Heavy Metal Contamination Along the Coast of North-East England

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by

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Abstract

The last century has seen the north east coast of England heavily affected by anthropogenic activities, none more notable than the coal mining industry, and the millions of tonnes of colliery waste estimated to have been dumped every year. Since the decline of the industry and subsequent remedial work carried out by the Turning the Tide Partnership, investigation of the coastline has been minimal. The purpose of this investigation is to consider the industrial forcing of the natural ecosystem which exists along the north east coast of England, and analyse the impacts of remediation in accelerating the recovery of the area from a state of economic exploitation, to natural habitat and environmental resource.

Giusti et al. (1999) conducted a study which collected heavy metal data from the shell and tissue material of *Mytilus edulis* (the blue mussel) at five coastal locations along the north east of England, during the early stages of remediation (December 1997). A second study (Giusti, 2001) monitored the heavy metal contamination of *Fucus vesiculosus* (bladderwrack) along the coast during the same period.

This investigation has provided comparative heavy metal data to these baselines, allowing assessments of the level of recovery to be made, while highlighting current areas of concern and the implications of post-remediation activity. The concentrations of Fe, Mn, Zn, Cr, Cu, Pb, Ni and Cd were determined in both the soft tissue and shell material of the blue mussel and common limpet (*Patella vulgata*) at several sites between Whitburn and the Tees estuary. Bladderwrack is included as a sensitive short term indicator of water based heavy metal contamination.

Although the investigation finds that the long term metal contamination of the coastline has decreased, a change in the spatial pattern of pollution is observed, manifested by an increase in metal concentrations at the Tees estuary site of Bran Sands. The mobilisation and transport of offshore sediment is discussed as a possible causal factor. High levels of iron and manganese are recorded in all three indicators, suggesting an aqueous source. These high values include a 9-fold increase in iron contamination of bladderwrack (to $\sim$9,000 mg kg^{-1}), and a 12-fold increase of manganese in bladderwrack at Roker estuary (to $\sim$1,600 mg kg^{-1}). Subsequently, tentative links are drawn to the pumping of treated minewater into the sea at Horden and Dawdon.

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Contents

List of Figures

List of Tables

Chapter 1

Introduction

The purpose of this investigation is to consider the industrial forcing of the natural ecosystem which exists along the north east coast of England, and analyse the impacts of remediation in accelerating the recovery of the area from a state of economic exploitation, to natural habitat and environmental resource. Focusing on County Durham, this stretch of coastline is of particular interest due to the degree of degradation which occurred, with the coal industry using beaches at numerous sites for the disposal of colliery spoil. Furthermore, the anthropogenic influence in regenerating the coastline served to accelerate its evolution after the coal industry's decline, although there appears to be little research investigating the potential for change in the chemical composition of the coast as a result. While working with Niall Benson (Durham Heritage Coast Officer), he acknowledged the lack of such data since remediation work carried out during the Turning the Tide Project, whereas the current form of the coast and the remediation itself received acclaim. Despite this, a number of studies considered the heavy metal contamination of the coast using a variety of indicators prior to the Turning the Tide Project, providing a baseline dataset for comparison with present day values. Through this investigation it will be possible to comment on the impact of regeneration on the chemical record of the coast.

The remainder of chapter 1 notes the significant changes which have occurred along the County Durham coastline, including an overview of the Turning the Tide Project which was responsible for its remediation between 1997 and 2002. The aims and objectives of this investigation are also set out with reference to similar projects in the literature. Chapter 2 details the studies carried out in the late 1990s which provide the baseline data for comparison through the course of this study, while chapters 3 and 4 consider the ecology of the coastline and different analytical techniques respectively.

Chapter 5 introduces the research and analysis from this investigation, with the findings presented in journal article form in chapters 6 and 7. Finally, chapter 8 provides an overview of findings, considering the relative impact of remediation in producing the observed results.

1.1 Evolution of the County Durham Coastline: From Coal Spoil to Heritage Coast

This coastal zone has a long history of mining with collieries at sites such as Easington (1899) opening in the 19th century, exploiting the coal seams which run out beneath the North Sea (Durham Heritage Coast, 2010).

Wilkinson and McCay (1998) suggest it was the growth of the industry by the 1930s which raised the logistical issue of disposing of the coal spoil, the waste by-product of the mining industry, claiming the cheapest and easiest solution was adopted which saw the dumping of solid and liquid waste onto the local beaches. Figure 1.1 shows these four major dumping sites at Dawdon in the north, through Horden and Easington, with Blackhall in the south. This dumping continued, and eventually peaked in the early 1980s where values are estimated to have reached 2.5 million tonnes per annum (Norton, 1985). Prior to the Second World War, it is claimed that spoil on the beaches could be effectively removed by the erosive action of the waves (Wilkinson and McCay, 1998). However as the volume being dumped increased, human deposition exceeded natural erosion which led to increased accumulation until the gradual demise of the coastal mines, with the final closure occurring in 1993 (Rodgers and Proudfoot, 1999). It is this 150 year history of industrial action and environmental neglect which created what Humphries (1996) sees as the anthropogenically induced chemical and structural legacy which was visible prior to remediation (figure 1.2).

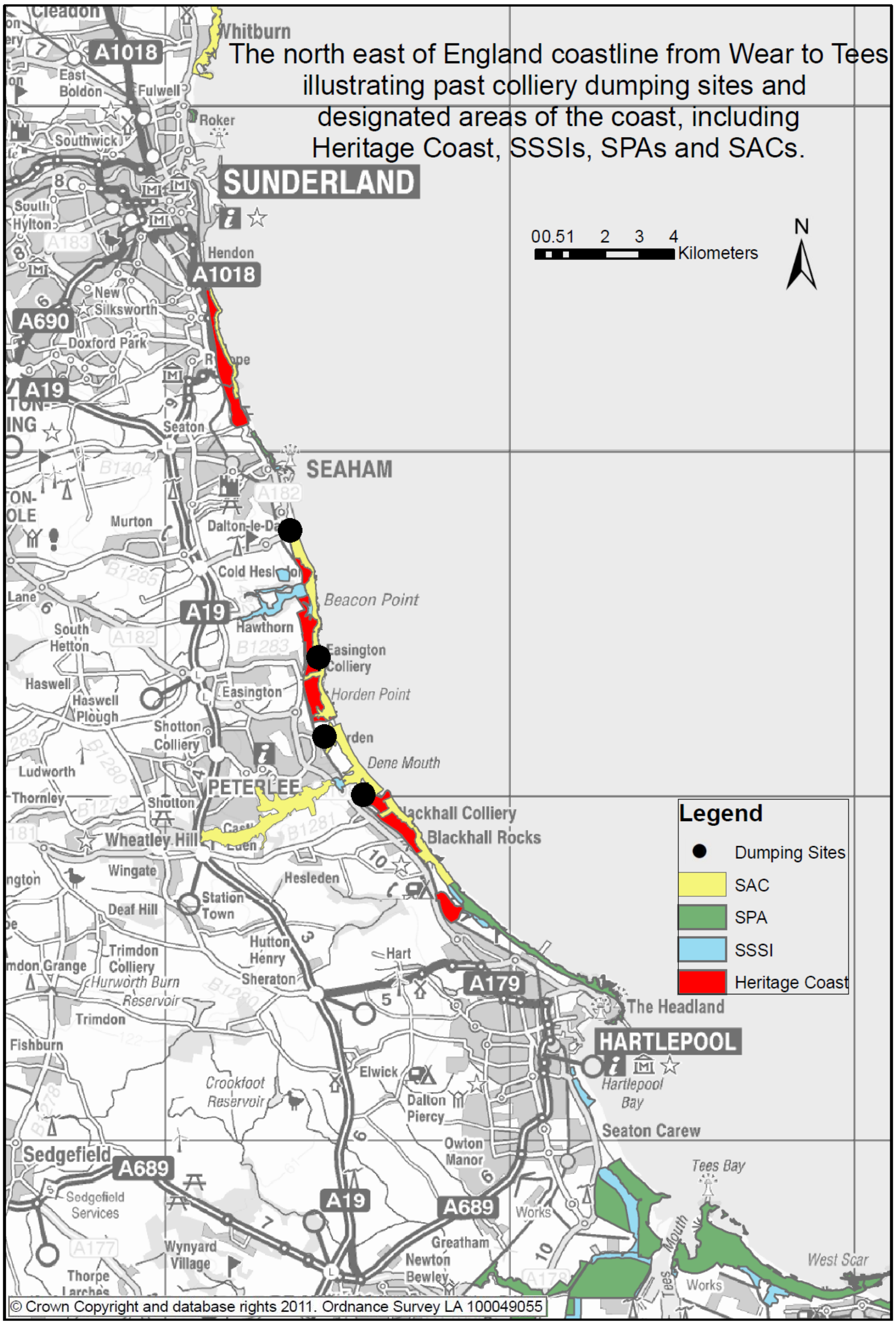

Figure 1.1: Map showing designated land and former mine waste dumping sites.

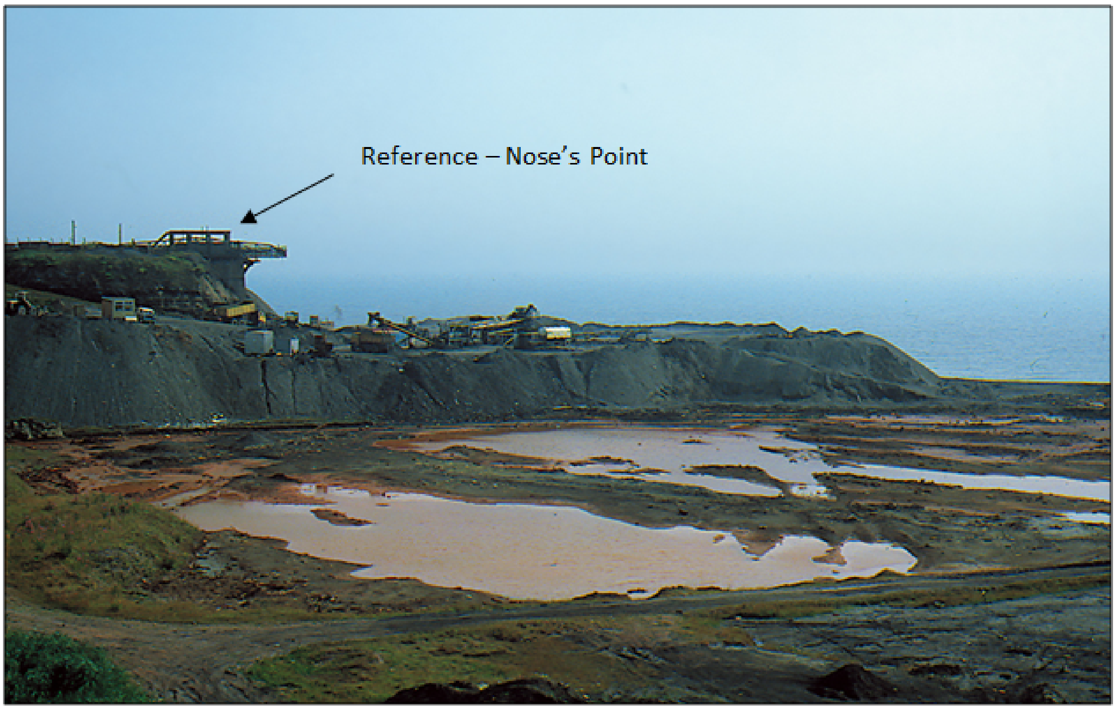

Figure 1.2: Colliery spoil at Dawdon while the mines are still open. Rising above the spoil to the left, the headland of Nose's Point can be seen (image from Durham Heritage Coast Partnership)

Away from the coast, the 1972 United Nations Conference on the Human Environment prompted the creation of international policy which would change the way coastal environmental management is conducted (Mendelsohn, 1971). The 'Convention on the Prevention of Marine Pollution by Dumping of Wastes at Sea' was signed by 80 countries in London in November 1972 (Duncan, 1973), which ultimately led to an announcement by the UK government in 1974 that beach tipping of coal spoil should cease (Rodgers and Proudfoot, 1999). This is one of the many contributory factors which triggered a decline in coastal dumping from the 1970s right up to the closure of the last coastal mine in County Durham at Easington in 1993.

1.2 Introduction to the Sampling Sites

1.2.1 Whitburn & Roker

Whitburn is a headland site which lies just north of the Wear estuary at Roker. As the site was not heavily affected by the dumping of coastal mining waste, the shoreline is dominated by large boulders with comparatively little fine grain sediment. The main source of pollution at this site is likely to be the outflow of sewage into the sea through pipelines (for pipeline information see Davis and Horswill, 2002).

Roker lies south of Whitburn and consists of fine sediment bathing beaches with outlying rocky areas. The estuarine site in this study relates to the confluence of the River Wear with the North Sea. As a result, past pollution influences include the inland North Pennine Orefield (Dunham, 1990). However, recent work with farmers and industrial bodies has aimed to reduce pollution discharges, accompanied by huge investment in sewerage infrastructure, leading to a dramatic recovery in river water quality (Environment Agency, 2011a).

1.2.2 Dawdon, Easington, Horden & Blackhall Rocks

The area between Dawdon and Blackhall Rocks includes four study sites which were previously mine waste dumping areas (see figure 1.1). As a result, extreme, anthropogenic changes to the physical characteristics of the shoreline occurred which severely affected local flora and fauna (e.g. Hyslop et al., 1997). Remnants of the physical burden of mine waste material remain at sites where the spoil was left to erode naturally, such as Dawdon blast beach. At this site, spoil material is present along the coast in the form of a small, retreating cliff. The areas in the low tide zone which are now free of this material are returning to a more natural, rocky shoreline, manifest by the recolonisation of a small number of mussel species.

1.2.3 Middleton, North Gare & Bran Sands

The Middleton site at Hartlepool is a location where there is a change in shape of the coastline which will ultimately have implications for sediment transport and deposition. This is important as longshore drift in the region transports material from north to south (e.g. Bird, 2010), and Middleton is situated south of all four former dumping sites. As a result, it is possible that the headland at Hartlepool is an area affected by the deposition of material that was dumped on the beaches further north in the past.

North Gare and Bran Sands lie either side of the River Tees estuary. North Gare is a site of dunes and grazing marsh situated north of the river, and Hartlepool nuclear power station.

Bran Sands is located on the south side of the Tees estuary opening. Due to the change in direction of the coast here, combined with the disruption of coastal sediment transport by the estuary opening itself, this is an area of material deposition and represents the southern point of the Shoreline Management Plan's sediment cell 1c (see figure 1.3). Bird (2010) highlights Bran Sands as an area of deposition, noting that the barrier spit that makes up the south side of the estuary mouth means that the material in the estuary has accumulated as a result of rising tides and longshore drift, rather than from riverine input.

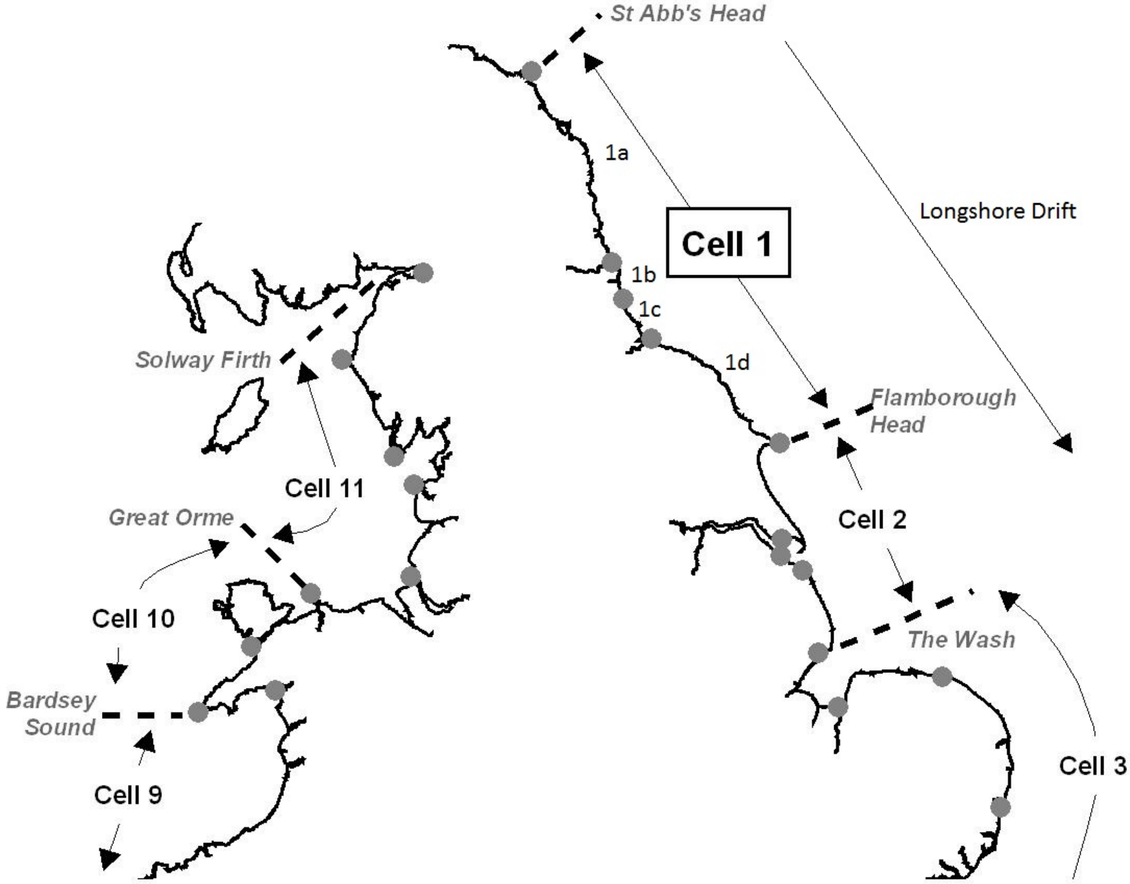

Figure 1.3: The coastal sediment cells of central and northern England. All sites but Whitburn and Roker currently lie in the sub-cell 1c. Modified from Aspect (2012).

Figure 1.3 shows the sediment cells as outlined in the shoreline management plan, with sub-cells 1b (Tyne to Seaham Harbour) and 1c (Seaham Harbour to Tees) being the focus of this study. While sub-cells are defined as a length of coastline where sediment movement is relatively self-contained, it has been suggested that 1b and 1c are combined as the reason for selecting Seaham Harbour as a boundary is not clear from the coastal processes (DEFRA, 2011). As a result, the generally low to moderate southward drift of material along a stretch of coastline which is characterised by embayments with rock headlands is not necessarily interrupted at Seaham (DEFRA, 2011), and the pollution history for each of the sites in this study could have implications for the sites further south along the coast.

1.3 The Remediation - Turning the Tide

The recovery from a site of extreme environmental decay to a distinguished and protected area of heritage has been attributed to the regeneration project called 'Turning the Tide', which facilitated the development of the coastline into the environmentally significant site which we currently see. The Durham Coast Management Plan (1993) outlined in its Coastal Process Report that the complete erosion of the spoil beaches, in the worst affected areas, could take between 52 and 210 years, dependent on erosion rates. This highlighted the need for human intervention, along with the now derelict mining sites, and the suffering ecology. As a result, the Turning the Tide Partnership was formed to regenerate the coast, making use of £10.5 million of funding (including £4.5 million from the Millennium Project) for remedial work to take place from 1997 to 2002 (Durham Heritage Coast, 2010). The project, split into four categories, aimed to rejuvenate the beaches, remove colliery spoil, undertake landscape enhancement and nature conservation, and promote coastal recreation and access.

The Turning the Tide Partnership, including English Nature, The National Trust and Durham County Council among others, started the remediation of the coast in July 1997. The work carried out included the reclamation of 80 ha of land and the removal of 1.3 million tonnes of coal spoil from the beaches, which was transported and spread over the sites of two former pits, capped and covered with soil to create a public open space. (Durham Heritage Coast, 2010). The three main goals of the project were as follows:

- To restore, enhance and conserve the environmental quality of the Durham Coast.
- To encourage sustainable use and enjoyment of the Durham Coast.
- To rekindle local pride and a sense of ownership of the Durham Coast.

(Durham Heritage Coast, 2010)

The project was deemed a success, as previous estimates of the time taken to erode spoil beaches to their natural states were dramatically reduced to 20 years (Durham Heritage Coast, 2010), and the remediation work was jointly awarded The

Royal Institute of Chartered Surveyors (RICS) Award for Outstanding Achievement in Regeneration 2001, shared with the Eden Project.

1.3.1 Since Turning the Tide, and Other Remediation

In the period following industrial decline and remediation, the County Durham coastline was awarded a 14 km stretch of Heritage Coast (Natural England 2011). This area which lies between the conurbations of Teesside and Tyneside was awarded the National Landscape Award 2010, and is recognised locally, nationally and internationally through statutory designations for its geological and nature conservation value (Scarborough Borough Council, 2006). The underlying magnesian limestone geology of the area and the associated grasslands are the focal point of the Blackhall Rocks Local Nature Reserve (LNR) (Natural England, 2011) and the wider National Nature Reserve (NNR). The coastal stretch is also recognised as a Site of Special Scientific Interest (SSSI), a Special Protection Area (SPA), a Special Area of Conservation (SAC) and a Ramsar site recognising the international importance of the coastal habitats and wetlands which lie in the area (Natural England, 2011). The intertidal area is frequented by over wintering seabirds such as oystercatcher, turnstone, redshank and purple sandpiper due to its importance as a feeding ground. The presence of nationally significant numbers of purple sandpiper, fulmars nesting in the cliffs at Hendon, and breeding pairs of the endangered little tern, means the ecological significance of this coastal zone is unquestionable (Limestone Landscapes, 2010). For reference, figure 1.4 shows Dawdon after remediation had been completed.

Since the end of Turning the Tide, further measures have been taken to protect the east Durham magnesian limestone aquifer, which provides 20% of local drinking water and supplies Sunderland, Durham and Hartlepool, from rising levels of contaminated mine water (Coal Authority, 2007). While the coastal mines were open, underground pumping of water from the pits was active, however this ceased with the final closure of these mines in the early 1990s, and subsequently mine water levels began to rise and collect contaminating minerals. The aquifer was being threatened by contaminated water with high levels of iron and dissolved salts, with twice the chloride concentration found in sea water (40,000 mg/l), via direct connections and old shafts. Through the treatment and pumping of this water into the sea, a 125 km^2 area has been protected from contamination, including public supply wells which are exploited to the value of c. 35 million litres/day (Parker, 2003). Initially, a temporary treatment plant was set up at Horden in 2004 which drew raw mine water from the shaft of the local colliery. This water passed through the High Density Sludge (HDS) treatment plant, removing contaminating iron, before

Figure 1.4: Nose's Point post-remediation (image from Durham Heritage Coast Partnership)

being pumped back into the North Sea (Coal Authority, 2007). With information gathered from this work and a series of technical studies, a longer term treatment solution was planned. The use of a single pumping site was deemed to have a high risk of blocking due to underground collapses, and subsequently Dawdon was identified as an ideal secondary pumping site. More recently, a third pumping site has been established further north at Whitburn (January 2011) (Environment Agency, 2011b), although this site opened after the data collection from this study. The HDS treatment facilities are designed to reduce the iron contamination levels of the water to less than 1 mg/l from values reaching 160 mg/l, before discharge back into the sea (Coal Authority, 2007).

