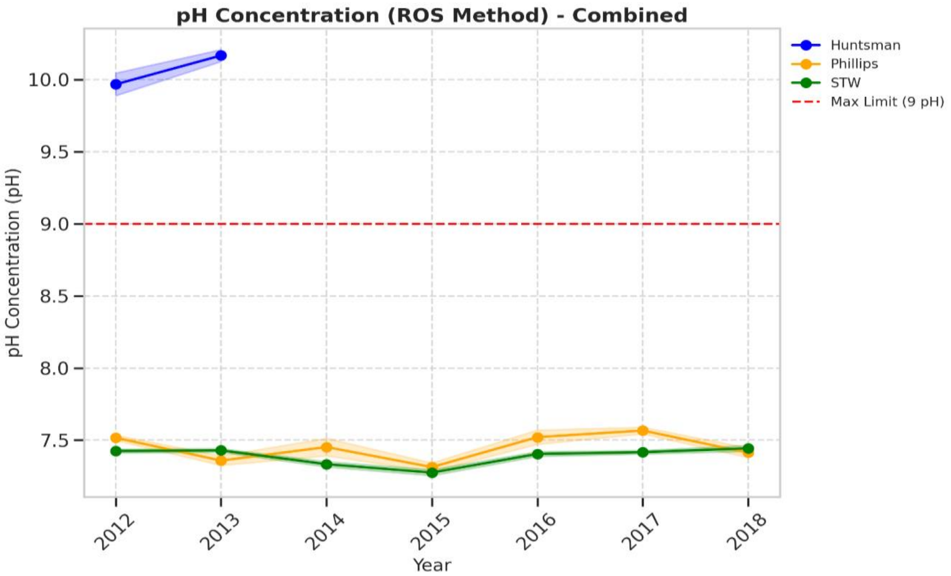

Figure 4.12 the annual mean level (with 95% confidence interval) of pH at Bran Sands Phillips Petroleum Crude Inlt Bran Sands Huntsman Crude Inlet and Bran Sands Stw Crude Inlet from 2012 to 2021

As illustrated in Figure 4.12, the pH levels at the Bran Sands inlets show variations across the monitored sites. Both the Phillips and STW sites display relatively stable pH values, consistently remaining within a narrow range between approximately 7.3 and 7.6. These values are well below the maximum compliance limits, indicating a balanced pH level with minor fluctuations over the observed period. However, in the Huntsman site, the pH levels were exceeding the regulatory limit of 9.0. however, limited data were available to fully explain the trend.

Bran Sands Outlets

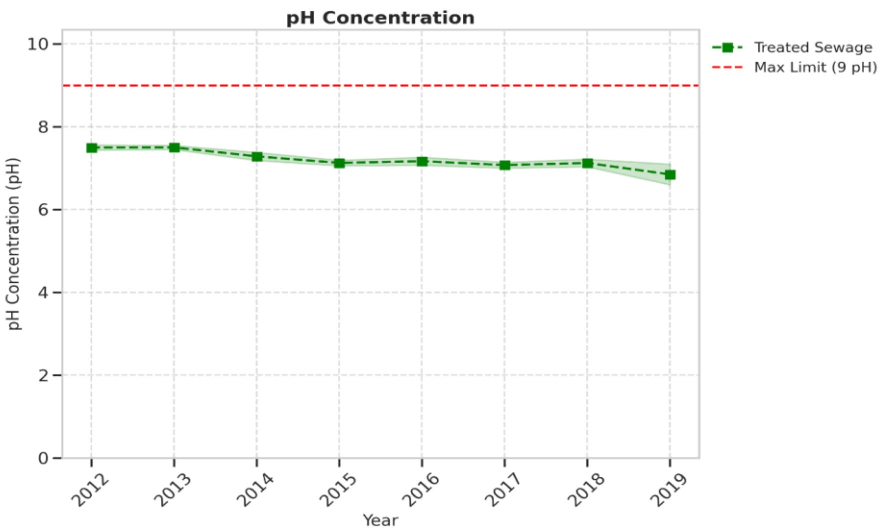

Figure 4.13 the annual mean level (with 95% confidence interval) of pH at Bran Sands Outlets from 2012 to 2021

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As shown in figure 4.13, trend in pH levels at Bran Sands outlets, showed a steady decline throughout the study period. The highest values were seen in 2012 and 2013 (7.50 each). However, from 2014 onwards, there was a marked decline, with pH values falling to 6.85 in 2019. All values were below the maximum compliance limit.

