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An Investigation about Neutralisation Rates of Acid Sulfate Soils Extracted as Sediment from Flood Mitigation Channels on the Shoalhaven Flood Mitigation System

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Abstract

Acid Sulfate Soils are a major environmental issue for NSW coastal regions. Many problems have arisen due to the installation of flood mitigation drains in prime agricultural areas, assisting the exposure and oxidation of sulfidic materials. As a result of this, options for management of drains and surrounding areas have become a leading area of research. Focus has been on not only identification and mapping, but remediation of affected areas. Many options such as the use of weirs, floodgates and permeable barriers have been described in the literature, however significantly less research has been invested into treatment of material once it is removed from flood drains or channels during management and routine maintenance activities. In order to aim for consistency across the country there are now a number of guidelines that have been made available by the Acid Sulfate Soils Management Advisory Committee (ASSMAC) that target the management of Acid Sulfate Soils.

The ability to predict the liming requirement for acidic dredge material in project areas of the Shoalhaven River estuary floodplain was investigated to facilitate the treatment and management of sediment removed from flood mitigation drains as a result of maintenance activities. The "Routine maintenance of flood mitigation drainage structures Review of Environmental Factors" document produced by the Shoalhaven City Council in 2011 has provided the basis upon which to conduct this study. Previous work and landholder experiences have come to show that a simplified method for treating acidic dredge material dumped along the sides of drains is required in order to neutralise the material which, left untreated, has significant impacts on the surrounding environment following oxidation and acidification. Three different methods were used to calculate the weight of lime necessary for neutralisation of every unit of material removed from drains in each of the separate project areas of the Shoalhaven River estuary. 65 samples were collected from a range of 17 drains. X-ray diffraction was used to detect levels of pyrite and the subsequent level of acid produced from its oxidation, while X-ray fluorescence was used to detect trace levels of sulfur, and the potential amount of pyrite that could be produced from those amounts. A third method involved testing field pH following hydrogen peroxide initiated oxidation and calculation of lime that would be required based on values provided in a 'Look-up table'. The maximum lime requirements calculated from each different method were graphed against each other to analyse correlation of values. Values calculated from XRF and XRD data analysis showed the greatest level of correlation when graphed against each other. Drain P2G1 has been identified as the drain with the highest recorded sulfur and pyrite concentrations, as well as zinc concentration, indicative of its ability to produce acid concentrations beyond that of any other drain sampled. The significance of this drain being a naturally formed entity rather than an artificial construction component of the flood mitigation scheme is discussed as well as the characteristics of all project areas that have given rise to differing levels of lime and overall management required. These results give information to those responsible for maintenance of the drains about which areas are of highest concern and the monitoring that needs to be implemented to ensure success of neutralisation efforts.

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AN INVESTIGATION ABOUT NEUTRALISATION RATES OF ACID SULFATE SOILS
EXTRACTED AS SEDIMENT FROM FLOOD MITIGATION CHANNELS
ON THE SHOALHAVEN FLOOD MITIGATION SYSTEM

by

RONNI MACIEJOWSKI

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Requirements for the Award of the Degree Of

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THE UNIVERSITY OF WOLLONGONG

October 2012

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- Ronni Maciejowski

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Abstract

Acid Sulfate Soils are a major environmental issue for NSW coastal regions. Many problems have arisen due to the installation of flood mitigation drains in prime agricultural areas, assisting the exposure and oxidation of sulfidic materials. As a result of this, options for management of drains and surrounding areas have become a leading area of research. Focus has been on not only identification and mapping, but remediation of affected areas. Many options such as the use of weirs, floodgates and permeable barriers have been described in the literature, however significantly less research has been invested into treatment of material once it is removed from flood drains or channels during management and routine maintenance activities. In order to aim for consistency across the country there are now a number of guidelines that have been made available by the Acid Sulfate Soils Management Advisory Committee (ASSMAC) that target the management of Acid Sulfate Soils.