1.3.2 Remediation of Estuarine Sources

The cessation of coastal mining in the area coincided with the decline of the estuary based industry of the River Tees in particular, with many of the areas formerly occupied by sites of steel production, ship building and chemical and power plants being transformed into diverse habitats for important wildlife (Tees Valley Joint Strategy Unit, 2008). Similar decline occurred in industry which impacted the River Wear such as the lead, zinc, cadmium and copper mining of the North Pennine Orefield, an area which was once the UK's leading producer of lead and zinc (Dunham, 1990).

Despite this and subsequent remediation efforts, Shepherd et al. (2009) highlight the importance of continued monitoring as fine grained river sediment can contain up to 600 mg/kg of lead, illustrating an industrial legacy of environmental pollution. Outfalls of domestic sewage which used to be discharged untreated into both of these rivers, and more significantly the River Tyne due to higher populations, now flow through treatment plants sited by the coast (Giusti, 2001).

1.3.3 Implications

Although a large amount of remediation has occurred and the expectation may be that heavy metal pollution has decreased significantly, new processes which were absent during previous monitoring need to be considered. The remobilisation of large volumes of contaminated material on the beaches during remediation, exposing more material to the action of the waves, the pumping of controlled levels of iron contaminated water, and the influence of riverine pollutants, may still have some effect on coastal pollution levels.

1.4 Scientific Context

The majority of the discussion thus far has been concerned with change: the rejuvenation of a coastline from polluted dumping ground to a site of recognised scenic importance. Remedial work of this sort ultimately requires monitoring to gauge its success, justifying the input of funding, and assessing the suitability of the techniques used and their potential impact. Continued monitoring can allow a temporal record to be constructed, allowing the rate of recovery to be measured.

1.5 The Current Study

The transformation of the County Durham coastline over a relatively short period of time (approx. 50 yrs), provides an opportunity to monitor recovery and discuss the remediation work which was carried out along this coastal stretch. A unique feature of the proposed investigation is the existence of heavy metal contamination data in both *Mytilus edulis* and *Fucus vesiculosus* from **after** final colliery closure on the coast, and **prior** to the commencement of remediation, in several sites along the County Durham coastline. This past work by Giusti et al. (1999) and Giusti (2001) will provide the base line data for the current study, allowing a temporal comparison across the five year remediation project, and allowing changing spatial patterns to be identified.

1.5.1 Aim

To provide a new heavy metal record in *Mytilus edulis* and *Fucus vesiculosus* post-remediation, and compare this to data collected between final colliery closure and the start of Turning the Tide. This comparison, along with an assessment of the present spatial patterns will allow a discussion of the remediation process and the impacts it may have had on the County Durham coastline.

1.5.2 Research Questions

For this investigation, based on current understanding from the literature and of the site, the following research questions have been derived. The answering of these questions will allow the aim to be met.

- What is the current spatial pattern of heavy metal contamination in *Mytilus edulis*, *Patella vulgata* and *Fucus vesiculosus* along the County Durham coastline?
- What trends are observed between the data collected for each species?
- How do the current point concentrations and spatial trends compare to data collected prior to Turning the Tide?
- What impact could the process of remediation have had on the observed spatial and temporal trends?

Through the discussion of past studies which have monitored coastal pollution levels in littoral communities, both at the site of interest and further afield, justification for the current investigation can be derived. This will include discussion of key factors such as the complexity of the intertidal zone, the role of heavy metal bioaccumulation in pollution monitoring, an insight into the niche of the bioindicators for this study, and a summary of popular analytical techniques.

1.6 Monitoring Coastal Recovery

Throughout history, natural resources have been exploited despite the subsequent detrimental impacts on the environment, both physically and ecologically, as well as climatically (Ludwig et al., 1993). The coastal ecosystem is no exception to this, whether a result of tourism (Priskin J., 2003), power generation (Rotchell et al., 2001), the shipbuilding and petrochemical industries (Davies et al., 2005) or, more relevant to this study, coastal mining (Giusti et al., 1999). Although this investigation is site specific given the short timescale and circumstances which lie beneath the transformation of the Durham Coast, a number of similar monitoring projects have been carried out using littoral ecology to assess the impact of polluting activities, and recovery from them.

Bryan (1980) acknowledges that the development of fast analytical techniques during the 1970s brought a significant increase to the amount of research conducted in heavy metal contamination in the sea. Indeed, In the 6-7 years that followed the 1972 UN Conference in Stockholm, advances in the use of bivalve molluscs for heavy metal pollution research were made, with new techniques allowing an increased understanding of tissue distribution and the kinetics of metal uptake (Cunningham, 1979). The four most prominent indicators of coastal contamination are littoral flora such as *Fucus vesiculosus*, littoral fauna (mainly gastropods e.g. *Patella vulgata*, and molluscs e.g. *Mytilus edulis*), beach sediment and the seawater itself. However, the difficulties of monitoring using seawater, due to the need for multiple samples to eliminate variations in pollutant concentrations, currents, tidal patterns, and inputs of freshwater have been identified (Phillips, 1977). Similarly, problems occur with variations in sedimentation rate and percentage organic matter when analysing beach sediment (Phillips, 1977). An additional problem when measuring heavy metal concentrations in beach sediment is the lack of direct relation to the contamination of present biota. Despite these issues in monitoring sediment, it should be noted that to some extent the problems concerning spatial variability are being lessened due to the advances in digital mapping and reduction in cost of analysis, allowing reliable sampling of multiple recorded sites within one beach. This was utilised by Romano et al. (2004), where potential sinks of pollution were identified in marine sediment near an industrial plant in Bagnoli, Naples. This compares to Giusti (2001) at the current study site where a single surficial sample was taken from a beach and used to represent overall contamination, despite earlier studies suggesting that polluted sediment was being remobilised from offshore and transported along the coast (Johnson and Frid, 1995).

Forsberg et al. (1988) utilised *Fucus vesiculosus* to study heavy metal contamination in the Archipelago of Stockholm, concluding that the species is an excellent indicator for heavy metal pollution, given its sensitivity, particularly when transplanted. Miramand and Bentley (1992) used a combination of *Patella vulgata* and *Fucus serratus* to establish levels of heavy metal contamination in the rocky shore of Goury, thought to be influenced by the outlet of the nuclear reprocessing plant of La Hague in France. The investigation reported the influence of the industrial activity was negligible by comparison of the values with other regions. Additionally, the suitability of the indicators for seasonal studies due to their fluctuating uptake, peaking in winter, is discussed. Phillips (1970) highlights the advantages of using both *Fucus vesiculosus* and *Mytilus edulis* in a study due to the different mechanisms by which metal contamination is accumulated, with mussels being more susceptible to pollution from particulate matter, and seaweed from water contamination. This study confirms the use of the indicators to compare results spatially and temporally, to past investigations from the same area. This is a key factor in the current investigation. Finally, the Bristol Channel in the south west of England is a prime example of an area which has undergone repeated heavy metal monitoring as a result of industrial influence. Here, multiple different species of indicator were sampled, including *Fucus vesiculosus*, *Patella vulgata* and *Nucella lapillus*, to monitor the gradual decrease of metal contamination as a part of the Sabrina Project (Nickless et al., 1972). An additional aspect in Bristol, which has yet to be mentioned, is the use of this monitoring to assess the spatial extent of pollution rather than just comparing between study sites and years. Indeed, Fuge and James (1973) identify steep gradients between samples taken from just 100 m away, from within and outside a harbour. The ability to identify these boundaries at any site is useful in planning and implementing any future remediation work. In addition, these studies highlight the importance of adopting a multi-species approach due to the different rates of metal uptake and population sizes between species in different environmental conditions. Reliance on a single species when conducting a monitoring project could result in accurate data which is specific to that species, but not necessarily reflective of general coastal conditions.

1.7 Previous Studies of the County Durham Coastline

Due to the significance of the environmental disturbance created by industry along the north east coastline, a number of studies have been carried out investigating environmental impact. Due to the level of change both spatially and temporally, the data present in existing studies are dated. Indeed, the majority of studies relating to the biosphere along this stretch of coast (e.g. Ellis and Hoover, 1990; Johnson and Frid, 1995; Hyslop et al., 1997; Barnes and Frid, 1999; Giusti et al., 1999; Giusti, 2001) were carried out around the time of the final closure of coastal mines in County Durham but significantly, prior to the start of coastal regeneration. Some of their findings are considered before an introduction to the two key papers which provide baseline data for the current study.

The effects of the spoil in limiting the biodiversity of the polluted coastal areas are clearly visible. For example, the number of different species of algae found across the County Durham coastline varies between 10 and 60, compared to a national coastal average of 90 species (Durham Biodiversity Partnership (DBP), 2009). There are a number of ways in which the presence of coal spoil is thought to have had such an impact on the ecology of the coastal zone. These include the bioaccumulation of heavy metals in flora and fauna (Giusti et al., 1999), and habitat disturbance and often loss due to modified shoreline topography and an increase in suspended solids (Barnes and Frid, 1999; Rodgers and Proudfoot, 1999). This relationship between habitat disturbance and spoil material is particularly complex and differs greatly by type of shoreline. Indeed on sediment shores, small scale population extinctions were found to be caused by sediment instability as a result of mine waste deposition (Ellis and Hoover, 1990). Conversely on rocky shores, Hyslop et al. (1997) found that where significant correlations were found between faunal species richness and colliery waste input, they were positive. Combine these factors with seabed smothering and increased water turbidity (Hyslop et al., 1997), and the extent of the impact of coal spoil on coastal ecology becomes clearer.

Despite the interest taken in this stretch of coastline prior to remediation, only two studies measured heavy metal contamination in bioindicators just before remediation commenced. Giusti et al. (1999) and Giusti (2001) collected data from *Mytilus edulis* and *Fucus vesiculosus* with which the present study will compare its results. The following chapter outlines the findings of these studies.

1.8 Summary of Objectives

Through answering the outlined research questions, a comparison between datasets of heavy metal contamination on the County Durham coastline before and after remediation can be carried out. While enabling the project to meet its aim of discussing the impacts the remediation may have had, the production of new data will provide an up-to-date benchmark of contamination levels along the coast. As a result, this data may highlight areas where remediation has been successful, where further work is required, and raise questions concerning the current problems, and how to solve them.

Chapter 2

Key Baseline Studies

These two studies provide the foundation for the current project for two reasons. Firstly, they both call for further investigation due to the limited data collection which has been carried out at these sites. Secondly, both studies occurred before the Turning the Tide Project. As a result, a current dataset can be collected and compared to this past data to monitor what impacts the regeneration work may have had on these contamination levels. Although it may be expected that the remediation work would decrease coastal contamination, the large scale anthropogenic disturbance of coal spoil and the pumping of treated mine water into the sea may provide differing results.

2.1 "Biologically available trace metals in *Mytilus edulis* from the coast of north east England" (Giusti et al., 1999)

This study measured the heavy metal concentration in the shell and tissue of *Mytilus edulis* samples which were collected during the winter of 1996-1997. The study used an open aqua-regia digest and flame atomic absorption techniques to determine the concentrations of Fe, Mn, Zn, Cr, Cu, Pb, Ni, Cd, and Ag in the seaweed at all sites. The sites were chosen due to the declining influence of both estuarine industrial sources of pollution (Roker, Middleton & Bran Sands), and areas affected in the past by coastal mining (from Easington to Blackhall Rocks). Holy Island was chosen as a control site due to its location approximately 100 km north of the other sites. Fewer sampling sites were used compared with the Giusti (2001) study, most likely due to an insufficient population at other sites.

The overall outcome of the study was that mussels from the coastline under study accumulated heavy metal concentrations similar to or higher than the literature's most contaminated sites. This included Cu levels found in the mussel tissue that are higher than the standards set for metals in shellfish in the 1987 UK guidelines. These elevated levels are thought to be particularly significant due to the time of year in which they were collected, as uptakes rates are likely to be slower during the winter. The authors note that a fraction of the metal loads will be of natural origins due to the past mining activities in the inland Pennine region causing the accumulation of contaminated material in the estuaries of the Wear and Tees rivers. High levels of Pb at Roker are attributed to this source, although the busy coastal roads between Sunderland and South Shields are also highlighted as they may have some influence through atmospheric pollution. High levels of metals such as Fe, Pb, Cd, and Ag at Blackhall were thought to be a result of the oxidation of pyrite contained in mine waste at the site. These metals, while attached to sand and silt particles, would be released when ingested by the filter-feeding mussels under study. High values of Fe, Mn, Cu, Zn and Ni were thought to be a product of industrial sources, particularly the close proximity to the petrochemical works. The unexpectedly low metal concentrations at Bran Sands, an estuarine site which has been influenced by sewage and industrial effluents for decades, suggests a reduction in metal loading to this estuary, although future studies were called for to help confirm these trends.

The use of Holy Island as a control site is questioned due to the high metal levels at sampling sites there, thought to be a product of the weathering of the dolerite dyke at the location. Other possible causes are cited, including agricultural run-off, sewage output, and increased traffic across the causeway connecting the island to the mainland.

2.2 "Heavy metal contamination of brown seaweed and sediments from the UK coastline between the Wear river and the Tees river" (Giusti, 2001)

Samples of the brown seaweed *Fucus vesiculosus* and surface sediment were also collected in December 1997 at 17 sites along the north east coastline of England (figure 2.1).

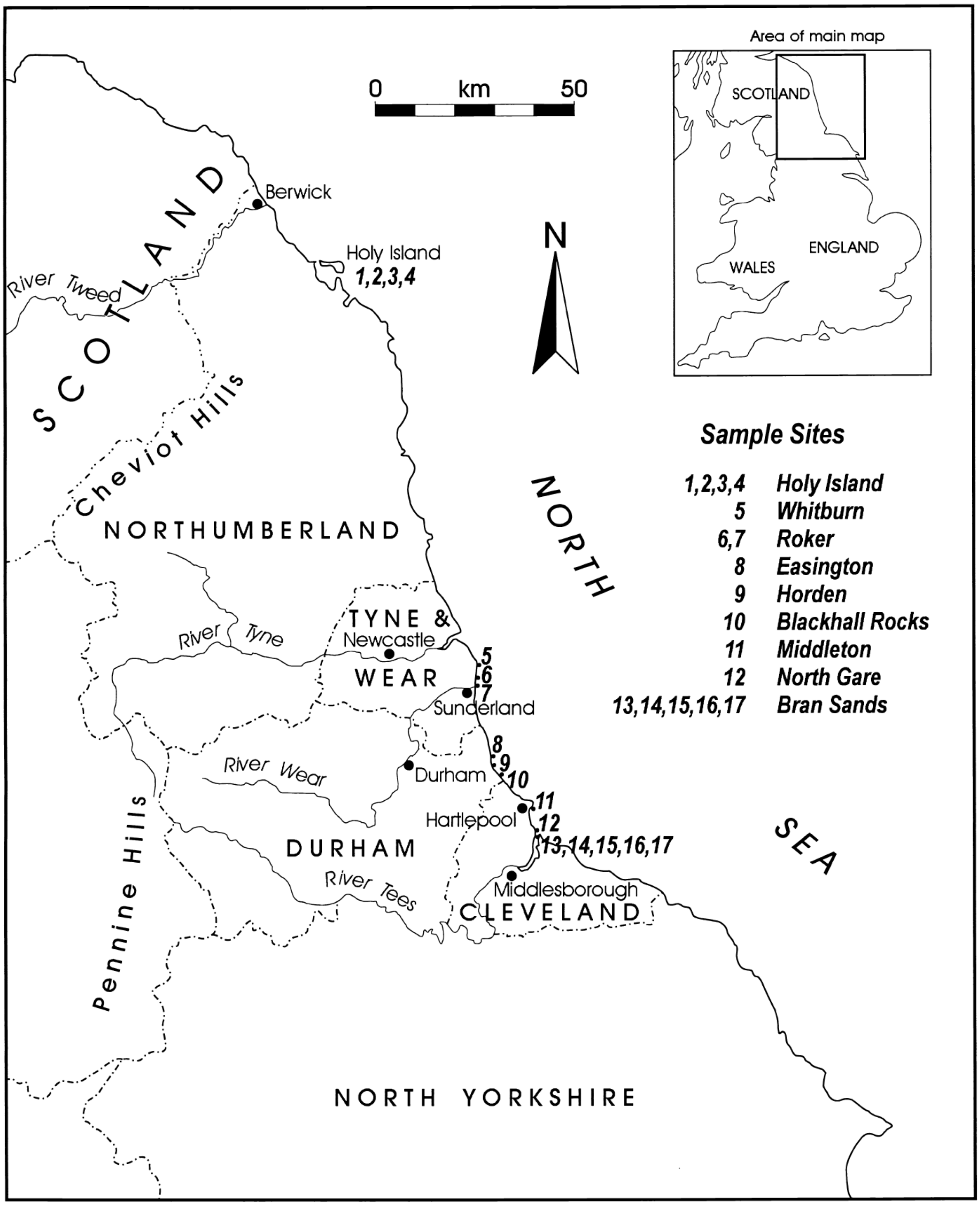

Figure 2.1: Map of study sites for the 1997 *Fucus vesiculosus* sample collection (after Giusti (2001))

The main finding of the investigation was that although all mines in the area had closed, along with the decline of many industrial activities in the area, both sediments and algae were contaminated with elevated levels of heavy metals. Seaweed samples from Whitburn, Roker, Easington and Horden had high burdens of Zn, Cu, and Cr. As with the mussel study, levels of metals at Bran Sands are lower than at other sites, and concentrations of Pb, Zn, Cu, Cd and Ag observed in seaweed are normally lower than those found in the mussels of the previous paper. Conversely, Mn in seaweed is frequently an order of magnitude higher than that observed in the mussels.

The study called for further data to be collected due to the small time frame of the study, and again to confirm the apparent reduction in industrial impact on the marine environment at Teesside.

2.3 Review

Although these studies provided important heavy metal data for a coastline naturally recovering from significant industrial impact, it appeared difficult to place the results in environmental context due to the lack of locally collected comparison data available, restricting analysis to comparison with similar studies of other contaminated sites, and with international legislative guidelines for metals in edible shellfish. Equally, by limiting shellfish data collection to Mytilus edulis (the common mussel) and not exploring the contamination of other species, interpretation can be difficult. For example, *Patella vulgata* (the common limpet), *Nucella lapillus* (dog whelk) and the mussels collected in Giusti (2001) all have different ecological niches, as will be explained in Chapter 3, meaning that they are affected differently by varying levels of specific metals, an attribute which promotes the use of multiple faunal indicators when investigating the contamination of a coastal stretch.

While the pumping of minewater into the River Wear is mentioned in the introduction of Giusti (2001), the discussion of treatment strategies and the implications of the process on the collected data is not a significant feature. This may be surprising given that *Fucus vesiculosus* is known to be a good indicator of water quality, and it will be interesting to see if the ongoing treatment and pumping efforts since this study will appear to have any impact in the dataset produced in the current investigation.

Chapter 3

Ecology

3.1 Rocky Shorelines

The dependence of shore communities on tides and wave action, which cause variations in the temperature, level of drying and exposure, creates specific zones where communities can be found. The four most distinct of these communities are found at the splash zone, the upper, middle and lower shore (Cremona, 2005). Additional physical variables to consider include aspect, salinity, substrate type, light exposure and slope (e.g. Durham Biodiversity Partnership (DBP), 2010; Cremona, 2005), while climate and predator-prey interactions are also shown to be significant factors in the stability of these habitats (Bertness et al., 1999a). Consideration must be given to the great variability of some of these factors within rocky shorelines as well as between them, such as slope and aspect, when constructing a sampling method for multiple sites. This is important as fauna living on opposite sides of rocks, or at different heights, may witness different slope, aspect and exposure to both waves and potential heavy metal pollution.

Intertidal communities can be particularly complex when coping with different levels of habitat disturbance. As Bertness et al. (1999b) illustrate, different habitat modifications, such as the removal of seaweed canopies, can have differing ecological effects on shoreline communities depending on the location within the beach. Indeed, their research shows that the presence of canopies aided the survival of underlying fauna in the upper tidal zone but had little effect on fauna in the lower tidal zone. This is perhaps due to the upper tidal zone exhibiting greater ranges of moisture and temperature; factors which can be mediated with floral shelter. In this sense, positive interactions between neighbouring organisms can have a buffering effect, reducing the impact of stressful conditions in certain habitats (Bertness and Leonard, 1997).

While the susceptibility of coastal communities to similar minor disturbances can vary greatly, larger scale physical and pollutant disturbances may have a broader scale effect. Castilla (1996) discusses the ecological impact of the El Salvador untreated copper mine tailings on intertidal communities around a dumping site in northern Chile between 1975 and 1990. Changes in ecology were monitored in polluted and unpolluted sites during this period. Comparisons showed a complete absence of all littoral species in the polluted site, with *Enteromorpha compressa* dominating the rocky substrate in their absence. This conveys the susceptibility of floral and faunal species to the large scale physical and chemical disturbance created by industrial pollution.

Perhaps more spatially relevant to this investigation is the study carried out by Hyslop et al. (1997). When carrying out an ecological survey on rocky shorelines prior to remediation on the County Durham coastline, the presence of colliery spoil was shown to have implications in lowering the species diversity of macroalgae compared with unpolluted sites. However, unlike the Castilla (1996) study, the presence of mine waste material significantly increased the diversity of faunal communities in some instances. This occurrence may be a product of the mine waste material being of boulder size, and therefore providing a surface on which intertidal communities can inhabit, particularly as species diversity was reduced on typically sandy beaches with mine waste present.

Intertidal communities are clearly fragile, yet unpredictable and are sensitive to small variations in physical and chemical disturbance. The dumping of colliery spoil on the County Durham coastline was a particularly large disturbance on both fronts, yet the remediation work itself, with the remobilisation of large volumes of contaminated material, poses another disturbance event not yet investigated. Due to wide range of ecological niches which are apparent in intertidal communities, this section discusses the characteristics of the three bioindicators under study in this investigation.

3.2 *Mytilus edulis*

Figure 3.1 illustrates the internal structure of the blue mussel, *Mytilus edulis*.