Temperature

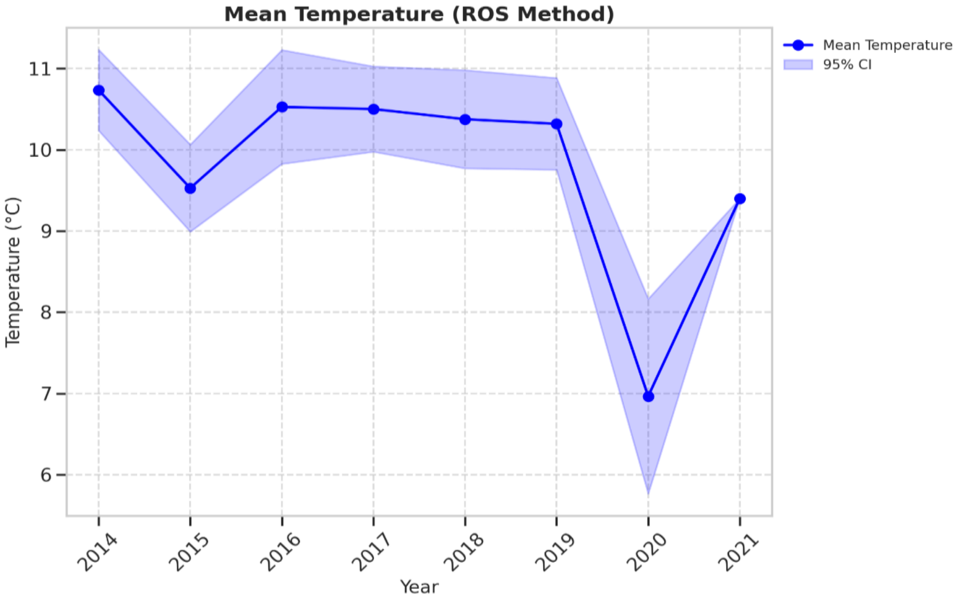

Figure 4.14 the annual mean level (with 95% confidence interval) of temperature from River Tees at Dabholme Gut Confluence from 2012 to 2021

As shown in figure 4.14., the mean temperature trend shows fluctuations, with a sharp decline in 2020. This may be attributable to the COVID-19 lockdown, which saw many industries shutting down. This can also be seen with a partial recovery in 2021. Before 2020, the annual arithmetic mean temperature ranged between 9.00°C and 11.00°C. The highest and the lowest temperature values recorded were in 2014 (10.73°C) and 2015 (9.53°C). There were no significant changes in temperature from 2016 to 2019.

Salinity

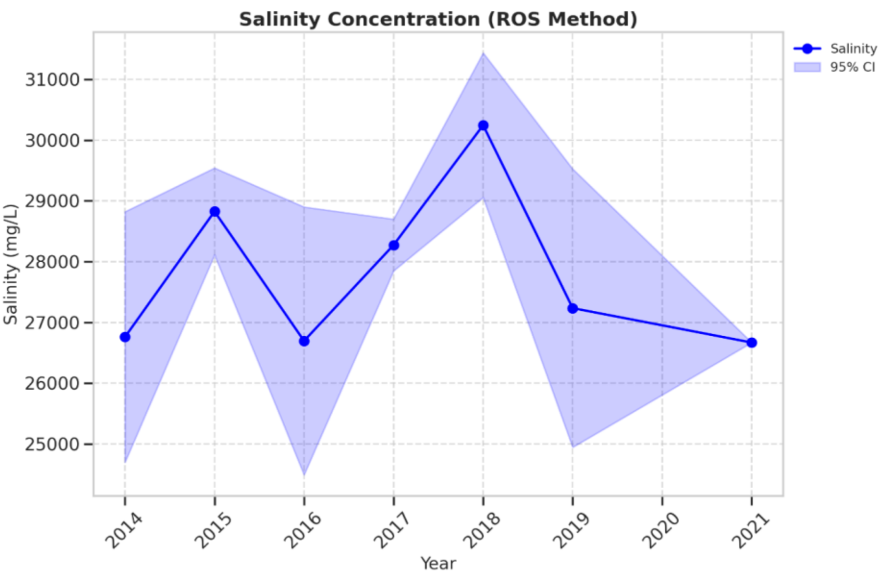

Figure 4.11 the annual mean level (with 95% confidence interval) of in Salinity in Situ of River Tees at Dabholme Gut Confluence from 2012 to 2021

As shown in figure 4.6, the annual arithmetic mean salinity levels generally range between 26670 and 30245 mg/L in 2018 and 2021 respectively. Significant peaks were observed in 2015 and 2018 (28826.67 and 30245 mg/L respectively), followed by declines in 2016 and 2019 (26697.27 and 27236.36).