The ability to predict the liming requirement for acidic dredge material in project areas of the Shoalhaven River estuary floodplain was investigated to facilitate the treatment and management of sediment removed from flood mitigation drains as a result of maintenance activities. The “Routine maintenance of flood mitigation drainage structures Review of Environmental Factors” document produced by the Shoalhaven City Council in 2011 has provided the basis upon which to conduct this study. Previous work and landholder experiences have come to show that a simplified method for treating acidic dredge material dumped along the sides of drains is required in order to neutralise the material which, left untreated, has significant impacts on the surrounding environment following oxidation and acidification. Three different methods were used to calculate the weight of lime necessary for neutralisation of every unit of material removed from drains in each of the separate project areas of the Shoalhaven River estuary. 65 samples were collected from a range of 17 drains. X-ray diffraction was used to detect levels of pyrite and the subsequent level of acid produced from its oxidation, while X-ray fluorescence was used to detect trace levels of sulfur, and the potential amount of pyrite that could be produced from those amounts. A third method involved testing field pH following hydrogen peroxide initiated oxidation and calculation of lime that would be required based on values provided in a ‘Look-up table’. The maximum lime requirements calculated from each different method were graphed against each other to analyse correlation of values. Values calculated from XRF and XRD data analysis showed the greatest level of correlation when graphed against each other. Drain P2G1 has been identified as the drain with the highest recorded sulfur and pyrite concentrations, as well as zinc concentration, indicative of its ability to produce acid concentrations beyond that of any other drain sampled. The significance of this drain being a

naturally formed entity rather than an artificial construction component of the flood mitigation scheme is discussed as well as the characteristics of all project areas that have given rise to differing levels of lime and overall management required. These results give information to those responsible for maintenance of the drains about which areas are of highest concern and the monitoring that needs to be implemented to ensure success of neutralisation efforts.

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1. Introduction

1.1 Background

Acid sulfate soils are a key environmental issue for coastal, inland and mine areas across the world (Fitzpatrick et al. 1998; Melville and White 2007). In Australia they have gained increased acknowledgement since their damaging impacts have become apparent in densely populated coastal areas and prime agricultural pastures. In NSW in particular, in regions where agricultural land has been drained to increase land productivity, problems have arisen as a result of artificial drainage schemes, including the installation of floodgates and connected flood mitigation drainage systems. On the south coast of NSW, the Shoalhaven River estuary has been subject to a range of problems that have arisen from the presence of acid sulfate soils and their exposure to the atmosphere arising from drainage projects that were introduced in the 1960's (Indraratna et al. 2005).

Previous experimental work in the Shoalhaven area has primarily been centred upon in-drain systems or works to neutralise waters. Indraratna et al. (2005) produced a document which focused upon the remediation techniques that have been employed, which included groundwater level adjustment using weirs, and tidal buffering using modified floodgates. Blunden (2000) also explored the validation of improved drain management techniques with respect to management of pyritic soils by manipulating groundwater with the installation of weirs. Additionally, reactive barriers have been researched as an option in the area (Indraratna et al. 2006), among other alternatives.

1.2 Basis for Study

Acid sulfate soils are primary causes for concern by landholders in the Shoalhaven agricultural area. Consequential complaints include the overgrowth of weed and vegetation within the drains and subsequent flooding of pasture (see Figure 1.1). In order to manage the use and state of the flood mitigation drains, the Shoalhaven City Council produced a "Routine maintenance of flood mitigation drainage structures Review of Environmental Factors" document in September 2011. This document was produced in regard to the proposed maintenance activities which include:

- The regular inspection of drains,
- Removal and/or treatment of noxious and aquatic weeds,
- Sediment removal to maintain design levels, and
- Removal of emergent, aquatic and terrestrial vegetation debris (eg. floating logs) to maintain appropriate flow and operation of the system (S.C. Council 2011).

The Review of Environmental Factors (REF) document, and the accompanying maintenance activities with which it is associated, provide the grounds from which this project has stemmed. The removal of sediment along with vegetation debris from the drains during maintenance dredging gives rise to consequential oxidation and acidification of material once the dredged material is placed alongside the banks of drains. Dredged material, if abandoned, has the potential to affect the growth of surrounding vegetation and leach acids back into the drain, having substantial impacts on the entire ecosystem. The prime aims of this project are to provide information to aid in the management of dredged acid sulfate soil material that is removed as a result of the afore-mentioned maintenance activities.



Figure 1.1: Photograph taken at sample site P1D1 (4) displaying the potential overgrowth of drains that are in desperate need of maintenance works and the kind of material that may be removed with dredging activities (taken 27th July 2012).