Due to the ease with which these mussels can be kept alive in laboratory conditions, their relative abundance and their widespread distribution, they are well studied and are often used as bioindicators (e.g. Goldberg, 1975; Hueck, 1976). They are found on rock surfaces and in crevices occupying most of the intertidal range on the rocky shores of open coastlines, attaching to suitable substrata by byssal threads (see figure 3.1) (Brenner and Buck, 2010). They are filter feeders and with 80-100% efficiency, can remove particles down to $2-3$ μm from ingested water (Mohlenberg and Riisgard, 1979). Daly and Mathieson (1977) showed that zonation patterns of the common mussel could be limited in the lower regions of the intertidal range due to sand burial. This could be a particular problem in coastlines where large amounts

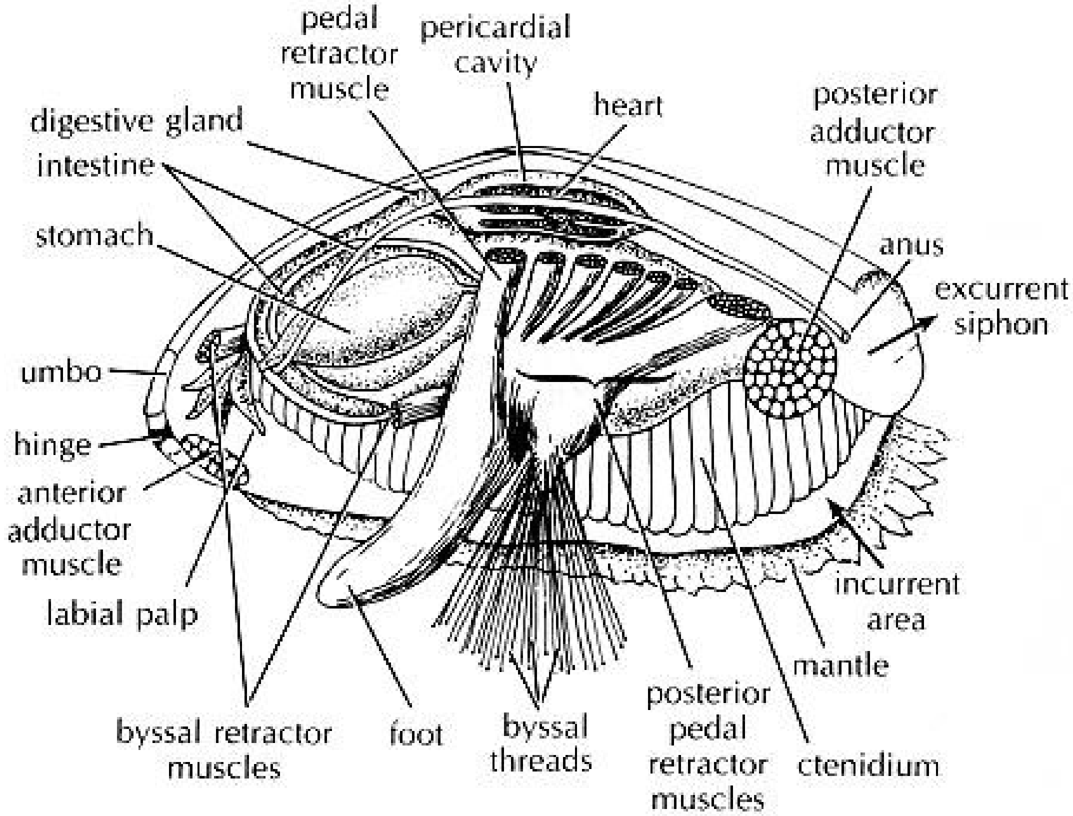

Figure 3.1: Internal structure of the blue mussel, *Mytilus edulis*. After Morton (2005)

of coal spoil have been dumped on shores normally predominated with larger rocks, giving a rough, discontinuous surface, the preference of the common mussel (Maas Geesteranus, 1942). Studies which use *Mytilus edulis* as a bioindicator tend to measure concentrations of heavy metals found in the byssal threads (Szefer et al., 1999), the soft tissue with byssal threads removed (Giusti et al., 1999), or digestive gland (Fitzpatrick P. J. et al., 1997), along with shell material. The life span of the species varies depending on local conditions and the degree of predation, although the majority of studies which consider the age of the specimen look at samples which are <10 years, perhaps due to the availability of a large enough sample (e.g. Sukhotin and Pörtner, 2001).

3.3 *Patella vulgata*

This gastropod is abundant on substrata which are firm enough to allow the attachment of the organism's foot muscle to rocks (Smith, 1992). The common limpet is abundant on rocky shores of all levels of wave exposure. They have a radula which aids the scraping of biofilm nutrients off rocks. The common limpet forages for its algal food supply when the tide covers it, travelling an average of 0.4 m and then returning to the home scar at least an hour before exposure caused by the outgoing tide (Hartnoll and Wright, 1977). The idea of the home scar makes the limpet well adapted for inhabiting exposed shorelines. When the organism finds a suitable habitat, it will grind down on the rock so that it fits perfectly on the surface, allowing only a small gap for water to enter to prevent drying out. This method of attaching to rocks provides protecting against winged predators. The other common predator is the dog whelk, which can emit shell dissolving acid onto its prey (Gabriel, 1981). As with mussels the life span of the species can vary drastically, from 4-5 years to nearing 15-17 years in peak conditions (Lewis and Bowman, 1975).

Numerous studies have been conducted using *Patella vulgata* as bioindicators of heavy metal pollution. For example, a study of the shell and soft tissue was conducted in monitoring the heavy metal contamination from a French nuclear fuel reprocessing plant (Miramand and Bentley, 1992). Other studies have focused on contamination levels of the radula, or feeding muscle of the limpet (Davies et al., 2005).

3.4 *Fucus vesiculosus*

Fucus vesiculosus, commonly known as bladderwrack due to the prominent air sacks present on the plant's fronds, is a species of brown algae which is tolerant of exposed shorelines and freshwater. The species spreads rapidly after colonisation and lives for around 3-5 years (FSC, 2008).

Species of brown algae such as *Fucus vesiculosus* have been used in numerous studies to estimate trace metal availability in coastal waters around the Northern Hemisphere (e.g. Rainbow P.S., 1995; Rainbow and Phillips, 1993). *Fucus vesiculosus* is the ideal choice for this study as it is abundant at all study sites along the County Durham coastline, is the species used by the past study for comparison, and being a brown algae, readily accumulates metals (Roberts et al., 2008) due to their high affinity to the large amounts of sulphated polysaccharides in the organism's cell walls (Davis et al., 2003). Indeed transplant experiments from unpolluted sites to estuaries affected by mine waste have shown in the past a significant uptake of metals by *Fucus vesiculosus* (Ho, 1984). The use of a hardy, early coloniser such as this is useful at locations like the County Durham coastline, where up until recently some sites where completely devoid of littoral ecology due to the unfavourable conditions produced by the coal spoil, both physically and chemically. Given the documented sensitivity of the species to metal fluctuations in the environment, and the relatively short life span of 3-5 years, it makes it the ideal species for a comparison study over a 10 year time scale, either side of remediation.

Figure 3.2: *Fucus vesiculosus* (bladderwrack), (FSC, 2008)

3.5 *Nucella lapillus*

Although only mentioned briefly within this study, it is worth noting the role of the dog whelk in the ecosystem under investigation, particularly when going on to discuss the bioaccumulation of heavy metals. Dog whelks are gregarious, bare a largely conical shell and are predators of species including both mussels and limpets, drilling through their shells and using digestive enzymes to allow feeding (Rovero et al., 1999). The species is also widely used as an indicator of coastal pollution, particularly tributyltin (TBT), where imposex is exhibited when the female of the species is exposed (Gibbs et al., 1987). The life span of the species is thought to be around 6 years (Feare, 1970).

3.6 Heavy Metal Bioaccumulation

Bioaccumulation of heavy metals in marine organisms occurs through the uptake of metal complexes across membranes, and into the tissues of the organism. The level of bioaccumulation is dependent on a number of factors, including the concentration and the physical form of the metal, as well as its bioavailability to the organism which can differ greatly between species (Neff, 2002). Indeed, the physical form of the chemical not only influences its method and rate of uptake, but also the level of harm it can do to the tissue of the organism (Nelson and Donkin, 1985; Waldichuk, 1985), and its potential rate of biomagnification up the food web. The most bioavailable form of most metals is thought to be that of free ions and aquo ions, e.g. M[OH]2 and M[OH-] (Cowan et al., 1984; Newman and Jagoe, 1994). While at normal levels marine organisms regulate these often essential micronutrients between a narrow range in soft tissue, this is not always possible when concentrations in food and water reach high, nearly lethal levels (Amiard et al., 1987). In bioindicators, metals such as Zn and Fe bioaccumulate due to their biological significance (Jothinayagi and Anbazhagan, 2009), however, toxic metals such as Pb and Cd can accumulate due to the inability of the organism to efficiently process and remove the contaminant (Regoli and Orlando, 1994). As the level of excretion of a number of metal complexes (e.g. Pb) is often much slower than its uptake (Regoli and Orlando, 1994), marine organisms can be very useful for monitoring coastal recovery from heavy metal contamination.

There is an additional complexity that in most marine molluscs, the level of metals found in the shell and tissue material can differ greatly. Numerous theories exist to try and explain this, including the use of the shell material as a matrix for storing toxic contaminants which are unaffected by soft tissue detoxification mechanisms (Walsh et al., 1995), and the differential concentrations being caused by the different physiological roles of the metals (Huanxin et al., 2000). Overall, marine molluscs can be useful bioindicators of heavy metal pollution but we have to be careful when conducting studies and comparing results due the variations in uptake and excretion between species, and shell and tissue.

The expected bioaccumulation of metals in the current study is illustrated in figure 3.3, with metals accumulating through the microfilm or seaweed as a primary producer (represented in this study by bladderwrack), through the limpets (grazers) and mussels (detritus feeders), and finally in the dog whelks as the predator.

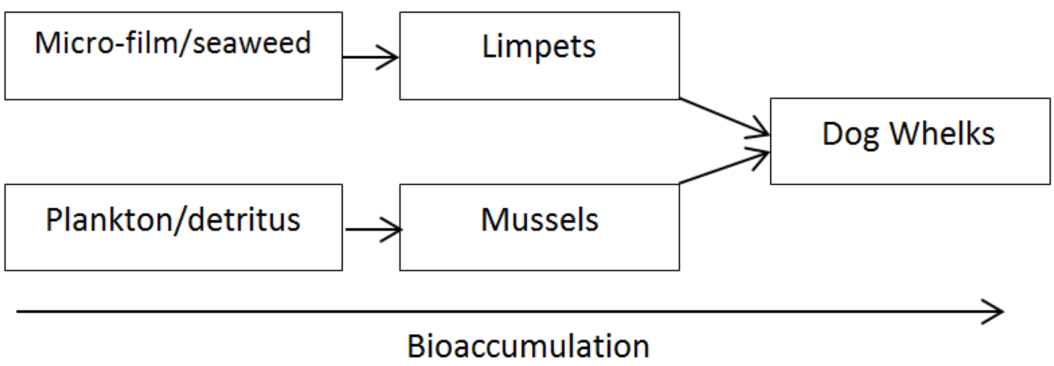

Figure 3.3: Predicted bioaccumulation of metals up the food chain

Chapter 4

Sample Preparation & Analytical Techniques

This chapter discusses the techniques used in this study to produce comparable data to that collected by Giusti et al. (1999) and Giusti (2001). Although the use of different techniques in the preparation and analysis of the samples was restricted by the desire to produce comparable results, it is worth acknowledging other possible methods utilised in the literature. By conducting appropriate pilot studies, and discussing their advantages and disadvantages, potential methods for future investigations have been identified.

4.1 Digestion Techniques

The method of sample preparation used by Giusti et al. (1999) and Giusti (2001) is an open, hot plate aqua-regia digest in glass beakers. This has been repeated in the current investigation to allow result comparison but pilot studies suggested that it is not the most efficient digestion technique. Initial observation highlighted issues with inconsistent heating across the hotplate, remedied by careful monitoring, while some consideration was given to the potential for material to effervesce during the reaction due to the open nature of the procedure. Despite these concerns, the literature suggests that the alternative, a closed microwave digest, produces little advantage in terms of chemical yield. Indeed, Afridi et al. (2006) report the recovery of heavy metals in microwave digests to be 96-98% of that achieved using a hot plate digest when analysing biological tissue samples. In addition, a study which compared aqua-regia hotplate and microwave digestion techniques on soil samples and standard reference materials found that precision and accuracy was similar using both methods. However, the ability of the microwave digest to dissolute Al, Ba and K, elements which are largely found bound to silicates, was found to be greater than the open technique (Chen and Ma, 2001). Although this would be worth considering in a study which looked to analyse beach sediments, these elements are not being considered in this organic study. One additional consideration was the relative success of an aqua regia digest of the materials within the investigation, compared to other methods which use Hydrofluoric acid, or a mixture of the two techniques. Although hydrofluoric acid is considered to be a weak acid, due to its lower dissociation constant than stronger acids, it is highly corrosive (Tam and Wong, 2000). Aqua regia digest of pilot studies using shell material showed near complete digestion, unsurprising considering that the calcium carbonate shell reacts strongly with acids. Furthermore, the removal of organics from the pilot study bladderwrack samples by ashing appeared to aid the digestion, greatly reducing the volume of material per glass vessel, and preventing a solidifying of material in the base of beakers. The pilot digestion of faunal tissue materials is more of an issue, given that the lack of ashing meant there was a lot of organic material in the samples. Although this was the method required to produce comparable data for this investigation, a future study could include hydrogen peroxide to aid the oxidation of the organic material (Hoenig and de Kersabiec, 1996).

4.2 Analysis Techniques

Three techniques of metal analysis were considered when constructing this study: atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF) spectroscopy and inductively coupled plasma-mass spectroscopy (ICP-MS). Each method has advantages and disadvantages in terms of running cost, sample preparation and resolution of detected elements.

4.2.1 X-ray fluorescence (XRF)

XRF is a technique commonly used to determine contaminant levels of coastal and estuarine sediments (e.g. Ackermann et al., 1983; Araujo et al., 1988; Middleton and Grant, 1990). The method involves drying and homogenising samples to a fine powder, mixing with wax, and forming a small pellet under high pressure. The pellet is subsequently illuminated by an intense X-ray beam. The sample then emits X-rays across a spectrum of wavelengths based on the molecular structure of the sample, allowing the contents to be identified (Wirth and Barth, 2011). This method is relatively robust, cheap and produces fast results, and does not require a digestion in sample preparation. It also has the advantage of analysing quite large sample masses (˜5g) allowing the analysis of relatively large homogenised samples which is particularly useful when using a small sampling technique to make assertions over a wider coastal area. The pilot study showed that the faunal shell material in particular would lend itself to this form of analysis.

4.2.2 Atomic Absorption Spectroscopy (AAS)

Flame AAS uses an air/acetylene flame to evaporate the prepared solvent, dissociating a sample into its component atoms. To do this, sample is typically drawn up through a nebulizer to the flame, meaning the material has to be a completely clear solution. Light from a series of cathode lamps (based on the elements under investigation) is allowed to pass through this cloud of atoms. The amount of light which is absorbed by the atoms under investigation is measured, and used to calculate its concentration in the sample (Thermo Elemental, 2001). This technique is more expensive than the XRF method and requires a prior digest to obtain the sample in the form of a solution. Despite this, it is widely used to analyse heavy metal concentrations in ecological samples (e.g. Amiard et al., 1987; Giusti et al., 1999; Giusti, 2001; Vlahogianni et al., 2007). The advantages of this technique include its robust interface, speed of analysis and ease of use, although detection limits are moderate when compared to the high resolution of the ICP-MS analysis.

4.2.3 Inductively coupled plasma-mass spectroscopy (ICP-MS)

The ICP works on a similar premise to the AAS as it analyses a digest of the material under investigation, but there are some notable differences which produce a higher resolution analysis of elements in a sample. Rather than an air/acetylene flame, the ICP uses a plasma source to dissociate the digested sample material into atom or ion form. These ions are removed from the plasma and, unlike the AAS where light emission is measured, the particles themselves are detected. Elements are separated and detected based on their atomic mass to charge ratio in the mass spectrometer (Thermo Elemental, 2001)

Based on the specification of the machine available in the department, much smaller sample sizes (˜0.5g) are required than either XRF or AAS (˜3g) due to samples being limited to <0.2% dissolved solids. Although this is seemingly beneficial, especially considering the lower detection limits which are achieved with this technique, it may not be ideal when planning to analyse large homogenised samples due to the need to include a large number of repeat samples. An additional possible issue recognised when analysing pilot samples by AAS is the large content of sodium in the sample material. Due to the intricate nature of the ICP-MS machinery, the production of a solid sodium based material when the solution is heated could produce interferences, or worse still, block the machinery. An interesting feature of the ICP-MS technique is the presence of a micro-drill, which can be used to analyse small sections of shell material from a single organism. As Toland et al. (2000) note, this Laser Ablation-ICP-MS is a useful method of extracting and analysing material within yearly growth bands, applicable to both mussels and limpets. By using this technique, short term elemental signals can be measured which would be lost when homogenising and digesting material for analysis in solution.

Overall, ICP-MS is a technique which is very expensive when compared to either AAS or XRF in both start-up and running costs, but for that, excellent detection levels with few interferences are available to the user.

4.3 Summary

To summarise, the techniques used in this investigation reflect those used by Giusti et al. (1999) and Giusti (2001). Although this was a constraint, the information suggests that some of the more modern techniques may be less favourable for such an investigation, exemplified by the use of the more robust techniques in the literature. Should this investigation be conducted again, without the aim of producing comparable data to previous studies, the use of microwave digestion techniques would be investigated due to greater efficiency and perhaps a more complete digest. Secondly, the LA-ICP-MS technique would be considered for the analysis of seasonal variations in metal contamination within solid shell samples.

Chapter 5

Introduction to Research

The following two chapters contain the research carried out for this thesis. The studies are presented in the style of two articles prepared for submission to academic journals. The research has been split across two papers because the interpretations of the different data sets have different environmental implications due to the different ecological niches and trophic levels of the bioindicators used.

The blue mussel (*Mytilus edulis*) has already been identified as a filter feeder which lives attached to rocks by byssal threads. Based on this habitat and feeding process, a hypothesis could be drawn which would suggest that heavy metal contamination of this species within collected samples would have decreased post remediation, due to a reduced loading of contaminated sediment available on the beaches. This may apply more to metals which are largely found bound to sediment particles, and not in soluble oxidised ionic form such as iron and manganese. Unlike the blue mussel, the common limpet (*Patella vulgata*) feeds on algal film attached to large boulders near the home scar. As a result it is less influenced by sediment based pollution than the blue mussel. Consequently a second hypothesis may be that heavy metal pollution of limpets will be lower than that of mussels should the coastline be strongly influenced by the remobilisation of contaminated sediment. These two indicators are used in the first of the two studies. This paper aims to draw comparisons between mussel data collected either side of the regeneration project, with limpet samples included to conduct the species comparison, and provide indicative data for areas where mussel populations are too low to sample.

The brown seaweed (*Fucus vesiculosus*) is a primary producer and has been shown as a good indicator of water quality. The second study uses samples of this species to consider the degree of soluble heavy metal pollution which exists along many of the same coastal sites as the first study, including areas adjacent to the treated minewater pumping sites discussed in chapter 1. Should this effluent be having an adverse effect on the coastal habitat ecosystem, the use of algae, where growth rates (and therefore a monitoring timescale) can be estimated (e.g. Bryan and Hummerstone, 1973), is a suitable method of investigation and is the focus of the second study. This is of particular importance as an additional site of minewater treatment has been opened since this data was collected (Whitburn January 2011), so any negative effects observed could be increasing should they be a result of this process. Aside from the monitoring of water based metal pollutants, the addition of seaweed to this investigation means species across trophic levels have been collected, and therefore the implications of heavy metal bioaccumulation can be considered.

All of the data for this study were collected in the winter of 2010-2011, 14 years since the data collected in the studies prior to remediation, and 8 years since the end of the Turning the Tide remediation project.

Chapter 6

Heavy metal contamination in *Mytilus edulis* and *Patella vulgata* between the estuaries of the River Wear and River Tees, UK.

6.1 Abstract

The north east coastline of England has been heavily influenced by coal mining and input from estuary based industry throughout the 20th century. Pollutant levels and ecological impacts in the area were monitored in various studies during the decline of these mining sites, yet little research has been carried out since the 10 million Turning the Tide Project which regenerated coastal zones affected by coal spoil dumping. This study determines concentrations of Fe, Mn, Cu, Zn, Ni, Pb, Cr and Cd in the shell and soft tissue of the mussel (Mytilus edulis) and common limpet (Patella vulgata), collected since the end of remediation. Comparable methods are used to a similar study carried out prior to remediation (Giusti et al., 1999), allowing comparison of individual values and spatial trends. An overall decrease in total metal pollution is observed however significant increases in Fe and Mn are present in mussel tissue, with average Fe values reaching 8293 mg kg^{-1} at Blackhall Rocks. Similarly high average values of Fe (8662 mg kg^{-1}) in limpet tissue suggest an aqueous source of pollution. We tentatively link high levels of Fe in tissue material to treated minewater discharge along the Durham coast, a potential source of pollution which was absent at the time of the Giusti et al. study.

6.2 Introduction

The degradation of the north-east coast of England through the dumping of colliery spoil over the past 200 years has been subject to a number of studies (e.g. Norton, 1985; Ellis and Hoover, 1990; Hyslop et al., 1997; Giusti et al., 1999; Giusti, 2001). Estimates suggest that millions of tonnes of colliery waste were dumped annually in these coastal locations, peaking in the early 1980s with values reaching 2.5 million tonnes per annum (Norton, 1985; Wilkinson and McCay, 1998). Although the last coastal mine at Easington closed in 1993 (Rodgers and Proudfoot, 1999), the anthropogenically induced chemical and structural legacy remained (Humphries, 1996).

The presence of colliery spoil on the beaches has served to limit the biodiversity of the coastline. Habitat disturbance caused by the modification of shoreline topography and an increase in suspended solids (Barnes and Frid, 1999; Rodgers and Proudfoot, 1999), is manifested in surveys suggesting coastline algal species are limited to between 10 and 60, compared to the national coastal average of 90 species (Durham Heritage Coast, 2010). Ellis and Hoover (1990) suggest that small scale benthic faunal population extinctions can be attributed to sediment instability as a result of mine waste deposition, with added influence from seabed smothering and increased water turbidity (Hyslop et al., 1997). After final mine closure, Giusti et al. (1999) note that heavy metal content in Mytilus edulis was slightly above those from other sites in the UK, while sediment samples contain significant levels of heavy metal contamination 4 years on from the cessation of dumping (Giusti, 2001).