DISCUSSION

The trends of key water quality parameters at Bran Sands indicate significant improvements throughout the study period, demonstrating a substantial decline in pollution loadings from the Bran Sands sewage treatment works into the River Tees between 2012 and 2021. The recorded values for Ammoniacal Nitrogen, BOD, COD, and pH at the outlets were all within permissible limits for an estuarine environment (Ujjania & Dubey, 2015). Notably, Ammoniacal Nitrogen levels were occasionally above the maximum compliance limit at the Wilton Complex Main Effluent and Bran Sands inlets. However, at the outlets, ammoniacal nitrogen concentrations remained below the limits, reflecting effective wastewater treatment measures. Similar trends were also observed for BOD, COD, and pH.

These reductions align with documented national improvements in pollution control, as reported by the Environment Agency, which noted that pollution loads from water company sewage treatment works have decreased by 80–85% for ammonia and 46–55% for BOD (Environment Agency, 2022; 2024). The findings of this study also complement recent national-scale analyses of macroinvertebrate community trends in English rivers (1991–2019), which similarly indicate improvements in river water quality and ecological health (Pharaoh et al., 2023; Pharaoh et al., 2024; Qu et al., 2023).

The reduction in BOD concentrations at Bran Sands outlets is particularly significant because BOD is closely associated with DO levels in aquatic ecosystems. A decline in BOD suggests that less oxygen is being consumed for the decomposition of organic matter, indicating a healthier water environment with increased oxygen availability (Rosli et al., 2012; Amadi et al., 2010). Similarly, the observed lower COD levels reinforce the conclusion that pollution from organic and chemical contaminants has decreased, leading to improved water quality (Waziri & Ogugbuaja, 2010). These observed reductions suggest that enhanced wastewater treatment technologies have been effective in mitigating organic pollution and improving DO conditions in the estuary.

pH levels at the outlets, have remained within a neutral to slightly alkaline range, which is typical for unpolluted rivers. The declining trend in pH can also enhance DO concentrations and improve aquatic life in the ecosystem, as long as it does not go below the minimum compliance limit of 5 (David et al., 2003). Temperature values of river tees did exceed critical temperature threshold, thus protecting aquatic organisms in the region (Verma & Singh, 2013). salinity levels did not indicate any major water quality concerns at the river tees as salinity was maintained with acceptable limits due to tidal mixing (Wade, 2002).

However, chloride concentrations remain a significant concern in the Bran Sands. Although it is a common practice to maintain a residual level of chlorine in wastewater plants, however, awareness of the environmental effects of chlorine necessitates a move to reduce this residual (Australian Government Initiative, 2000; Hong, et al., 2023). Although chlorine itself does not persist for long periods, it undergoes rapid transformation into hypochlorous acid (HOCl) and hydrochloric acid (HCl). These transformations are influenced by pH, temperature, and ionic strength, with free chlorine existing in equilibrium as Cl_2, HOCl, and hypochlorite ion (OCl^-). In estuarine and marine environments, chlorine also reacts with bromine to form brominated compounds, or nitrogenous substances (e.g. ammonia) to form N-chloramines compounds, which persist longer and contribute to total residual chlorine (Australian Government Initiative, 2000).

Long-term inputs of these compounds are toxic to aquatic organisms, with sensitivity varying across species; for example, Freshwater fish exhibit sensitivity, with chronic no-observed-effect concentrations (NOEC) as low as 14–29 µg/L for *Oncorhynchus mykiss* over 24 to 96 hours. Freshwater crustaceans, particularly *Ceriodaphnia dubia*, show immobilisation effects at 48 µg/L in a 10-day exposure, while other species like crayfish and copepods tolerate higher concentrations over 24 to 96 hours. Freshwater molluscs and periphyton experience chronic toxicity at 32 µg/L after 168 hours, indicating potential bioaccumulation risks. Marine species are also affected, with chronic NOEC values of 87–186 µg/L for *Menidia beryllina* over a 7-day growth period and 20–87 µg/L for *Mysidiopsis bahia* over a 7-day reproductive period, suggesting chlorine-induced growth and reproductive impairments in estuarine ecosystems (Australian Government Initiative, 2000).