In order to assist in managing acidification of drains, there have been a range of studies and proposals put forward which include the use of compost/limestone/iron mixtures (Gibert et al. 2003), calcareous, gypsiferous waste (Offiah and Fanning 1994), permeable reactive barriers or lime-fly ash barriers (Banasiak 2004; Regmi, et al. 2009), lime-stabilised bio solids (Orndorff, et al. 2008), closed tank reactors (Green et al. 2008) and the direct application of alkaline reagents (Green et al. 2006). While all these studies produced an extensive range of options for acid sulfate soil management, there is little information from literature that is focused on the treatment or management of acid sulfate soil material once it is removed from the drain as dredge material, especially in Australia. The process of liming has been described as a limited and strategic option only, used to assist with scald revegetation and treatment of drain spoil (Tulau 2007). Thus, while it

may be inappropriate for other projects, lime is a suitable option for the treatment of dredge material from the Shoalhaven drains.

In order to address the problem of treating dredged material, agricultural lime is readily available and may be used to treat and neutralise material that has been removed from drains during routine maintenance. The amount of neutralising agent required will depend on the total oxidisable material that is contained within the sediment. At the present time, there are insufficient data sources to provide information on differing rates of application for specialised drainage areas. Therefore, this provides the foundation for research as part of this project.

1.3 Scope

This study was conducted in the Lower Shoalhaven River catchment area, containing a system of flood mitigation drains, many of which are currently managed by the Shoalhaven City Council. To assess the use of liming guidelines and to determine the amounts of lime that may need to be applied in general project areas of the catchment, sediment samples were collected from 17 of the recorded 50 drains that make up the entire flood mitigation scheme in the Shoalhaven (see Figure 1.2 for project area distribution). Samples were analysed in the University of Wollongong laboratories. Data that were produced were used to assess the severity of potential acidity in separate drains and separate project areas on the greater floodplain. Further, the amount of neutralisation in the form of agricultural lime application was determined by use of mineral identification and pH analyses that were carried out. This study provides the Shoalhaven City Council with a set of new values that aim to provide a more specific and simplified way for lime to be applied in separate project areas with differing oxidation potential of removed material. A review of previous studies of management of acid sulfate soils in the Shoalhaven area, primarily those based on treatment and management of actual waterways has also been conducted as part of this study. The Acid Sulfate Soil Manual produced for NSW by the acid sulfate soils management advisory committee (ASSMAC) has provided the guidelines upon which many methods and recommendations of this study have been derived.