After final mine closure in 1993, a significant effort was made to transform the County Durham coastline to an area of conservation rather than exploitation with the Turning the Tide regeneration programme, which spanned 5 years between 1997 and 2002, being the focal point. This series of projects received approximately 10 million of funding to undertake remedial work, regenerating beaches and coastal habitats, stretching 17 km along the County Durham coastline. One aspect of this series of projects was the reclamation of 80 ha of land through the removal of 1.3 million tonnes of coal spoil from the beaches at Horden and Easington. This material was moved to cliff top heaps, spread out, and capped before covering with soil to allow habitat creation and open public space (Scarborough Borough Council, 2006). This process served to significantly reduce estimates of the time taken to completely erode spoil beaches, to approximately 20 years, from initial calculations of between 52 and 210 years, dependent on erosion rates (Durham Coast Management Plan, 1993). Dawdon beach, which provided a dumping site for Seaham, Vane Tempest and Dawdon collieries, was left to erode naturally.

Since the end of Turning the Tide, further measures have been taken to protect the east Durham magnesian limestone aquifer. This was being threatened with contamination from rising levels of mine water, which is now being treated on the coastline and pumped into the sea at Dawdon and Horden (Environment Agency, 2011b). The aquifer provides 20% of local drinking water and so had to be protected from the high levels of iron, but also chlorides with concentrations reaching 40,000 mg/l. The treated mine water, with concentrations of iron below 1 mg/l, is pumped into the sea at the two sites at a rate of 35-70 litres per second (Environment Agency, 2011b). An additional pumping site has been trialled at Whitburn, north of the Heritage Coast region.

Since the industrial decline and remediation work, County Durham has been awarded 14 km of Heritage Coast designated land (Durham Heritage Coast, 2005) and is recognised locally, nationally, and internationally through statutory designations for its geological and nature conservation value (Natural England, 2011).

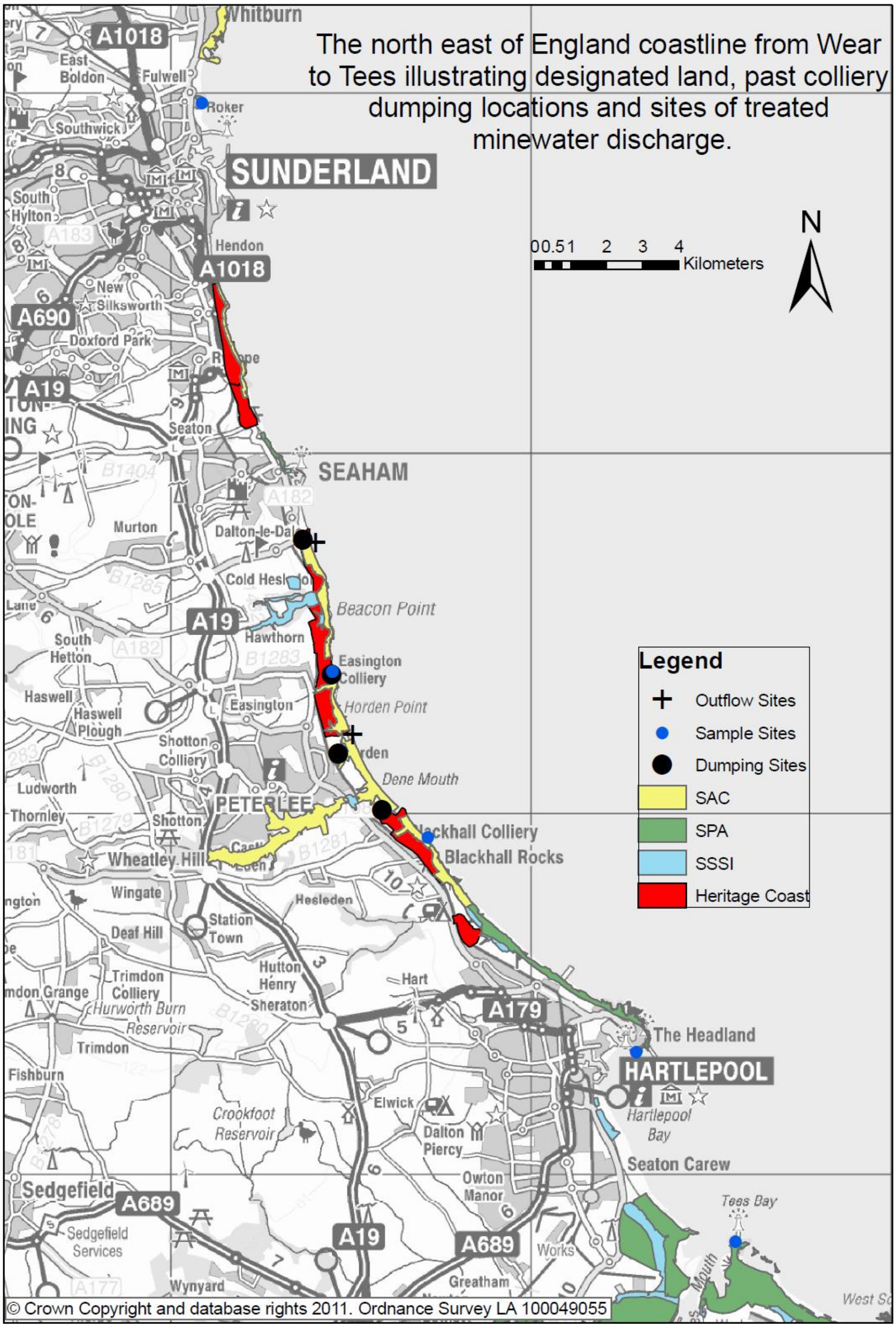

Figure 6.1: A GIS produced map with overlapping layers of designated land, study sites and current treated minewater pumping sites at Dawdon and Horden. The base layer is Heritage Coast, then SSSIs, SPAs, and SACs. The four former coastal dumping sites are included to help illustrate the transformation of land use from polluting heavy industry to conservation.

Figure 6.1 shows designated Sites of Special Scientific Interest (SSSIs), Special Areas of Conservation (SACs) and Special Protection Areas (SPAs), along with the four past colliery dumping sites, current study sites, and locations of treated minewater outflow. Of particular relevance to studies of beach contamination, are the SPAs of the foreshores to the extreme north and south of the Heritage Coast region. Here, Ramsar site designation has been awarded for the important coastal habitats, specifically for overwintering seabirds such as purple sandpiper and little tern which are in nationally significant numbers at the location (Natural England, 2011). Grasslands associated with the underlying magnesian limestone geology in the area make up 92% of Britain's total area designated as an SSSI and contribute to a wider National Nature Reserve (Natural England, 2011).

Despite previous interest in the anthropogenic impact of the coastal ecosystem at study areas spanning this coastal zone, few have assessed the impact of the regeneration work carried out by the Turning the Tide Partnership, and monitored the apparent recovery which has taken place. The study carried out by Giusti (2001) was a landmark in the research of the chemical record of the coastal coal mining industry in County Durham in terms of its content and timing, yet it predates the removal of spoil in the region. The investigation found that samples of Mytilus edulis accumulated elevated levels of metals between the Wear and Tees estuary, despite the cessation of mining in the area. The study also showed that these contamination levels all met 1987 UK guidelines for metals in shellfish, apart from Cu, which exceeded the levels. The study is unique as it is the only one which measured the heavy metal content in faunal species in several locations along the north east coast after final mine closure and prior to remediation. Despite this, it is evident that a great degree of change has occurred in the physical form of the coastline, and so, the Giusti et al. study is now out of date. The aim of the current investigation is to provide an up to date assessment of heavy metal contamination in Mytilus edulis. This provides a post-remediation study, allowing a detailed comparison with the past data to highlight recent chemical and ecological change resulting from the regeneration work, while demonstrating the areas where further investigation is required.

In addition we consider the effects on those areas occupied by sites of industry on the Tees estuary that are becoming more diverse habitats for important wildlife (e.g. Evans et al., 1998). The partial decline of industry in the River Tees is similar to that of industry which affected the River Wear, such as the lead, zinc, cadmium and copper mining of the North Pennine Orefield, an area which was once the UK's leading producer of lead and zinc (Dunham, 1990). Despite this and subsequent remediation efforts, Shepherd et al. (2009) highlight the importance of continued monitoring as fine grained river sediments contain up to 600 mg kg^{-1} of lead, illustrating present transportation of pollutants from source, and thus an industrial legacy of environmental pollution. The discharge of these sediments into the North Sea may have repercussions in heavy metal concentrations along the coast.

6.3 Methodology

6.3.1 Ecological Consideration

This study used the common limpet Patella vulgata as a bioindicator in addition to the mussel, Mytilus edulis, used by Giusti et al. (1999). Limpets are gastropods which are known to consistently migrate and forage short distances for food, normally lichen (Little et al., 1988) and microalgae (Hill and Hawkins, 1991). Conversely, mussels are filter or suspension feeders, straining incurrent water for plankton and other small fauna (Hawkins et al., 1996). Mohlenberg and Riisgard (1979) suggest that this filtering process can achieve 80-100% efficiency, removing particles down to 2-3 μm. This potentially creates a bias in results from mussels to suspended particles rather than bioavailable dissolved ions. Daly and Mathieson (1977) showed that zonation patterns of the common mussel could also be limited in the lower regions of the intertidal range due to sand burial. This could be a particular problem in coastlines where large amounts of coal spoil have been dumped on shores normally predominated by larger rocks, giving a rough, discontinuous surface, shown to be the preference of the common mussel (Maas Geesteranus, 1942).

6.3.2 Legislative Values

The Giusti et al. (1999) study showed that heavy metal concentrations were similar to, or in the case of copper, exceeded national and international guidelines for shellfish. As a result, these will be considered again as an additional indicator of the health of the coastline. Guideline values are shown in table 6.1.

mg kg^{-1}	1987 UK Regional Water Authorities (NRA 1994)	Australian Legal Requirements (NHMRC 1987)	Spanish legislation (BOE 1991)	Lead in Food Regulations (GB Parliament 1979)	Ministry of Food (1953)	MAFF (1956)	Joint Monitoring Programme- Oslo & Paris (CEFAS 1997)
Pb	20	-	25	50	-	-	-
Zn	450	750	-	-	250*	-	-
Cu	16	350	100	-	-	100*	-
Cd	10	10	5	-	-	-	>5**
Cr	8	-	-	-	-	-	-

Table 6.1: National and international guidelines/limits for metal contamination of shellfish. *Where limits may be exceeded due to high background levels. **An upper level guideline. All concentrations are for the dry weight of tissue.

6.3.3 Sampling & Analysis

The relative uptake of heavy metals by both indicator species varies throughout the year, peaking in winter and decreasing through to summer for the majority of metals (e.g. Bourgin, 1990; Miramand and Bentley, 1992; Regoli, 1998). Field data collection took place during December 2009, to capture the period of maximum concentrations and to be consistent with the timing of data collection carried out by Giusti et al. (1999).

For consistency with Giusti et al. (1999), all samples were collected from the mid to upper tidal range at each location. As mussels were not readily abundant at all locations, a single composite sample of 50-60 mussels was collected from across each site, helping to negate influences from variation of habitat. The same method was used to collect limpets, and samples were transported back to the laboratory in seawater from the site.

The need for an additional indicator was exemplified by the lack of sufficient mussels at Roker to provide an adequate sized sample without causing significant disturbance to the local population. As a result no mussels were collected here but limpets were readily available. In addition to the collection of samples from the 5 sites in the original study, limpets were collected from Easington, the site of final colliery closure. Again, mussel populations were too sparse for an adequate sized sample.

Giusti et al. (1999) suggest that the high levels of metals measured at Holy Island could be attributed to increasing vehicular traffic, agricultural run-off and sewage output, along with the weathering of the dolerite dyke. These heightened levels exclude its use as a control, and no samples were collected from this site.

6.3.4 Extraction & Measurement

The living samples were transferred to beakers and stored in seawater from the relevant site for 24 hours to allow depuration/cleansing (Bordin et al., 1992; Robinson et al., 1993; Donkin et al., 2003). Mussel samples for each location were separated into two shell length size groups, a 20-29 mm and a 40-50 mm category. Giusti et al. (1999) found no relationship between tissue concentration of Cr, Cd, Mn, Zn, Ni and Pb and body size, so the middle size category of 30-39 mm has been omitted from this study. These groups were then weighed and dissected by cutting the abductor muscle to separate shell and flesh. Excess water was allowed to drain and the byssal threads were removed as these are known to have raised values (Szefer et al., 1999). Limpet samples were treated in a similar way, except instead of separating by shell length, they were separated by approximate age into <4 years and >7 years. The average age of the limpets in each age group was determined by counting shell rings.

Additionally the soft tissue was sliced using a scalpel to increase surface area to aid drying.

All mussel and limpet samples were transferred to for oven drying at 105^{o}C for 48 hours and left to cool. All samples were then ball milled for 4 minutes at 200 rpm to ensure homogenisation. 5 g of shell and 3 g of soft tissue were weighed into 50 ml vessels along with five repeats. These were pre-digested with 15 ml of concentrated HNO_3, and left overnight. Samples were then refluxed in 5 ml an aqua regis mixture of 16 M HNO_3 and 15 ml of 12 M HCl. After refluxing for 1 hour the samples were allowed to cool and vacuum filtered through a 0.45 μm-membrane filter, with deionised water. The samples were then diluted to the 50 ml with deionised water.

The digested samples were analysed using the same method as Giusti et al. (1999) using the Varian SpectrAA 220FS Atomic Absorption Spectrometer. The metals analysed for were Fe, Mn, Zn, Cr, Cu, Pb, Ni and Cd. Ag has been omitted from this study due to the consistent low results observed in Giusti et al. (1999), which may be reflective of background levels. Standards of known concentrations of each metal were run through the machine prior to the analysis. The matrix effect was accounted for through the addition of some HCl and HNO_3 to the standards in the 3:1 ratio equivalent to that of aqua regia in the samples. For some elements with high concentrations, for example Fe, the 50 ml sample needed to be further diluted with deionised water before being analysed. Machine readings of each metal were expressed in mg kg^{-1} (dry weight).

As with Giusti et al. (1999), no systematic variation in contamination with size of mussel is observed. Thus, results plotted are a mean taken of both size groups. For reference, the results of a certified reference material run through this methodology are presented in table 6.2, while results for repeat shell and tissue samples are presented in table 6.3 to indicate precision.

Metal	IAEA-413 Reference	This Study	% Recovery
Fe	1370	1123.05	82
Mn	158	128.93	81.6
Zn	169	155.42	92
Cu	11	9.96	89.8
Pb	242	214.81	88.8
Ni	113	99.88	88.4
Cr	377	328.71	87.2
Cd	204	182.84	89.6

Table 6.2: Recovery of metals in certified reference material IAEA-413 (Algae). Reduced recovery of metals may reflect the differing method of extraction used for the reference material; while this study extracted using open aqua regia digestion only, the reference values are averages of different extraction techniques including closed vessel microwave digestion. Values expressed in mg kg^{-1}(dry weight).

	Sample mass	Fe	Zn	Cu	Mn	Pb	Ni	Cr	Cd
Shell repeat sample 1	3.05	2487.09	83.09	11.54	35.24	5.51	1.2	2.28	6.67
Shell repeat sample 2	3.09	2486.2	86.67	11.88	35.85	4.03	0.89	1.67	6.78
Shell repeat sample 3	3.03	2553.21	87.71	11.66	38.4	6.15	1.12	2.7	6.53
Shell repeat sample 4	3.04	2478.18	84.13	11.03	37.64	5.83	1.16	2.48	6.26
Shell repeat sample 5	3.04	2540.22	85.96	11.51	38.76	5.83	1.16	2.38	6.62
Standard Deviation		**34.93**	**1.88**	**0.31**	**1.56**	**0.83**	**0.12**	**0.39**	**0.2**
	Sample mass	Fe	Zn	Cu	Mn	Pb	Ni	Cr	Cd
Tissue repeat sample 1	5.08	20.99	Undetectable	6.35	9.29	Undetectable	0.05	7.32	Undetectable
Tissue repeat sample 2	5.09	19.8	0.54	6.34	11.01	Undetectable	Undetectable	7.36	0.01
Tissue repeat sample 3	5.03	26.25	0.22	6.38	8.68	Undetectable	Undetectable	7.21	Undetectable
Tissue repeat sample 4	5.05	36.89	0.17	6.23	9.41	Undetectable	Undetectable	7.08	Undetectable
Tissue repeat sample 5	5.04	56.49	0.64	6.52	11.94	Undetectable	0.05	7.48	0.03
Standard Deviation		**15.22**	**0.24**	**0.11**	**1.36**	**0**	**0**	**0.15**	**0.02**

Table 6.3: Repeat digestion and analysis of a single sample from the study, included as a reference for the precision of the investigation. Values expressed in mg kg^{-1} (dry weight).

6.4 Results

Tables 6.4 and 6.5 summarise metal concentration results.

These results are initially discussed in aggregated form prior to discussion of specific metal type and location variability. Total recorded metal concentrations are shown as a Metal Pollution Index (MPI) calculated for both past and present data sets (e.g. Usero et al., 1996, 1997; Giusti et al., 1999) using:

$$\text{MPI} = (\text{M1 x M2 x M3 x....Mn})^{1/n}$$

Where Mn is the concentration of metal n in mg kg^{-1} (dry weight). This was then used to compare the overall metal contamination at each site, and to assess trends down the coast.

Mussel Shell	**(mg kg^{-1}, dry wt)**	**Fe**	**Zn**	**Cu**	**Mn**	**Pb**	**Ni**	**Cr**	**Cd**	**Sample**
	Blackhall Rocks									
	20-29 mm	346	3.9	6.8	27.4	undetectable	0.08	6.7	undetectable	~45
	40-50 mm	121	2.1	6.5	16.5	undetectable	undetectable	6.8	undetectable	~45
	Middleton									
	20-29 mm	68	4.5	6.9	19.5	0.3	undetectable	6.7	undetectable	~45
	40-50 mm	105	3.5	6.8	17.2	undetectable	undetectable	6.7	undetectable	~45
	Bran Sands									
	20-29 mm	264	3.2	6.9	61	undetectable	undetectable	7.2	undetectable	~45
	40-50 mm	264	2.4	6.6	50.9	1.2	0.07	7	undetectable	~45
Mussel Tissue	**(mg kg^{-1}, dry wt)**	**Fe**	**Zn**	**Cu**	**Mn**	**Pb**	**Ni**	**Cr**	**Cd**	
	Blackhall Rocks									
	20-29 mm	11691	184.3	12.8	174.5	7.7	2.8	3.4	0.8	~45
	40-50 mm	4894	191.3	9.2	110.2	7.4	2.2	2.9	1.1	~45
	Middleton			9.2						
	20-29 mm	1461	148.1	7.9	72.1	9.2	1.2	2.7	0.5	~45
	40-50 mm	913	128.6	6.4	54.3	7.8	1	1.5	0.5	~45
	Bran Sands									
	20-29 mm	2479	156.8	8.9	80.9	16.9	1.7	4.6	0.6	~45
	40-50 mm	1946	197.9	7.8	58	20.4	1.5	4.7	0.8	~45

Table 6.4: Metal concentration results for the analysis of mussel shell and tissue material. Values expressed in mg kg^{-1} (dry weight).

Limpet Shell	**(mg kg^{-1}, dry wt)**	**Fe**	**Zn**	**Cu**	**Mn**	**Pb**	**Ni**	**Cr**	**Cd**	**Sample**
	Roker									
	<4 years	31.725	2.312	6.269	11.243	undetectable	0.014	6.769	undetectable	˜45
	>7 years	21.461	undetectable	6.106	8.331	undetectable	0.03	7.236	0.05	˜45
	Easington									
	<4 years	95.976	1.979	6.119	36.89	undetectable	undetectable	6.999	undetectable	˜45
	>7 years	48.573	1.738	6.366	24.551	undetectable	0.104	7.4	0.013	˜45
	Blackhall Rocks									
	<4 years	186.772	9.396	6.273	49.257	undetectable	0.06	6.919	0.064	˜45
	>7 years	106.394	5.973	6.266	29.834	undetectable	0.04	7.039	undetectable	˜45
	Middleton									
	<4 years	44.353	0.099	6.083	15.367	0.708	0.39	7.128	undetectable	˜45
	>7 years	20.994	undetectable	6.35	9.291	undetectable	0.051	7.317	undetectable	˜45
	Bran Sands									
	<4 years	46.469	1.776	6.197	21.156	undetectable	undetectable	6.841	undetectable	˜45
	>7 years	40.466	2.784	6.224	22.096	undetectable	undetectable	7.053	0.013	˜45
Limpet Tissue	**(mg kg^{-1}, dry wt)**	**Fe**	**Zn**	**Cu**	**Mn**	**Pb**	**Ni**	**Cr**	**Cd**	
	Roker									
	<4 years	3255.67	92.133	7.712	59.252	7.438	1.098	2.185	3.242	˜45
	>7 years	2447.667	89.145	6.971	37.566	6.71	0.997	2.204	6.6	˜45
	Easington									
	<4 years	5702.65	110.221	11.569	49.606	7.174	2.181	2.637	1.39	˜45
	>7 years	5203.237	130.602	12.349	34.384	7.141	1.729	1.742	2.725	˜45
	Blackhall Rocks									
	<4 years	10159.29	174.491	16.308	92.113	6.138	2.148	2.858	6.647	˜45
	>7 years	7165.556	149.67	13.615	89.285	7.536	1.829	2.902	7.343	˜45
	Middleton									
	<4 years	2803.415	97.75	9.304	39.54	6.801	1.432	2.43	2.888	˜45
	>7 years	2487.086	83.094	11.537	35.241	5.513	1.202	2.276	6.668	˜45
	Bran Sands									
	<4 years	4063.875	116.461	8.636	36.845	7.13	1.234	2.405	1.296	˜45
	>7 years	1791.429	94.128	10.512	33.346	5.285	0.871	1.801	2.081	˜45

Table 6.5: Metal concentration results for the analysis of limpet shell and tissue material. Values expressed in mg kg^{-1} (dry weight).

6.4.1 Shell Composition

Figure 6.2 shows the MPI for shell material at the five sites.