In addition, chloride ions are highly corrosive and can accelerate the degradation of metal structures, including bridges, water distribution systems, and industrial equipment. High chloride concentrations contribute to corrosion-related failures, increasing maintenance costs and safety risks (Hong, et al., 2023).

CONCLUSION AND RECOMMENDATIONS

Conclusion

The present study which aimed at analysing the trend of water quality at Bran Sands between 2012 and 2021, found out that certain physicochemical parameters such as, ammoniacal Nitrogen, BOD, COD, and pH, showed a clear decreasing trend in the outlets of Bran Sands as compared to the inlets, indicating significant improvement over the time period. temperature, and salinity varied in a relatively stable range below the maximum compliance limits. However, Chlorine was on an inclining trend and over the maximum compliance limit at both inlets and outlets monitored sites. The successful management of ammoniacal nitrogen, BOD, COD, and pH could be attributed to, upgrading, and improvement of sewage treatment systems.

Therefore, this study has provided comprehensive information on the physicochemical properties and water quality of Bran Sands, Tees Estuary. Despite the overall improvements, chloride concentrations If left unaddressed could pose long-term risks to aquatic ecosystems, and infrastructure. Therefore, there is a need for continued monitoring and targeted interventions to sustain these gains and mitigate persistent pollution concerns.

Recommendations

Once chloride is dissolved in water, it cannot be effectively removed by conventional biological treatment or sedimentation processes used in wastewater treatment facilities (Minnesota Pollution Control Agency, 2018). Due to the persistent nature of chloride contamination in the Bran Sands outlets, implementing advanced treatment technologies is necessary to enhance chloride removal. The following methods offer potential solutions:

chemical precipitation technologies can be used to convert chloride into less soluble compounds like metal chloride, metal oxychloride, and Friedel's salt

adsorption technologies can trap chloride ions onto solid surfaces. It involves using technologies like the Ion-exchange resins and bimetal oxides

Advanced oxidation processes (AOPs) use highly reactive hydroxyl radicals (•OH) with a higher redox potential than chloride (Cl^-) at 1.36 V, allowing for effective oxidation and breakdown of chloride compounds. Techniques for chloride removal include ozone-based AOPs, electrochemical AOPs, and SR-AOPs.

Membrane separation technologies, such as diffusion dialysis, nanofiltration, reverse osmosis, and electrodialysis, can selectively filter out chloride ions through membrane-based processes (Li et al., 2022; He et al., 2023).

Future Direction

Although the application of advanced chloride removal technologies can improve water quality, the large-scale application of these technologies may be limited by factors such as engineering practicality, cost, and legal requirements (Minnesota Pollution Control Agency, 2018). Thus, more studies are needed to perform a techno-economic analysis of these technologies, to determine their feasibility, viability, and applicability for the long-term implementation in wastewater treatment plants such as Bran Sands.

In addition, more research is needed to find better relationships between the chemical and physical water quality parameters and the biological water quality parameters like macroinvertebrate index of biotic integrity and fish index of biotic integrity (Environment Agency, 2025).

In order to maintain and further enhance these achievements, more resources should be allocated to water quality management and to the advancement of science. The long-term monitoring and analysis should be given priority to monitor the changes that are still ongoing and to detect new pollution threats that may arise in the future to enhance the water management. Therefore, there is a need for more interaction with the stakeholders such as the regulatory bodies, industries, and the public in order to enhance the adaptive and effective water quality management of the Tees Estuary.

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This dissertation is dedicated to the loving memory of my beloved mother, Felicia Dulcie Omoataman, who passed away on 15 August 2024. Her love and sacrifices continue to inspire me.

To my precious diamond—my wife and children—thank you for your unwavering support and encouragement.

I extend my heartfelt appreciation to my father, James Omoataman, whose prayers and wisdom have been a source of strength, and to my wonderful sisters, Brenda Jessica, Tracy, and Sonia —you are truly the best.

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