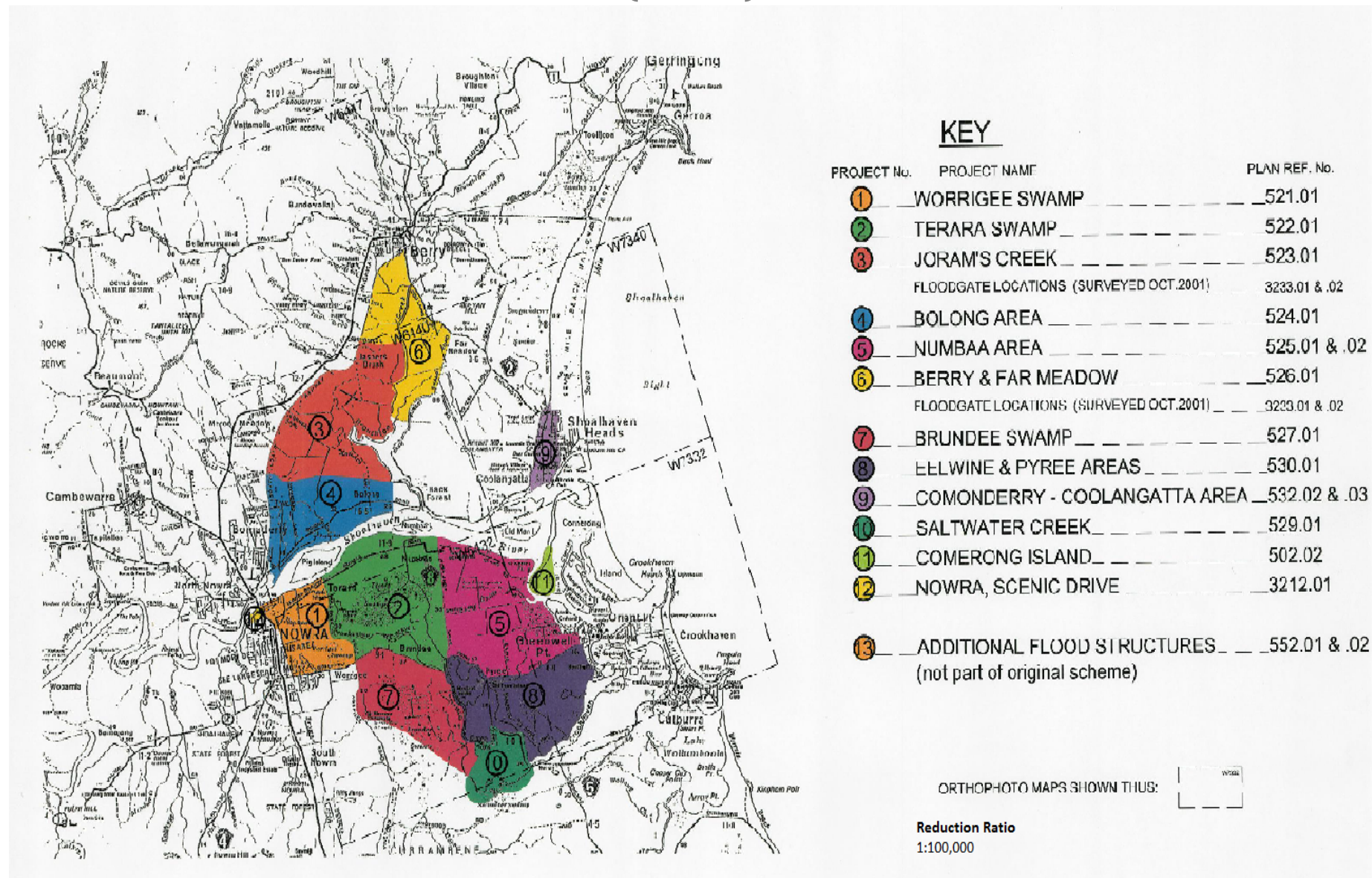


Figure 1.2: Map displaying the 13 separate project areas within the Shoalhaven estuary zone. Key shows the name and reference for each of these areas. (Shoalhaven City Council Flood Mitigation Key Map, Drawn by P. Jennings, 4/9/02)

1.4 Aims and Objectives

This study was conducted to aid the Shoalhaven City Council in their drain maintenance activities by analysing the methods that have been used previously to address the presence of acid sulfate soils in the Shoalhaven region, assessing the relationships between potential acidity in different areas of the floodplain, and addressing the methods of neutralisation treatment of acidic material.

The basic aims of this study are to:

- review previous and possible methods of acid sulfate soil management for flood mitigation drains;
- analyse material that may potentially be removed from drains along with the removal of vegetation during maintenance, to assess its associated mineralogy and acidity levels in terms of total pyrite concentrations;
- use acidity results to determine the amount of agricultural lime that would be required per tonnage and volume of material removed and dumped along the sides of drains for each sample location based on values contained in the ASS manual and neutralisation chemistry;
- determine the amount of agricultural lime that would be required for neutralisation in a worst case scenario for each general project area to enable easy application for excavator operators;
- assess the reliability of the current method which uses a uniform application rate in comparison with determined results; and
- provide recommendations and conclusions derived from results of the study.

2. Literature Review

2.1 Acid Sulfate Soils Definition

Soil is a mixture and layering of (primary) weathered rock and (secondary) transported and transformed minerals and organic matter (Scott 2009). Different types of soils derived from this basic understanding of soil are characterised by the individual chemical, physical and biological processes to which they are exposed. Classification schemes used to differentiate between soils are complex and difficult to develop on a universal scale due to differences in climate and environments. The five biophysical factors that influence the formation of soils are climate, organisms, parent material, time and relief. In addition to these, human activity also represents an intense influence (Young and Young 2001), as is evident in many different environments.

“Acid sulfate soil” (ASS) is a relatively recent term for soils which are gaining increasingly more recognition as their environmental effects are becoming apparent. Scientific attention first began for these soils in the 18th century when Linnaeus recognised them in the Netherlands and described them as “clay with sulfuric acid” (Fanning 2005). From the very beginning, these soils have been disfavoured based upon the fact that they cause the practice of agricultural crop growing to become difficult. In broad terms, acid sulfate soil is any soil or sediment containing iron sulphides (principally pyrite) or products of the oxidation of sulphides (White et al. 1996). This definition has been expanded to describe acid sulfate soils as soils that have been drained, that have free and adsorbed sulfate, that show pale yellow mottles of jarosite, and that usually have a pH below 4 in water (Bloomfield and Coulter 1974). This description is much more detailed; however it still remains apparent that the primary cause of production of acid sulfate soils is the oxidation of sulphides contained within the soil. The oxidation of contained sulphides occurs when material is exposed to air, and sulfuric acid is produced whenever the soil’s capacity to neutralise the resulting acidity is exceeded (White et al. 1996). In most sulfidic soils, nearly all the sulfur occurs as pyrite (Dent 1986). However, other forms such as monosulfides exist in smaller concentrations (Melville and White 2007). Pyrite, being the primary iron sulphide material found within these kinds of soils forms the basis upon which analysis has been conducted for the purposes of this project.