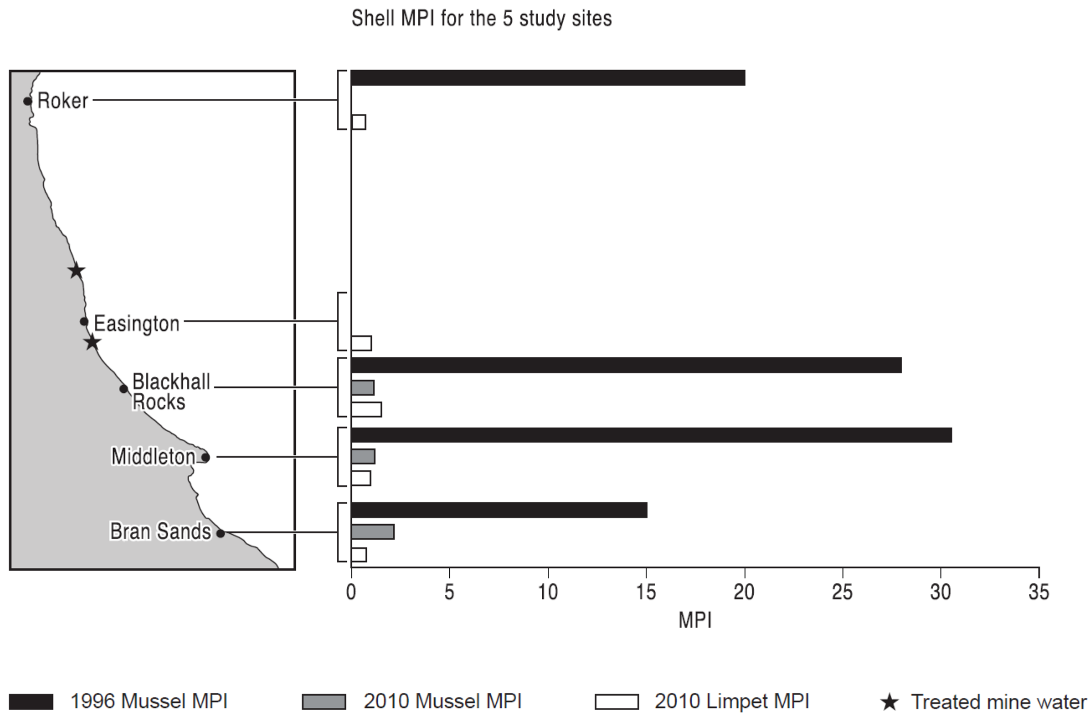

Figure 6.2: Metal pollution index (MPI) values calculated using concentrations for the 8 metals analysed used in the current study and corresponding data from Giusti et al. (1999) in shell material. Significantly reduced values are observed in mussel and limpet data compared with mussel data collected in 1996.

A significant decrease in MPI of the mussel shells is observed over time at all sites, the greatest being at Middleton (dropping from >30 to <2). The smallest decrease (down 12 points) is seen at Bran Sands. This site had the lowest MPI in 1999 and the highest in 2009. Limpet data shows a similarly low MPI to that of the mussels, although the spatial trend for highest and lowest MPI differs slightly; mussel shell MPI increase down the coast, whereas limpet shell MPI peaks at Blackhall Rocks. The limpet data for Roker and Easington is comparable in magnitude to that of the limpets in the three sites with mussels present. Sturesson (1976) and Sturesson (1978) identified, through laboratory experiments, that the sorption of heavy metals in shell material is much slower than in soft tissue, suggesting that this medium may be more useful in the monitoring of long term variations of metal contamination. This is a result of the low accretion rates in shell material. With an approximate 3-10 year lifespan for mussels at each study site, the shell samples analysed in 1996 represent an average record potentially dating back as far as 1986, prior to remediation and when dumping was still occurring. Samples analysed from

2010 represent an average record dating back to ~2000, this will largely cover the period after remediation although some individual mussels may date back to end of the Turning the Tide project, 7 years after final colliery closure.

6.4.2 Tissue Data

MPI calculated for tissue data (figure 6.3) is much more variable.

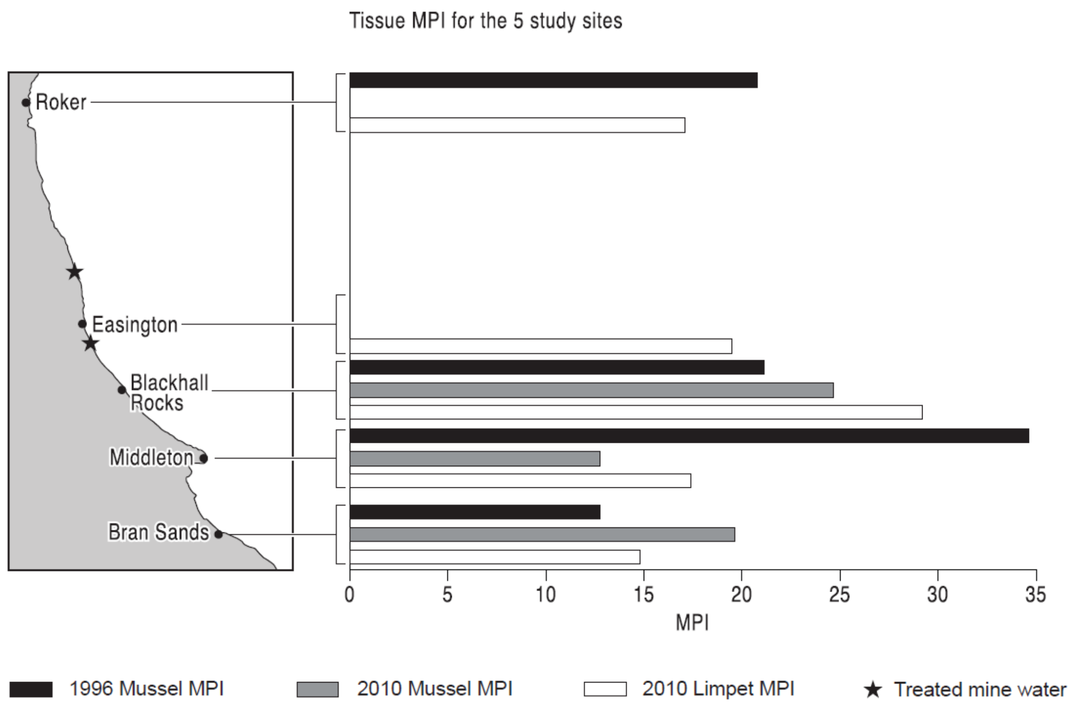

Figure 6.3: Metal pollution index (MPI) values calculated using concentrations for the 8 metals analysed in the current study and corresponding data from Giusti et al. (1999) in tissue material.

Values at all sites appear similar in magnitude to the pre-remediation data, with the MPI in mussels actually increasing at Blackhall Rocks (up 4 points) and Bran Sands (up 7 points). Middleton shows a clear decrease in MPI of the mussel tissue. However, the data is less clear at the other two sites. No mussel data for Roker and Easington were collected due to low population numbers. However, limpet data appears to have comparable values to that of mussels, with average values normally higher in the Limpet tissue. This may suggest tissue values at Roker represent a drop in metal pollution.

Where shell material is thought to be more indicative of a long term contamination, increasing number of studies monitoring heavy metal levels in transplanted bioindicators suggest that tissue material may reflect shorter term fluctuations.

Studies such as Regoli and Orlando (1994) find that, for example, 4565 mg kg^{-1} (dry weight) of Fe could be taken up by bivalves in two weeks after being transplanted from a clean to a polluted site. This concentration in turn reduced to below 1000 mg kg^{-1} after approximately one month of depuration. Although the study finds that different metals are excreted or detoxified at different rates, the different nature of metal contamination in shell and tissue material is useful for temporal analysis of contaminated sites. The tissue data collected in 1996 is unlikely to be reflective of pollution levels during spoil dumping, but during the period between final colliery closure (1993) and the start of remediation. This suggest that the short term availability of total metal contaminates appears to be similar prior to remediation and after the remediation.

6.4.3 Variations in Type and Location of Contaminants

Results for the individual metals Cr, Cd, Pb and Ni in soft tissue are shown by site in figure 6.4 and data for Zn, Cu, Fe and Mn are shown in figure 6.5.

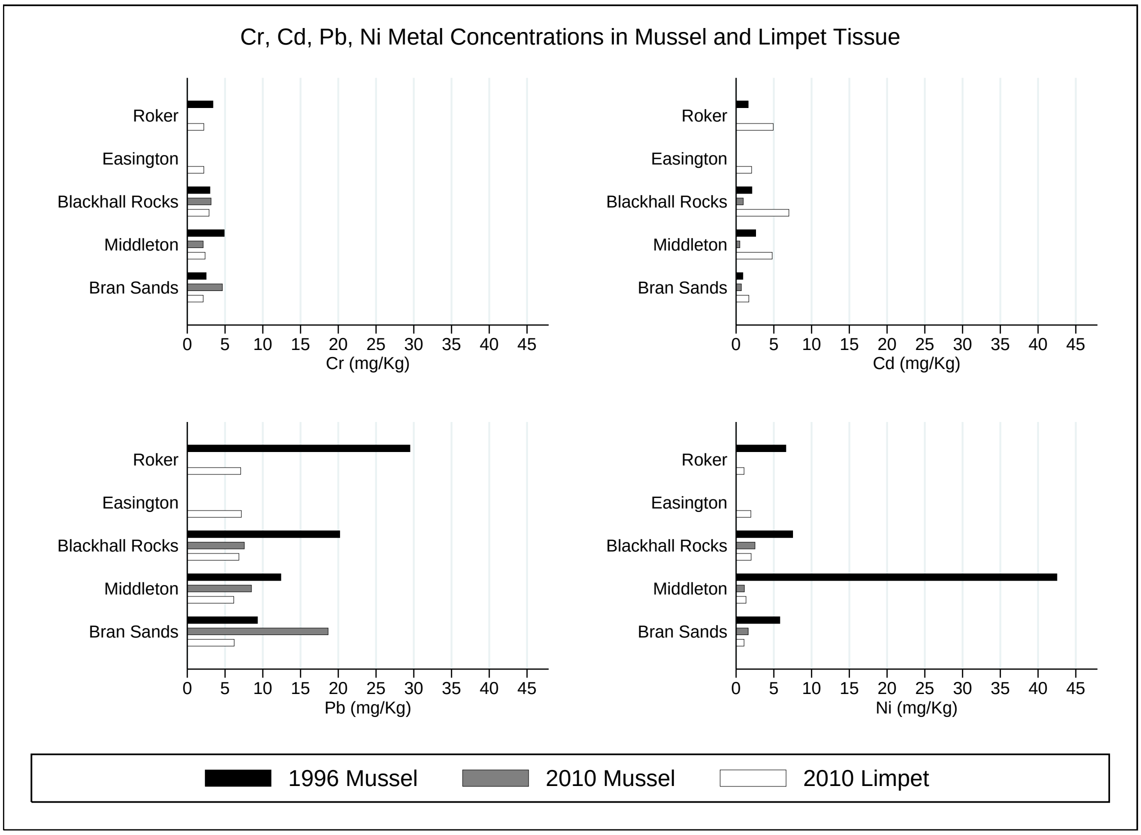

Figure 6.4: Metal concentration values for Cr, Cd, Pb and Ni in tissue material of mussels and limpets from the current study, and mussels from 1996 (Giusti et al. 1999). Values expressed in mg kg^{-1} (dry weight).

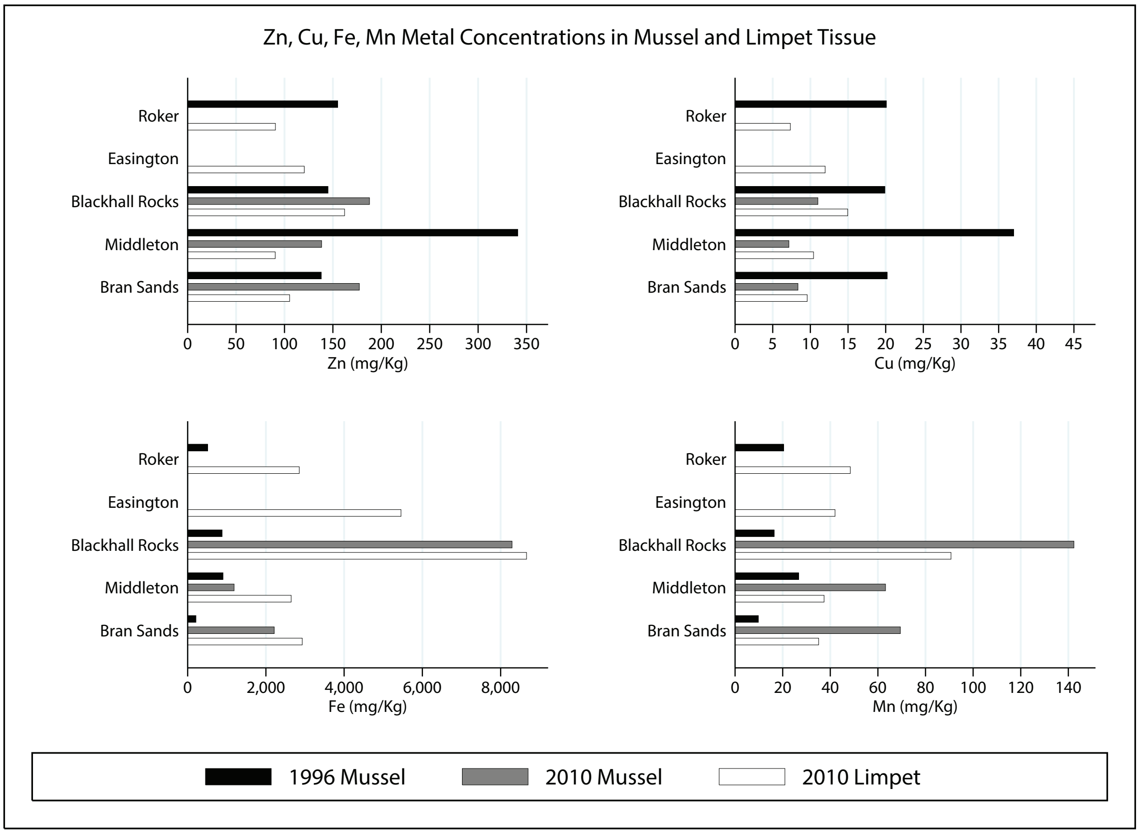

Figure 6.5: Metal concentration values for Zn, Cu, Fe and Mn in tissue material of mussels and limpets from the current study, and mussels from 1996 (Giusti et al. 1999). Values expressed in mg kg^{-1} (dry weight).

Concentrations for Cr and Cd in mussels from 2010 show negligible change (<2.5 mg kg^{-1}) from data collected in 1996. Such small differences at low detection levels are likely to fall within the error of both studies in terms of detection limits and levels of methodological uncertainty. Concentrations of Cr in limpets appear comparable with that of mussels, while concentrations of Cd in limpets are higher than in mussels at all sites, but still at low levels (<7.5 mg kg^{-1}). Pb contamination is shown to be negligible in limpets at all sites, while in mussels, concentrations at Bran Sands are higher in 2010 than in 1996 but lower elsewhere.

For the 1996 data, results for Ni appear similar down the coast aside from a clear peak at Middleton. Although Middleton was the site with the highest total MPI in 1996, these high values for Ni are not apparent in either limpet or mussel tissue in the 2010 data. Instead, Ni levels are negligible at all sites. In figure 6.5, a similar pattern is seen in Zn and Cu levels with an apparent peak at Middleton in 1996 being absent from the 2010 record. At present, Zn and Cu levels are lower at Middleton than Bran Sands and Blackhall Rocks, the site which currently appears to be the most polluted area.

Results for Fe and Mn in this study for both fauna, show an increase in values at all sites. Fe and Mn peak at Blackhall Rocks in the 2010 data, with Fe concentrations in the mussels at this site showing values ten times higher than in 1996. Similarly, concentrations of Mn in the mussel tissue at the same site are eight times larger. Middleton, the site with the highest concentration of both metals in 1996, while showing a small increase to 2010, now has the lowest concentration of Fe and Mn in this study.

6.4.4 Comparison with Legislative Values

Although Fe concentrations have shown up to tenfold increases in mussel tissue compared with 1996, the lack of Fe specific safe guideline levels in shellfish means that overall, the quoted national and international guidelines for each metal are all met. For consistency, although not as popular for consumption, the 2010 limpet data meets all guidelines apart from Cd at Blackhall Rocks. Here, the Joint Monitoring Programme- Oslo & Paris (CEFAS, 1997) guideline of 5 mg kg^{-1} is exceeded (7 mg kg^{-1}). Despite this, the overall results for mussel tissue show a marked improvement from 1996.

6.5 Discussion

The shell results of this investigation, compared to Giusti et al. (1999), suggest a significant long term (~15-20 year) decrease in coastal heavy metal contamination.

Both data sets are produced from samples in relatively stable external conditions. The 1996 study collected samples at a period where pollutant beach conditions were consolidated, after the cessation of spoil dumping and prior to its removal through remediation. While this remediation reduced significantly the total sedimentary reservoir of pollutants, in 2010 the samples were collected in a similarly consolidated state, 8 years after the end of remediation with no new polluted sediment input. The 1996 total MPI data for mussel shell suggests, on average, a greater level of pollution during the life span of the collected samples in this period, prior to remediation. Total MPI data calculated for the corresponding mussel shell samples in the 2010 study suggests a decrease in the contamination at all sites since the previous study. The removal of 1.3 million tonnes of coal spoil from the beaches as part of the Turning the Tide Project between 1997 and 2002 may have influenced these differing temporal records. Given that mussels are filter feeders, separating nutrients from sediment in suspension, they are heavily affected by pollutants adsorbed directly on sediments. As a result, the gradient in volume of spoil material between studies, created by remediation efforts, is the likely cause of the change in pollution record.

The comparison of total MPI from the 1996 mussel tissue and the 2010 investigation suggest a more variable record, with increases at some sites. Closer analysis of individual metal data however, shows either decreases or negligible levels of the toxic metals Ni, Cd, Pb and Cr at the majority of sites. This corresponds to metal concentration values found in the shell material. The high MPI values in tissue (this study) result from significant increases in Fe and Mn levels between 1996 and 2010. The high concentrations of both metals are present in limpet and mussel samples. These two species have very different ecological niches, with limpets living on hard substrates and feeding on algae that are known to be reflective of water quality and mussels being detrital feeders processing particulates through their gut before expelling indigestible sediment. This suggests that limpets are less affected by sediment pollution. The increases in pollutant levels in both species tissue despite a decrease in polluted sediment volume would support this argument, as would the decrease in corresponding shell contamination. As the shell contamination of Fe and Mn has decreased, the increases in tissue contamination of these metals suggest short term fluctuations in the source which are either smoothed in the shell record, or the result of more recent contamination. This degree of fluctuation is characteristic of metals in aqueous form, given the influence of tides, salinity, temperature and mobility on metal availability from marine water. Since remediation, there has also been an introduction of treated mine water and outfall into the sea at two points along the coast is a potential input of such aqueous metal sources. These process, implemented to protect the East Durham aquifer from groundwater contamination, pumps 35-70 litres of water per second into the sea at Horden (commenced 2004) and Dawdon (2009), see figure 6.1. Although treatment aims to restrict Fe levels in the output water to ¡1mg/l, Environment Agency monitoring of water content has recorded a number of instances at both sites where this is exceeded, and at an extreme, reaching 34 mg/l on the 10th of June 2011 at Dawdon (Environment Agency, 2011b). No monitoring data for Mn in the treated water is available. The degree of fluctuation and the volume of water which is pumped out at these sites is a potential cause of the pollution record in this study, given that both pumping sites lie between Roker and Blackhall Rocks, the most polluted site by Fe and Mn. The high values observed in the faunal data compared to the lower levels in minewater output can be explained by bioaccumulation. Wang et al. (1996) record accumulation of 6 trace metals in Mytilus edulis, while Regoli and Orlando (1994) record rates of uptake and excretion of Fe during transplant experiments. This excretion or detoxification during periods of reduced exposure to trace metals may explain the absence of peaks in Fe from the 2010 shell data. The fluctuation of Fe contamination levels from minewater could simulate the conditions of transplant experiments, resulting in the absence of high levels of Fe from the long term record. Guthrie et al. (1979) suggest that biomagnifications of metals through trophic levels is greater in attached species such as mussels, than for example, crabs. As a result further study in lower trophic levels such as algae, which are known to be good indicators of water quality (e.g. Phillips, 1970; Rainbow P.S., 1995), is recommended.

6.6 Conclusion

The long term heavy metal record of the County Durham coastline is shown to have decreased at the sites studied using the two bioindicators, mussels and limpets. The use of these two indicators from different habitats allows clear insight into the type and mobilisation of the contaminants. Increases in tissue contamination of Fe and Mn between 1996 and 2010, which is not reflected in shell material, suggest short term fluctuations are the source. As these high concentrations are also present in limpet tissue, the contamination is likely to be in aqueous form and subsequently, links are drawn to the pumping of treated minewater near the study sites. Further study is required to assess contamination of water on beaches and at these pumping sites. The use of seaweeds which are known to be good indicators of water quality would enable better spatial coverage and clear causal links to be drawn. Despite these findings, all guideline values are met for the toxicity of heavy metals within mussel tissue, showing an improvement on the 1996 study. These values are within the requirements for edibility.

Chapter 7

Monitoring the heavy metal contamination of the north east coast of England: a case study using the floral indicator, *Fucus vesiculosus.*

7.1 Abstract

Heavy metal data collected from the faunal indicators *Mytilus edulis* and *Patella vulgata* have suggested the long term heavy metal record of the coast has significantly decreased since remediation carried out by the Turning the Tide Partnership after the decline of the mining industry. Despite this, the short term tissue record from these samples suggests pronounced peaks in iron and manganese contamination. This study investigates whether this contamination could be from a primarily aqueous source by using the floral indicator *Fucus vesiculosus* to produce comparable data to a study carried out prior to remediation (Giusti, 2001). This study determines concentrations of Fe, Mn, Cu, Zn, Ni, Pb, Cr in the seaweed. The data confirms high values of Fe (9081 mg kg^{-1}) and Mn (1172 mg kg^{-1}), peaking at Horden. As a result, plausible links are made with minewater treatment facilities situated north of the most polluted sites, and the transportation and erosion of offshore mine waste material.

7.2 Introduction

Species of brown algae such as *Fucus vesiculosus* (or bladderwrack) have been used in numerous studies to estimate trace metal availability in coastal waters around the Northern Hemisphere (e.g. Forsberg et al., 1988; Rainbow P.S., 1995; Rainbow and Phillips, 1993). In particular, bladderwrack has been shown to be a sensitive indicator of contaminated coastlines, with transplant experiments between unpolluted and polluted sites observing significant uptake of pollutant metals (Ho, 1984). This high degree of uptake can be attributed to the metals high affinity to the large amounts of sulphated polysaccharides in the organism's cell walls (Davis et al., 2003). A resilient early colonizer such as bladderwrack, which is abundant in the UK and sensitive to environments with changing contamination levels, is a suitable choice for the monitoring investigation of a regenerated coastline such as County Durham, which was impacted heavily by the mining industry throughout the 20th century. Indeed, until 1993 and the closure of the final coastal colliery at Easington, the north-east coastline of England was a site of intense industrial activity, ranging from estuarine ship building and petrochemical activities, to the mining of coal seams which run out beneath the North Sea. Humphries (1996) suggests that in particular, the dumping of colliery waste directly onto the beaches at four coastal sites produced a chemical and structural legacy.

Despite a history of promoting resource exploitation over environmental stability, a five year remediation project entitled Turning the Tide commenced in 1997, tasked with aiding the return of the coastline to its natural state (Durham Heritage Coast, 2010). The remediation work carried out by the Turning the Tide Partnership included the removal of an estimated 1.3 million tonnes of coal spoil from the beaches at Horden and Easington (Scarborough Borough Council, 2006) and contributed to the designation of 14 km of Heritage Coast in County Durham (figure 7.1).

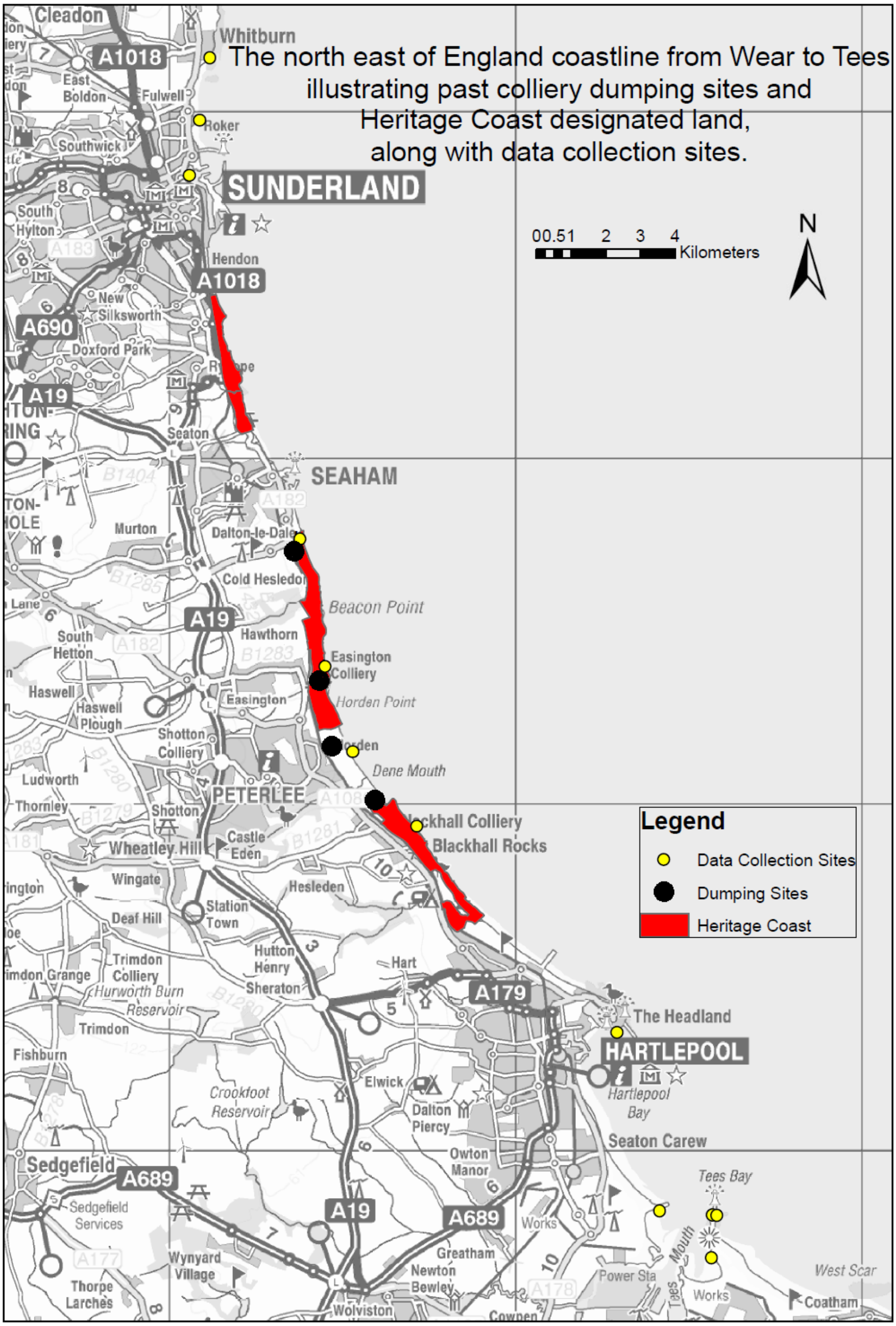

Figure 7.1: Map showing Heritage Coast designated land, former mine waste dumping sites, and *Fucus vesiculosus* sample collection sites.

This reduced the time expected for beaches to erode to their natural form to approximately 20 years (Durham Heritage Coast, 2010), from initial calculations of between 52 and 210 years, dependent on erosion rates (Durham Coast Management Plan, 1993). Since this remediation was carried out, further preventative measures have been taken by the Coal Authority (Parker, 2003) to intercept the contamination of the East Durham Aquifer by rising mine water in the disused shafts. This prompted the opening of treatment plants at Horden in 2004 and Dawdon in 2009 which would reduce the iron contamination of these waters from in the region of 160 mg/l to below a target of 1 mg/l (Coal Authority, 2007). These pumping stations are capable of returning treated water back to the North Sea at a rate of between 35 and 70 litres per second (Environment Agency, 2011b).

The aim of this study is to produce a dataset of heavy metal contamination levels in bladderwrack at a number of sites along the north east coast, providing comparable data to that produced by Giusti (2001). Justification for such a comparison, specifically relating to water quality rather than sediment or faunal contamination is threefold. The dumping of spoil material offshore during the height coastal mining is not something which could be easily addressed during remediation and the remobilisation and transport of this sediment has been previously cited as a possible source of contamination (Johnson and Frid, 1995). It is possible that contamination from this material could be manifested in elevated concentrations of heavy metals in water. Secondly, the bladderwrack samples in the Giusti (2001) study were collected in the winter of 1997, at the commencement of remediation. The production of corresponding data in this study would provide a means of comparing contamination across this physical transformation. The collection of samples reflective of water contamination is of particular significance as the removal of such large volumes of material would expose an increased amount of contaminated sediment to the action of the waves, potentially increasing the volume of soluble and suspended pollutants. Finally, since the Giusti (2001) study, treated minewater pumping has commenced. Current monitoring provides a means of establishing any impacts which this may be having on coastal heavy metal levels. Although the target iron concentration of 1 mg/l is low, the pumping of large volumes and occurrence of increased values in the effluent (as high as 34 mg/l (Environment Agency, 2011b)), suggests monitoring the possible impacts is valid, particularly as a new treatment site has recently been employed at Whitburn (January 2011).

Additionally, the collection of seaweed samples allows for the study of bioaccumulating metal contamination across trophic levels through comparison with previously collected *Mytilus edulis* (blue mussel) and *Patella vulgata* (common limpet) samples and an additional small sample of the carnivore *Nucella lapillus* (dog whelk). Bioaccumulation of heavy metals in marine organisms occurs through the uptake of metal complexes across membranes, and into the tissues of the organism. The level of bioaccumulation is dependent on a number of factors, including the concentration and the physical form of the metal, as well as its bioavailability to the organism which can differ greatly between species (Neff, 2002). Indeed, the physical form of the chemical not only influences its method and rate of uptake, but also the level of harm it can do to the tissue of the organism (e.g. Nelson and Donkin, 1985; Waldichuk, 1985), and its potential rate of biomagnification up the food web. In bioindicators, metals such as Zn and Fe bioaccumulate due to their biological significance (Jothinayagi and Anbazhagan, 2009), however, toxic metals such as Pb and Cd can accumulate due to the inability of the organism to efficiently process and remove the contaminant (Regoli and Orlando, 1994).

The present study presents a post remediation dataset of bladderwrack for comparison spatially and to previous data, while also examining the relationship to data collected from fauna in the food chain, including limpets, mussels and a preliminary samples of dog whelks.

7.3 Methodology

7.3.1 Sampling and Analysis

Miramand and Bentley (1992) show that heavy metal uptake by *Fucus* species varies throughout the year, peaking in winter and decreasing through the summer for the majority of metals. The degree of variation with season is shown to be inconsistent between metals, with Cr showing the least variation (<0.5 mg kg^{-1}), and Fe the most (>200 mg kg^{-1}). As a result, sample collection took place during December of 2010 to account for this seasonal variability and reflect the timing of data collection in Giusti (2001). The faunal samples with which metal concentrations in bladderwrack are compared were also collected in December, as similar patterns of seasonal variation are shown in limpet and mussel species (Bourgin, 1990; Miramand and Bentley, 1992; Regoli, 1998).

Samples were collected at twelve sites including Whitburn, Roker North Pier, Roker estuary, Dawdon, Easington, Horden, Blackhall Rocks, Middleton, North Gare and three sites at Bran Sands (figure 7.1). This differs from Giusti (2001) as the control of Holy Island has been omitted from this study due to heightened background levels of metals, thought to be a product of increased vehicular traffic and the erosion of a dolerite dyke (Giusti, 2001). Equally, the presence of the Giusti (2001) baseline data for comparison reduces the need for such a control. The number of sites at Bran Sands has been reduced from five to three, although the sites still range from estuary to coast. An additional site at Dawdon was used as this was a site heavily affected by colliery spoil dumping, and the only site where spoil heaps were allowed to erode naturally.

Acknowledging differing concentrations of metals through the plant, and recorded growth rates, Giusti (2001) collected the most recent 8-10 cm fronds of 20-30 randomly chosen plants to produce a single composite sample at each site. The use of the newest growth from each plant is significant as studies such as Forsberg et al. (1988) report normally lower metal concentrations than in older growth. Giusti (2001) also assumes this length of frond will provide an average metal concentration for a period of 3-5 months, with typical growth rates being recorded as 2-3 cm month^{-1} (Knight and Parke, 1950). For consistency with Giusti (2001), this 8-10 cm length of frond was collected and all samples were taken from the mid to upper tidal range at each location. As bladderwrack was abundant at all sites, the sample size was increased from 20-30 randomly chosen plants to 30-40, allowing for additional repeat aliquots to be analysed. Bladderwrack samples were cleaned in the field using seawater and transported to the laboratory in marine water from the site.

7.3.2 Extraction and measurement

Prior to digestion, seaweed was washed with deionised water and dried at 105°C for 48 hours. Samples were cooled and then weighed and ashed at 475°C, allowing for the calculation of the loss on ignition (LOI). From each sample, four 5g aliquots of ashed material were allowed to pre-digest with 5 ml of 16 M HNO_3 and 15 ml of 16 M HCl (a 20 ml aqua regia solution) in 50 ml beakers for 48 hours. Each sample was subsequently refluxed on a hot plate. The samples were gradually heated to 120°C, regulating the temperature when the reaction was getting too aggressive. The duration of the extraction was until the reaction appeared complete, but no longer than two hours (Giusti, pers. comm.). Subsequently, all samples were cooled and then diluted to 50 ml with deionised water.

The digested samples were analysed using the same method as Giusti (2001) using the Varian SpectrAA 220FS Atomic Absorption Spectrometer. The metals analysed for were Fe, Mn, Zn, Cr, Cu, Pb, Ni and Cd. Ag has been omitted from this study due to the consistent low results observed in Giusti et al. (1999), which may be reflective of background levels. Standards of known concentrations of each metal were run through the machine prior to the analysis. The matrix effect was accounted for through the addition of some HCl and HNO_3 to the standards in the 3:1 ratio equivalent to that of aqua regia in the samples. For some elements with high concentrations, for example Fe, the 50 ml sample needed to be further diluted with deionised water before being analysed. Machine readings of each metal were expressed in mg kg^{-1} (dry weight).

7.3.3 Faunal Samples

The results for the seaweed were compared to *Mytilus edulis* and *Patella vulgata* samples previously collected from some of these sites. A small sample of *Nucella lapillus* shells were also collected and analysed from Easington and Blackhall Rocks. These dog whelk samples were treated in the same way as the limpets.

Composite samples of 50-60 mussels were collected from Blackhall Rocks, Middleton and Bran Sands. Similar sized samples of limpet were collected from Roker Pier, Easington, Blackhall Rocks, Middleton and Bran Sands. The living samples were transferred to beakers and stored in seawater from the relevant site for 24 hours to allow depuration/cleansing (Bordin et al., 1992; Robinson et al., 1993; Donkin et al., 2003). Each species was separated into shell and tissue, removing the byssal threads of the mussels. The samples were dried at 105°C for 48hrs, ball milled to achieve homogeneity (4 minutes at 200 rpm), and then digested and analysed as for the seaweed.

For reference, the results of a certified reference material run through this methodology are presented in table 7.1.

Metal	IAEA-413 Reference	This Study	% Recovery
Fe	1370	1123.05	82
Mn	158	128.93	81.6
Zn	169	155.42	92
Cu	11	9.96	89.8
Pb	242	214.81	88.8
Ni	113	99.88	88.4
Cr	377	328.71	87.2
Cd	204	182.84	89.6

Table 7.1: Recovery of metals in certified reference material IAEA-413 (Algae). Reduced recovery of metals may reflect the differing method of extraction used for the reference material; while this study extracted using open aqua regia digestion only, the reference values are averages of different extraction techniques including closed vessel microwave digestion. Values expressed in mg kg^{-1}(dry weight).

7.4 Results

Table 7.2 is a summary of the raw data collected in the current investigation, including the % ash of seaweed material remaining after loss on ignition is calculated. The Bran Sands sites are number based on their proximity to the estuary. 1 signifies the site furthest inland in the estuary, whereas site 5 is the site on the coast. The table includes the data collected by Giusti (2001), and notes the change in values observed at each site. N/A represents a site where data was not collected in either this study or Giusti (2001).

Figure 7.2 is a preliminary look at the data in aggregated form, using the geometric mean of the heavy metal levels to produce a Metal Pollution Index (MPI) (e.g. Usero et al., 1996, 1997; Giusti et al., 1999):

$$\mathrm{MPI} = (\mathrm{M1 \ x \ M2 \ x \ M3 \ x....Mn})^{1/n}$$

Where Mn is the concentration of metal n in mg kg^{-1} (dry weight). This is used to compare the overall metal contamination at each site before and after remediation, and to assess trends down the coast.

Study	Site	Fe	Mn	Zn	Cu	Pb	Ni	Cr	Cd	% Ash
2001	Whitburn	636.50	490.60	560.20	29.60	3.60	3.00	5.00	2.53	
2011	Whitburn	930.77	636.14	251.53	20.82	7.69	13.02	4.84	3.56	22
Change	*Whitburn*	*294.27*	*145.54*	*-308.67*	*-8.78*	*4.09*	*10.02*	*-0.16*	*1.03*	
2001	Roker Pier	300.30	360.00	511.40	23.30	5.90	20.20	3.00	2.41	
2011	Roker Pier	513.32	454.61	355.57	25.29	9.33	18.09	4.68	4.86	24
Change	*Roker Pier*	*213.02*	*94.61*	*-155.83*	*1.99*	*3.43*	*-2.11*	*1.68*	*2.45*	
2001	Roker Estuary	490.60	176.00	740.00	30.70	7.80	30.60	3.60	2.02	
2011	Roker Estuary	1962.33	1582.82	655.66	33.38	45.90	21.47	6.73	3.65	21
Change	*Roker Estuary*	*1471.73*	*1406.82*	*-84.34*	*2.68*	*38.10*	*-9.13*	*3.13*	*1.63*	
2001	Dawdon	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
2011	Dawdon	2432.29	901.63	503.17	49.95	14.50	37.99	5.10	5.88	27
Change	*Dawdon*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	
2001	Easington	1208.90	80.60	1015.50	50.60	12.10	36.00	3.80	10.03	
2011	Easington	842.21	546.38	613.34	49.06	5.38	32.98	4.46	7.97	23
Change	*Easington*	*-366.69*	*465.78*	*-402.16*	*-1.54*	*-6.72*	*-3.02*	*0.66*	*-2.06*	
2001	Horden	920.10	105.40	904.80	35.90	8.40	70.50	3.50	9.18	
2011	Horden	9081.52	1172.17	386.08	57.93	23.93	52.43	6.15	6.24	26
Change	*Horden*	*8161.42*	*1066.77*	*-518.72*	*22.03*	*15.53*	*-18.07*	*2.65*	*-2.94*	
2001	Blackhall	815.10	107.90	140.30	20.20	5.70	32.10	2.60	2.16	
2011	Blackhall	2045.89	975.84	400.63	56.61	5.86	43.92	4.87	6.84	23
Change	*Blackhall*	*1230.79*	*867.94*	*260.33*	*36.41*	*0.16*	*11.82*	*2.27*	*4.68*	
2001	Middleton	1027.00	83.00	45.40	9.70	0.60	0.40	1.10	0.14	
2011	Middleton	1594.65	591.96	403.60	39.57	11.89	18.86	5.73	4.31	23
Change	*Middleton*	*567.65*	*508.96*	*358.20*	*29.87*	*11.29*	*18.46*	*4.63*	*4.17*	
2001	North Gare	80.40	31.60	23.60	8.40	4.90	0.70	2.10	0.21	
2011	North Gare	558.73	738.65	342.05	38.72	7.42	19.46	4.69	4.06	21
Change	*North Gare*	*478.33*	*707.05*	*318.45*	*30.32*	*2.52*	*18.76*	*2.59*	*3.85*	
2001	Bran Sands 1	658.80	136.20	62.90	15.80	3.20	2.90	2.40	0.06	
2011	Bran Sands 1	3045.84	985.30	366.27	40.71	23.18	22.84	8.57	3.48	28
Change	*Bran Sands 1*	*2387.04*	*849.10*	*303.37*	*24.91*	*19.98*	*19.94*	*6.17*	*3.42*	
2001	Bran Sands	123.20	118.10	46.80	12.30	1.10	2.10	1.20	0.04	
2011	Bran Sands	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	26
Change	*Bran Sands*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	
2001	Bran Sands 2	130.90	93.50	42.10	10.00	2.00	1.60	1.20	0.04	
2011	Bran Sands 2	565.50	445.46	309.22	24.77	9.33	13.23	4.76	3.48	24
Change	*Bran Sands 2*	*434.60*	*351.96*	*267.12*	*14.77*	*7.33*	*11.63*	*3.56*	*3.44*	
2001	Bran Sands	95.60	55.20	36.20	13.90	0.70	1.50	1.00	0.03	
2011	Bran Sands	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	22
Change	*Bran Sands*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	
2001	Bran Sands 3	67.50	18.80	41.80	10.20	0.50	0.60	0.90	0.02	
2011	Bran Sands 3	1476.83	549.57	308.58	29.50	12.53	15.18	4.62	4.21	26
Change	*Bran Sands 3*	*1409.33*	*530.77*	*266.78*	*19.30*	*12.03*	*14.58*	*3.72*	*4.19*	

Table 7.2: *Fucus vesiculosus* heavy metal concentrations (mg kg^{-1}) from the current study and Giusti (2001) (prior to remediation).

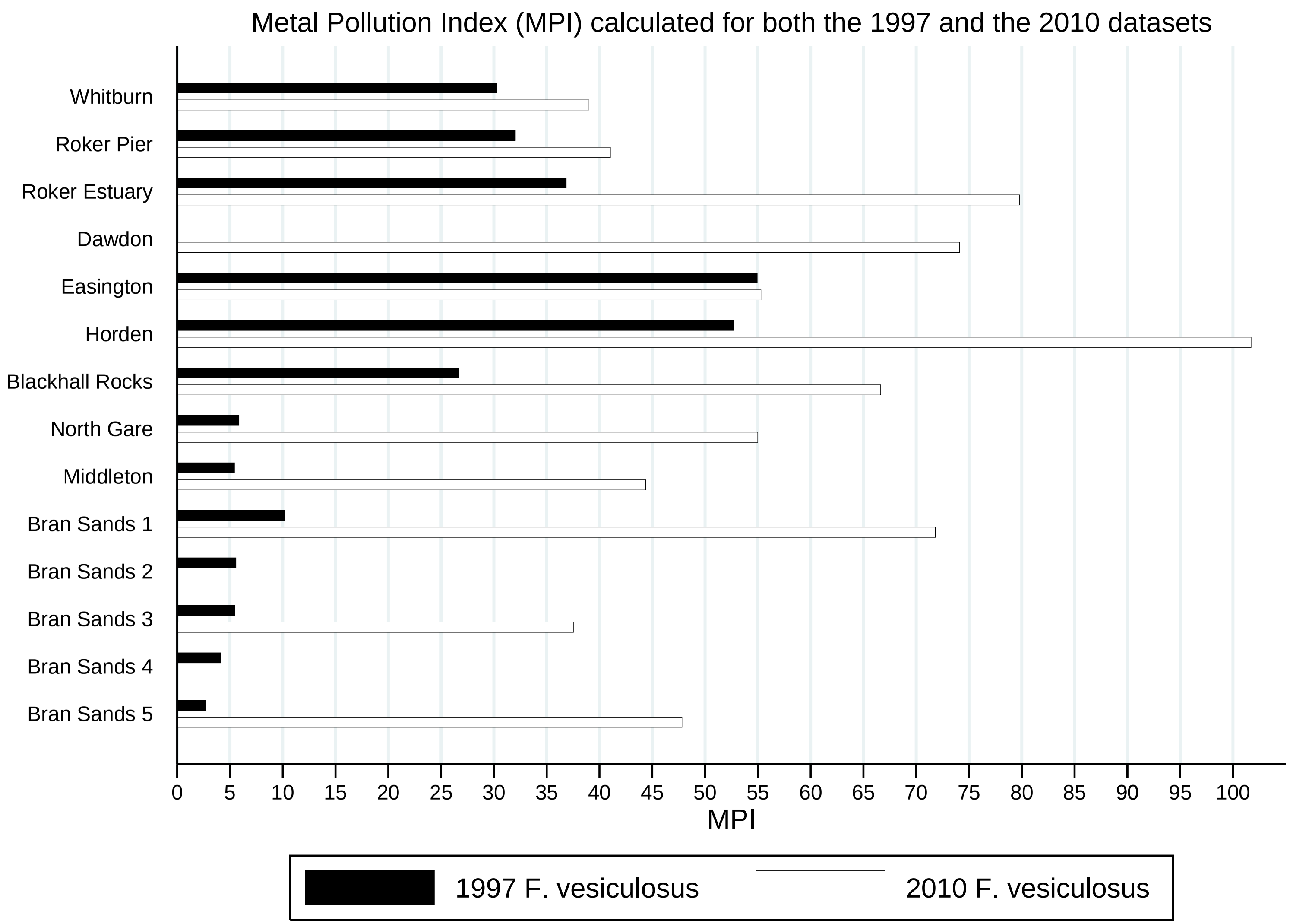

Figure 7.2: Metal pollution index (MPI) values calculated using concentrations for the 8 metals analysed used in the current study and corresponding data from Giusti (2001) in *Fucus vesiculosus* frond material.

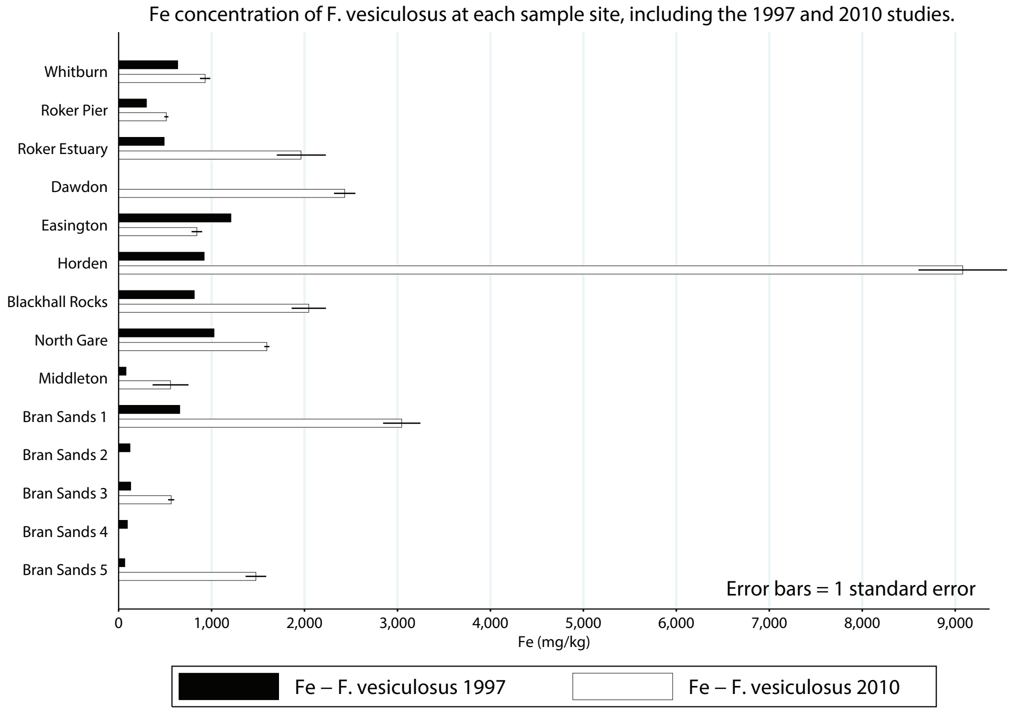

Figure 7.3: Fe concentrations (mg kg^{-1}) in bladderwrack before and after remediation

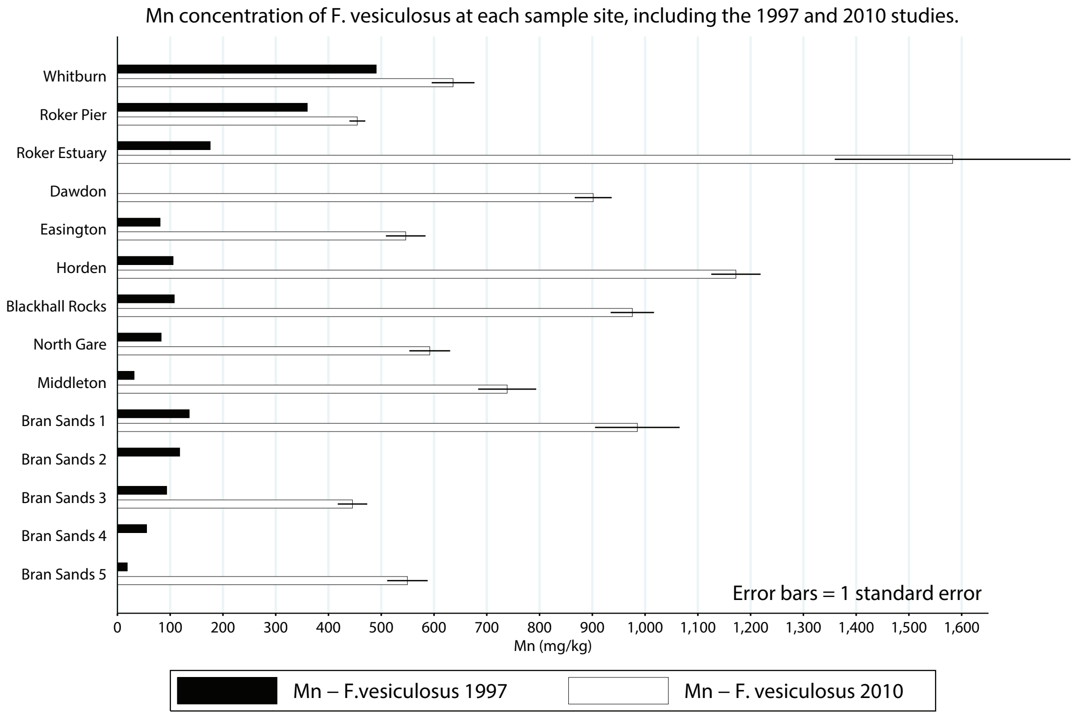

Figure 7.4: Mn concentrations (mg kg^{-1}) in bladderwrack before and after remediation

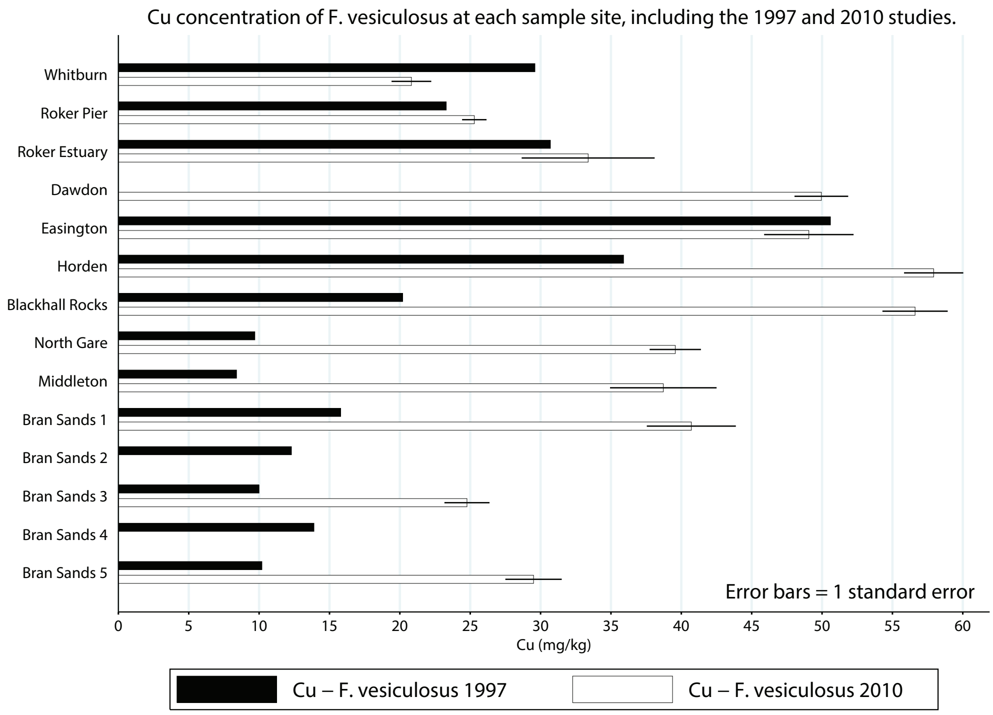

Figure 7.5: Cu concentrations (mg kg^{-1}) in bladderwrack before and after remediation

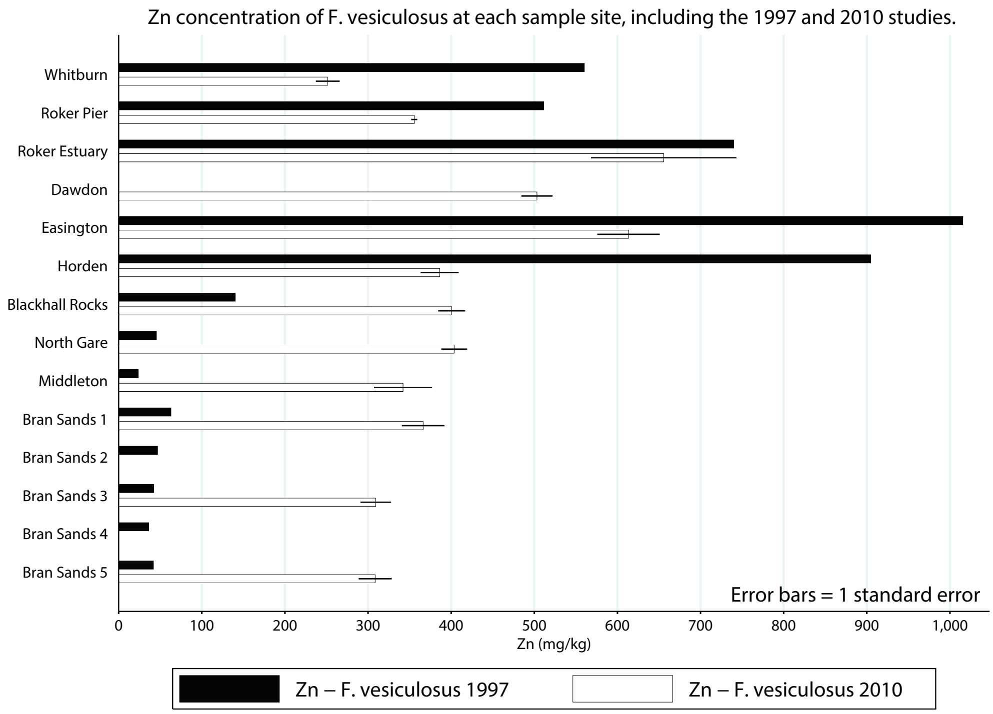

Figure 7.6: Zn concentrations (mg kg^{-1}) in bladderwrack before and after remediation

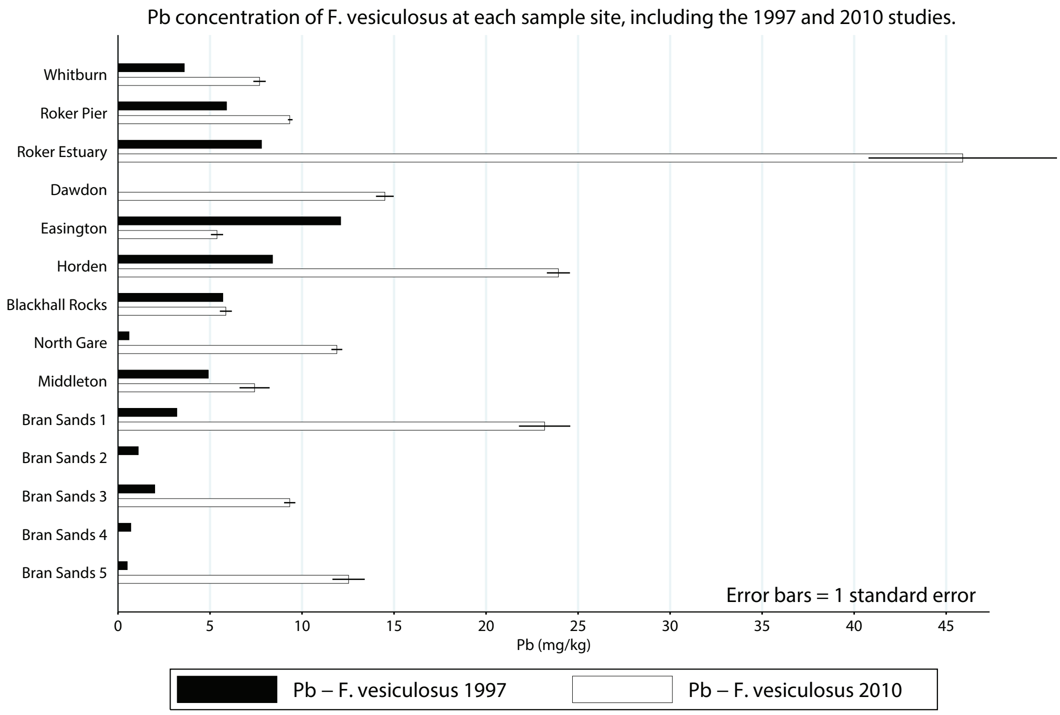

Figure 7.7: Pb concentrations (mg kg^{-1}) in bladderwrack before and after remediation

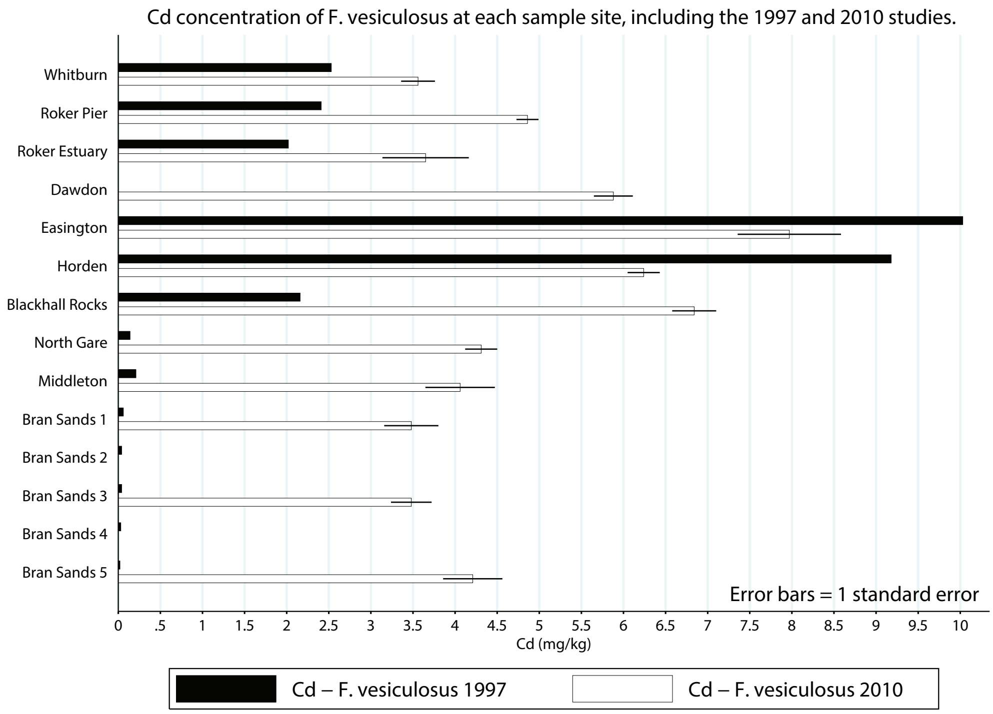

Figure 7.8: Cd concentrations (mg kg^{-1}) in bladderwrack before and after remediation

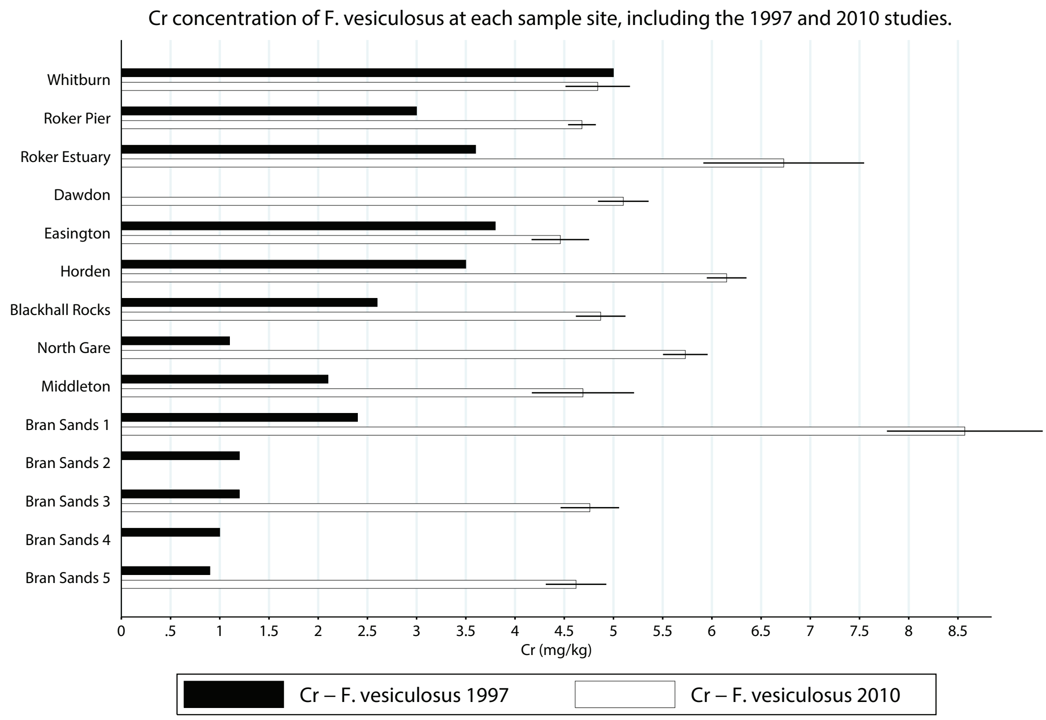

Figure 7.9: Cr concentrations (mg kg^{-1}) in bladderwrack before and after remediation

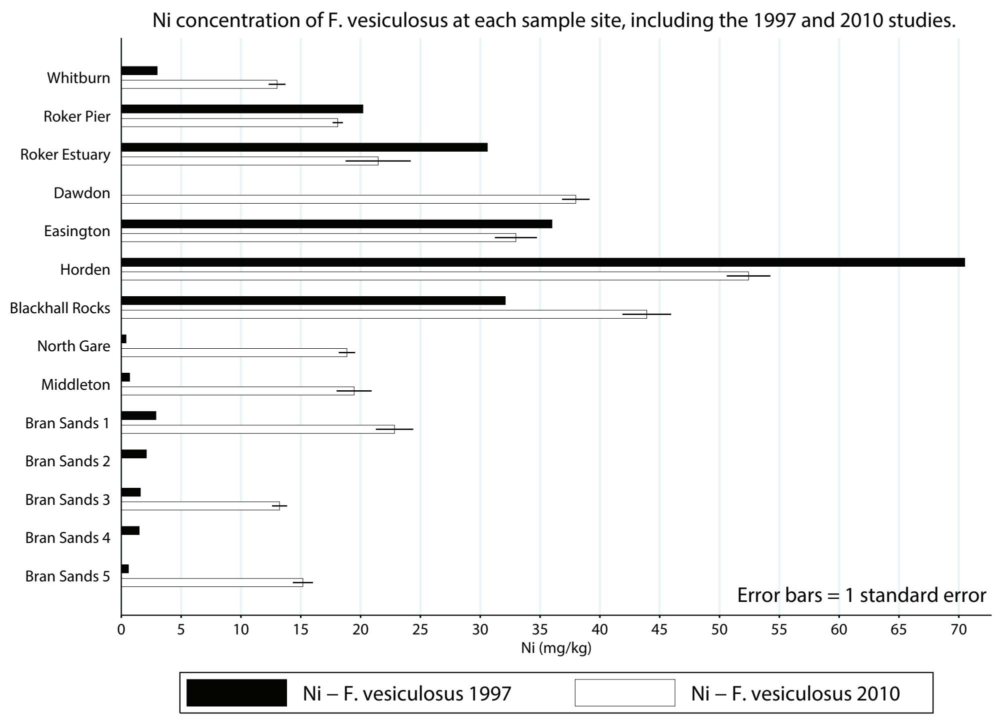

Figure 7.10: Ni concentrations (mg kg^{-1}) in bladderwrack before and after remediation

The MPI at all sites is shown to increase to some degree (figure 7.2) across remediation. The greatest increase between sites is observed at the first Bran Sands site, furthest from the coast (from ~10 points to >70). The smallest increase in MPI is observed at Easington, where both datasets result in an MPI of approximately 55. The largest MPI value in the current dataset is at Horden (>100), compared to Easington in 1997 (~55), and the lowest is Bran Sands 3 (~37) compared with Bran Sands 5 in 1997 (~3). Aside from the overall increase in MPI values, the general spatial trend appears to be a shift of less well defined peak values further down the coastline. Where peak values are observed at Easington and Horden in 1997, and MPI values drop significantly south of Blackhall Rocks, peak values in the 2010 dataset appear to stretch from Roker Estuary to Bran Sands 1 with MPI generally decreasing either side. The four largest values in 2010 are observed at estuarine sites (Roker and Bran Sands), and sites where treated minewater pumping has commenced between studies (Horden (2004) and Dawdon (2009)). It is worth noting again at this point that the length of frond sampled (based on recorded growth rates) is used to provide an average pollution record for the 3-5 months prior to sampling in both studies.

Concentrations of Fe, Mn, Cu, Zn, Pb, Cd, Cr and Ni from each study either side of remediation are presented in figures 7.3 to 7.10.

Fe and Mn are shown to be the metals which have the greatest overall increase in concentration between each study, increasing by an order of magnitude at some sites. For example, Fe concentrations at Horden increase from <1000 mg kg^{-1} to >9000 mg kg^{-1}, while Mn values at Roker estuary increase from <200 mg kg^{-1} to ~1,600 mg kg^{-1} between studies. The spatial pattern of Fe concentrations largely mirrors the observed pattern in the 1997 data, with larger values between Dawdon and North Gare. However, there appears to be an increasing input of iron from the estuarine sites of Roker (up by ~1,500 mg kg^{-1}) and Bran Sands (up by ~2,250 mg kg^{-1}) compared to the previous data set. There is a less well defined spatial peak of Mn concentrations in the current study compared to the 1997 data, where the highest values were observed at Whitburn (~500 mg kg^{-1}) and Roker pier (~360 mg kg^{-1}). In 2010, the general trend appears to be a greater increase in concentrations further south, between the estuarine sites, with the northern sites of Whitburn and Roker seeing the smallest increases in Mn. This shift is manifested by the large increase in Mn concentrations at Roker estuary and notably Horden (up by ~1,075 mg kg^{-1}), the sight of a significant increase in Fe concentration.

The concentration of Cu appears to have a similar spatial trend in this study to the dataset provided by Giusti (2001), although the values from Horden, moving south to Bran Sands, all show significant increases (smallest increase of ~15 mg kg^{-1} at Bran Sands 3, largest increase of ~35 mg kg^{-1} at Blackhall Rocks). Conversely, the range of observed concentrations in Zn at all sites in 2010 (~400 mg kg^{-1}) is significantly lower than that observed in the 1997 dataset (~1000 mg kg^{-1}), resulting in the apparent spatial pattern of lower values south of Horden being removed from the record. Zn is also the only metal for which concentrations in 2010 are consistently lower between Whitburn (decreased by ~300 mg kg^{-1}) and Horden (decreased by ~500 mg kg^{-1}) compared with the data from prior to remediation.

The majority of observed changes in concentration of Cr and Cd are likely to fall within the error of both studies in terms of detection limits and levels of methodological uncertainty due to such small differences at low detection levels. However, the apparent trend shown in the other metals of large increases at Bran Sands is again observed for these metals as well as Pb and Ni. Notable increases in Pb are found at both the estuarine sites, with Roker increasing by ~37.5 mg kg^{-1}, and Bran Sands increasing by ~17.5 mg kg^{-1}. The trend observed in the results for Mn and Zn of a narrowing concentration range due to increasing values south of Horden is again apparent in Cd, Cr and Ni.

Overall, the individual metal concentration results suggest a changing spatial pattern of contaminants compared to that observed in the 1997 dataset. Although the majority of metals peak concentrations lie between Roker estuary and Blackhall Rocks, the comparable or lower values observed north of these sites, and the large increases generally observed in the Tees estuary area (North Gare to Bran Sands), mean that the previous trend of decreasing contamination levels down the coast is now absent from the record.

This increasing level of contamination seen at the Tees estuary sites south of Horden, the significantly increased values of Fe and Mn, and the large increase in Pb at the Roker estuary site are the key findings from this dataset.

7.4.1 Bioaccumulation

Table 7.3 shows metal concentrations from three indicators for the comparison of metal accumulation in species at different trophic levels. Easington was chosen as the site to produce this comparison as it was the last site of mine closure, and it is down the coast from (and therefore potentially influenced by) the treated minewater pumping station at Dawdon.

Site	Species	Size/Age	Fe	Mn	Zn	Cu	Pb	Ni	Cr	Cd
Easington	F. vesiculosus	N/A	842.21	546.38	613.34	49.06	5.38	32.98	4.46	7.97
	P. vulgata	<4 years	95.96	36.89	1.98	6.12	undetectable	undetectable	7.00	undetectable
		>7 years	48.57	24.55	1.74	6.37	undetectable	0.10	7.40	0.01
	N. Lapillus	N/A	21.40	2.80	6.50	3.10	1.30	undetectable	undetectable	0.10

Table 7.3: Comparison of heavy metal concentrations (mg kg^{-1}) between species from the 2010 dataset, including a primary producer (bladder-wrack), herbivore (limpet shell) and predator (dog whelk shell).

If the site was subject to long term (species lifetime) pollution, it may be expected that some of the metals would bioaccumulate in the shell material of faunal species as it progresses up the food chain. The data suggests that a potential long term source is not an issue as all metal levels in the predator (dog whelks) are lower than in the prey (limpet), aside from a small increase in Zn. However, as with limpets and mussels, Fe concentrations are significantly higher than any other metal in the dog whelk shell.

7.4.2 High Fe and Mn Across Species

Although potential bioaccumulation of the high values of Fe and Mn observed in bladderwrack appear to be absent from the shell material of limpets and dog whelks, significantly high values are observed in the tissue material of both limpets and mussels (table 7.4). Blackhall Rocks was the site chosen for this comparison as it has the complete record of all three species and is located south of both the pumping stations at Dawdon and Horden.

Blackhall Rocks	Species	Fe	Mn
	F. vesiculosus	2045.9	975.8
	P. vulgata (tissue)	10159	92.1
	M. edulis (tissue)	11691	174.5

Table 7.4: Comparison of heavy metal concentrations (mg kg^{-1}) between species from the 2010 dataset, including bladderwrack and the tissue material of limpets and mussels.

Despite the differences between these values (which could be due to different rates of uptake, measurement timescales, and different rates of excretion), they are all significantly higher than observed in the work of Giusti et al. (1999) and Giusti (2001). Due to the apparent absence of long term bioaccumulation from the record, these high values are likely to be caused by a short term, or fluctuating, aqueous source. This may be inferred due to the absence of significantly high values in the shell record of the species analysed, and also due to the ecological niche of both bladderwrack and limpets, suggesting that metal concentrations should be primarily reflective of water quality rather than sediment bound pollutants.

7.5 Discussion

The observed concentrations of the eight heavy metals analysed in this study are typically higher than observed in Giusti (2001), with concentrations of Fe and Mn showing significant increases in bladderwrack. This 3 month record is reflective of the significant increases of these two metals observed in previously collected data in mussel and limpet tissue. The consistent presence of these high values suggests they are not anomalous, and the absence of such high concentrations in predators and shell material may indicate a new aqueous source, independent of past mining activities. One potentially polluting activity which is present now and would have been absent from both Giusti studies is the treatment of polluted minewater and subsequent pumping back into the sea. This process was initiated at Horden in 2004 and Dawdon in 2009, north of the sites which show the most significant increases in Fe and Mn. Although this process is designed so that the effluent has concentrations of Fe at or below 1 mg kg^{-1}, values measured by the Environment Agency have reached 34 mg kg^{-1} in the past (see figures 7.11 and 7.12) (Environment Agency, 2011b).

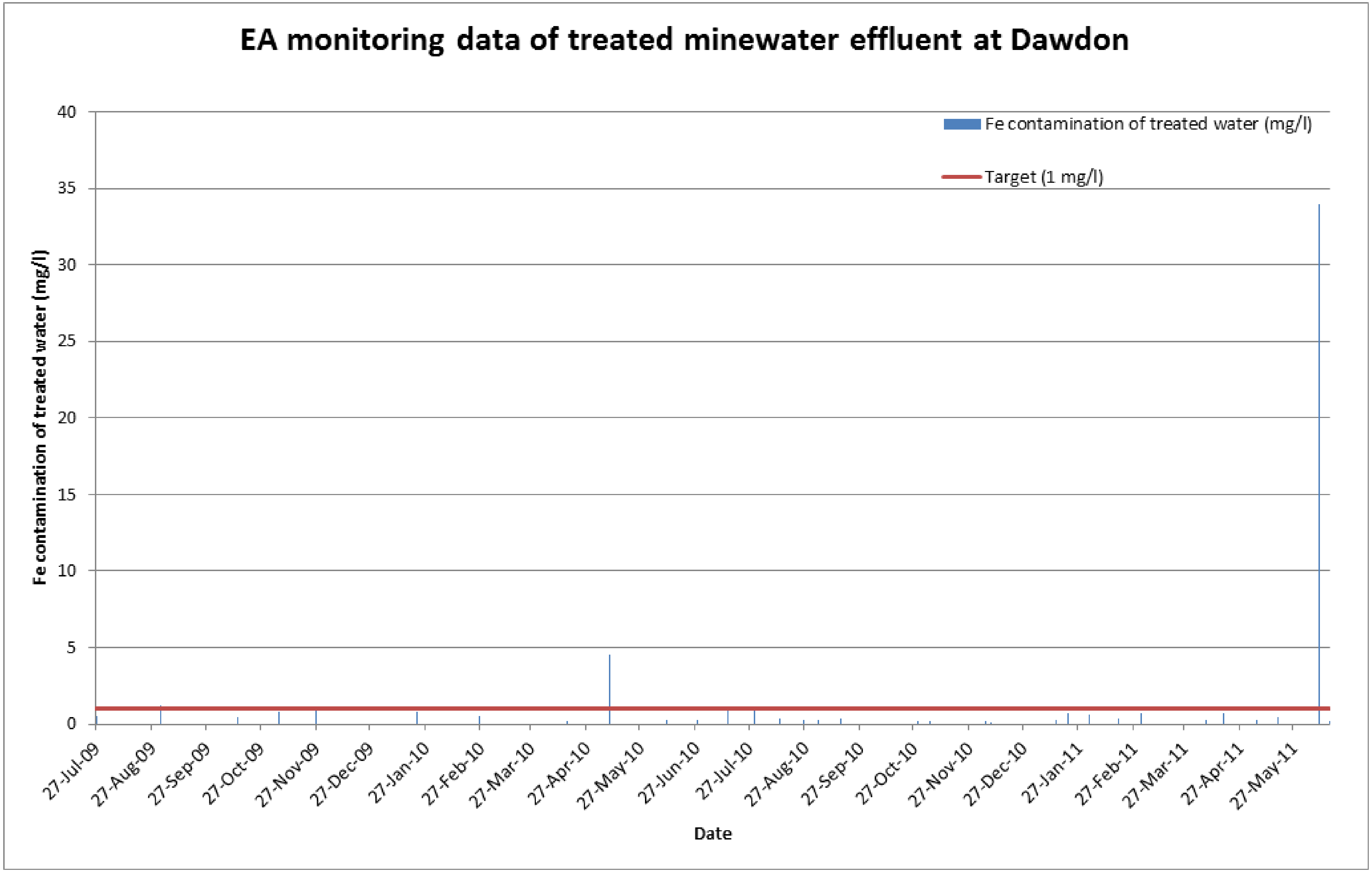

Figure 7.11: EA monitoring of treated minewater effluent at Dawdon (*Contains Environment Agency information ©Environment Agency and database right*)

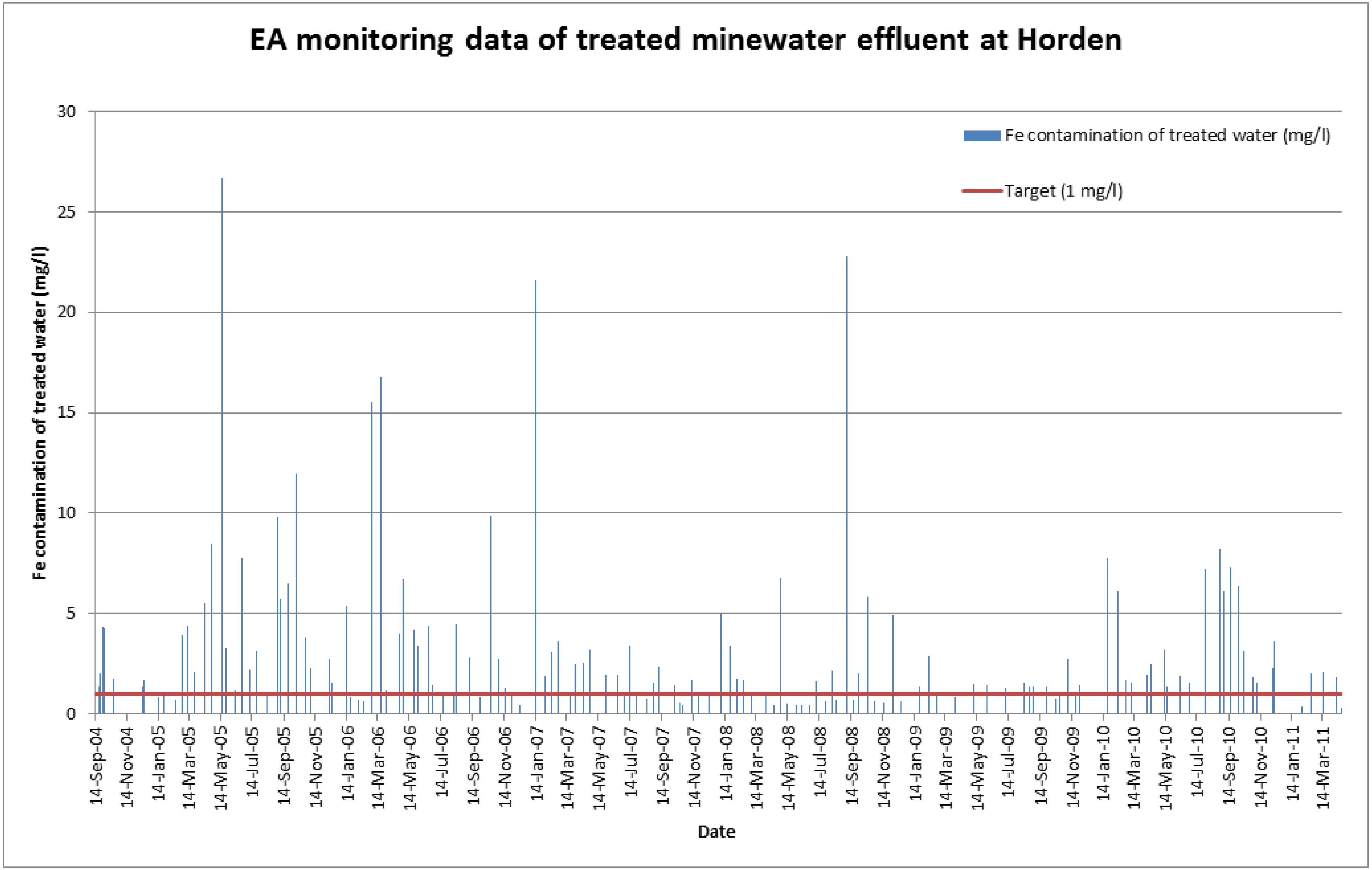

Figure 7.12: EA monitoring of treated minewater effluent at Horden (*Contains Environment Agency information ©Environment Agency and database right*)

The data shows that the output from the Horden station frequently exceeds the target level of iron contamination. Although these values are still at a relatively low level, the large volume of treated water which is pumped out suggests this source of metals should be considered throughout any monitoring investigation, particularly when considering future impacts as another station has recently been opened. Couple these high values with the high rate of pumping (35-70 litres per second), and the absence of manganese monitoring, and this appears to be a viable source from which these metals could accumulate in bioindicators. Based on these findings, future and more frequent monitoring of the effluent water and surrounding seawater is suggested.

The trend in metal accumulation has also seen significant change since the previous study and remediation. Where the trend of most metal levels to decrease as we move down the coast was present in Giusti (2001), a much less defined pattern is currently present. This observation is epitomised by the significant increases in most metals observed at the Bran Sands sites. This accumulation at the estuary may be a result of offshore sediment being transported south with metals being removed by wave action. This could provide a secondary hypothesis for observed increases in metals between studies, as the process of sediment removal in remediation would have allowed greater volumes of loose sediment to be picked up and moved by the waves. If this is the case, the high values observed may represent temporary peaks which are a necessary bi-product of removing huge volumes of polluted sediment from the beach for disposal. In order to test this theory, future offshore sediment grab samples and turbidity measurements are recommended.

High values of Pb observed at Roker estuary mirror the findings of the riverine research carried out by Shepherd et al. (2009), and suggest these inland sources may be having some coastal implications, despite remediation having taken place at the inland sites. Further research should be carried out to monitor these possible sources and consider the extent of the effected region.

7.6 Conclusion

Previous research using *Mytilus edulis* and *Patella vulgata* suggested that high values of metal pollutants may be a result of short term aqueous sources, with the long term record suggesting decreasing contamination levels and a successful remediation project.

The results of this investigation using *Fucus vesiculosus* have done little to change this theory, with high values of Fe and Mn observed in the indicator cited as a useful measure of water quality. The apparent lack of bioaccumulation of metals between predator and prey provide further support that these instances of high metal levels are short term or fluctuating. The results of this study should provide further evidence that stricter monitoring of post remediation water treatment processes is required, particularly as a new treatment facility has opened at Whitburn since this data was collected.

Chapter 8

Conclusions

The following section summarises the outcomes of the two conducted studies with reference to the research questions which the investigation aimed to answer. Subsequent, more detailed discussion leads back to the aim of the investigation, before suggestions for further work are noted.

8.1 Reference to Research Questions

8.1.1 What is the current spatial pattern of heavy metal contamination in *Mytilus edulis*, *Patella vulgata* and *Fucus vesiculosus* along the County Durham coastline?

The patterns of heavy metal contamination in the shell and tissue material of both limpets and mussels, along with bladderwrack, exhibit some distinct similarities and differences along the coastline under study. The metal pollution index in shell material for both mussels and limpets is uniformly low along the coast (<5 points at each site). However, within this trend, different spatial peaks are observed. Mussel shell appears to become more polluted as we progress down the coast, whereas limpet shell increases in contamination level as we move south to Blackhall Rocks where a peak is observed, before decreasing again to the Tees estuary sites. However, it should be noted that due to the low values detected for each metal at each site, these small variations may fall within the methodological error of the investigation.

The tissue data collected from the same species at the same sites illustrates a different level of contamination with different trends. The MPI for the tissue material across the study region does not fall below 13 points, peaking at around 30, although the high observed concentrations of Fe and Mn in this medium will influence these high values. As with the limpet shell material, the tissue data for both species suggests a peak contamination level at Blackhall Rocks.

Unlike the faunal data, peak values of contamination in bladderwrack are found at Horden, generally decreasing to the north and south, with MPI ranging from approximately 35 to in excess of 100. Again, these values will be influenced by the high concentrations of Fe and Mn observed at different sites, but the comparison of MPI across species gives an indication of the sensitivity of the different indicators in these environmental conditions. Indeed, these differences provide justification for the analysis of both shell and tissue material, as well as the adoption of a multi-indicator approach when conducting a heavy metal monitoring study.

8.1.2 What trends are observed between the data collected for each species?

Although the pattern for contamination in shell and tissue material differs for both mussels and limpets, the limpet shell material appears to reflect the pattern observed in tissue material more closely than the mussel samples. This may suggest that the accumulation of metals in shell material, transferred from tissues, is more consistent in this species. The high values of Fe and Mn are consistent across all three species, suggesting this is not an anomaly.

8.1.3 How do the current point concentrations and spatial trends compare to data collected prior to Turning the Tide?

There are clear differences between the point data and spatial trends observed in the current investigation compared with data collected by Giusti prior to remediation. The long term heavy metal record of the County Durham coastline is shown to have decreased at the study sites where the shell material of mussels and limpets was analysed. However, increases in mussel tissue contamination of Fe and Mn between 1996 and 2010 are also present. The absence of these increases in the shell data suggest the source may have arisen relatively recently, or these levels are a product of short term fluctuations which are averaged out of the long term record provided by shell material.

The previous spatial pattern of pollution found in bladderwrack, which suggests a decreasing level of contamination down the coastline, is now absent from the data. Indeed, the levels of metal concentration in all three indicators currently suggest that the most southerly site, Tees estuary, has become increasingly polluted since the studies in 1996-1997. Overall, the range of contamination levels observed in all indicators has decreased, with previous well defined peaks for certain metals at certain sites becoming less obvious in the new dataset.

In addition, the high value of lead observed in the bladderwrack data for the Roker estuary site compared to the earlier study confirms the need for further monitoring of riverine sources, noted by Shepherd et al. (2009).

8.1.4 What impact could the process of remediation have had on the observed spatial and temporal trends?

Due to the similarly high concentrations of Fe and Mn found in both limpets and bladderwrack, both known to be good indicators of water quality, the implication is that the predominant source of contamination for these metals is in aqueous form. As a result, these high values observed in all three indicators are linked to the post remediation pumping of treated minewater into the sea at Dawdon and Horden. Although the treated effluent has a guideline value of Fe, Environment Agency data suggests that this is frequently exceeded and Mn levels are not monitored at all. Closer monitoring of this pumping is called for, particularly as plans to open a new pumping site at Whitburn are being carried out.

Despite these findings, all guideline values are met for the toxicity of heavy metals within mussel tissue, showing an improvement on the 1996 study. These values are also within the requirements for edibility.

8.2 Further Discussion

When considering the results in this investigation which are indicative of long term pollution trends, the change in physical form of the County Durham coastline, and the improved image which this has brought, the £10 million regeneration project has been a success. However, in light of the data collected here, new problems have been created in terms of the maintenance of the coastline, and the goal of producing consistently low levels of heavy metal contamination. Although the unusually high levels of iron and manganese observed in these studies appear to be a result of low level fluctuations, the source needs to be identified to prevent levels increasing in the future, due to implications for fisheries and bathing sites. If, for example, the source of the problem is found to be a result of the treated minewater effluent from pumping stations, the opening of future sites after this study (e.g. the site at Whitburn in January 2011), may be having unknown adverse effects if the issue is not recognised.

The increase in heavy metal pollution at Bran Sands since 1997 is apparent for the majority of metals analysed and present in the record provided using all three indicators. This would suggest that these results are not anomalous, and the cause may be linked to the mobilisation of material which was initially dumped offshore prior to mine closure. The net transport of material along this coastal cell is from north to south (Johnson and Frid, 1995). The Tees estuary provides a natural barrier and thus an area of deposition for transported material in this cell to accumulate. It is possible that the general increase in metal contamination at this site is a product of this gradual transport and deposition. The physical breaking down and removal of mine waste from the beaches as a part of remediation could cause a magnification of this effect. Although the contaminated sediment was moved to the cliff tops and capped, the process of breaking up compact material may have heightened the potential for contaminated sediments to be transported by wave action during the remediation process. This theoretical fluctuation in the transport of polluted material may explain why the Tees estuary area appears to be more polluted now than during either of the Giusti studies, despite the sample collections for all studies being carried out after the input of mine waste into the system had ceased. Considering the bladderwrack data in particular, the general change in trend from decreasing levels of contamination down the coast, to the present spatial record which has a much narrower range, would suggest this theory has some grounding. Indeed, it seems logical that this shift in trend, with increasingly polluted sites to the south, would mirror the movement of the pollutants.

Another possible cause of the increased levels of metal contamination observed in the estuarine environment is the riverine transport of polluted material from inland sources. As Shepherd et al. (2009) suggest, this appears to be a factor in the Roker estuary, with heightened levels of lead observed in the bladderwrack data. Future studies of sediments at sites of deposition along the Tees river would be required to consider how influential such sources may be at Bran Sands.

The aim of the current investigation was:

"To provide a new heavy metal record in Mytilus edulis and Fucus vesiculosus post-remediation, and compare this to data collected between final colliery closure and the start of Turning the Tide. This comparison, along with an assessment of the present spatial patterns will allow a discussion of the remediation process and the impacts it may have had on the County Durham coastline."

This thesis has presented the new heavy metal records for three species, and through the comparison of results to data collected prior to remediation, the investigation has highlighted areas which require future monitoring, and potential problems which may be attributed to aspects of the remediation process. Through the presentation of data and the raising of new questions regarding the methods by which mine water is treated, the initial aims have been achieved.

8.3 Future Work

Based on the findings of the current investigation, three key areas of future study have been identified:

Firstly, work should be carried out to identify the source of the elevated levels of aqueous iron and manganese. The collection and analysis of periodic sea water samples at coastal sites could prove a useful starting point to such an investigation, particularly as it appears these high values may be a product of short term fluctuations. In order to identify any possible influences, closer monitoring of the treated minewater effluent at Whitburn, Dawdon and Horden and the surrounding waters would be beneficial.

Secondly, future consideration could be given to the mobilisation of polluted sediment which lies offshore. By considering levels of turbidity at different sites, collecting sediment samples from the seabed and utilising tracers, it may be possible to identify sources and sinks of polluted material. It would be interesting to see how any resulting spatial patterns map onto the pollution record collected from coastal ecology.

Finally, further studies which use bioindicators to collect heavy metal data at these sites would allow the construction of an increasingly detailed temporal record of post-remediation contamination levels. The relatively short record provided by such indicators is useful for noting changes in a dynamic environment, allowing areas which require further investigation to be identified, as has been experienced in this study.

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