As has been commonly recognised, there are two types of acid sulfate soils. These are actual and potential acid sulfate soils. These are distinguished based on oxidation and subsequent acidification of the soil that has or has not occurred. Actual acid sulfate materials are materials that once contained pyrite and may still contain some, but which have been exposed to the atmosphere causing pyrite to oxidise and decrease the pH to less than 3.5. Jarosite is often characteristic of this

type of soil. On the other hand, potential acid sulfate materials are constituents that contain pyrite that has not yet been oxidised, thus will have a pH close to neutral (Fitzpatrick et al. 1998). It is important to distinguish between these from mapping and agricultural aspects (Bloomfield and Coulter 1974).

2.2 Formation and Development of Acid Sulfate Soils

Acid sulfate soils are developed as a result of specific environmental conditions characteristic of particular common locations, such as along coasts. Three distinct acid sulfate soil weathering environments have been identified and assessed in Australia. These include coastal ASS (tidal mangrove swamps), inland ASS (non-tidal scalds driven by saline acid-sulfate discharge conditions) and mine site ASS (waste rock stockpiles or tailing impoundments; Fitzpatrick et al. 1998). Of these three environments, it is the occurrence of coastal ASS that has received the most adequate assessment. Coastal and deltaic areas, typically high population areas and often very important lands agriculturally, provide optimum conditions for formation of sulphides required for production of acid sulfate soils, due to their plentiful supply of sulfate and organic matter essential for the formation of sulphides (Bloomfield and Coulter 1974). In coastal environments, the source of sulphides arises primarily from tidal influences. In Australia, the acid sulfate soils of most concern are those which formed within the past 10,000 years, after the last major sea level rise (Sammut et al. 2004). Fitzpatrick et al (1998) also agreed with this statement as they too stated that the soils of most concern are those that were deposited during the Holocene period. In their paper, Fitzpatrick et al. (1998) continued further to describe the processes that occurred with sea level rise drowning coastal embayments and sediments blocking off coastal lagoons following the last Ice Age. These processes culminated with the end of the major sea level rise when sea water or brackish water containing dissolved sulfate covered organic debris in coastal and swamp environments and combined with iron from the sediments, under generally air-free conditions, to produce iron sulphides (Fitzpatrick et al. 1998). The pyrite that causes problems pertaining to acidity accumulates in waterlogged, saline sediments where there is a supply of decomposed organic matter (Dent 1986). The sea water that inundates these coastal environments contains 2700 mg/kg (27 mM/L) of SO_4^{-2} which provides the potential for acid sulfate soils to develop in both marine and estuarine environments (Melville and White 2007).

The primary reason that acid sulfate soils become prominent and recognised in particular locations is due to oxidation. This commonly occurs due to human action, such as dredging and draining for benefits including agricultural use that causes material to oxidise from exposure to the atmosphere, resulting in offensive odours and mineralisation. As long as sulphides remain in reduced conditions

below the water table they pose no problems. It is only when they are exposed to oxygen, such as in periods of prolonged drought, or after draining, dredging or excavation, that problems occur (White et al 1997). Under natural conditions, iron sulphide layers are covered by water and any acid produced is usually neutralised by tidal flows of alkaline sea water and the rest of the acid remains in the soil. However, in comparison, it is common for waterlogged areas where iron sulphide layers occur to be drained for agriculture. Drainage accelerates the natural rate of oxidation in these circumstances so that large amounts of acidic groundwater are released swiftly into estuarine streams (Sammut et al. 2004), causing a range of issues and environmental problems (see Section 2.6).

2.3 Location and Occurrence of Acid Sulfate Soils

Acid sulfate soils are widespread across the globe (Melville and White 2007), occurring on all continents. The worldwide extent is approximately 13 million hectares (Shamshuddin et al. 2004), representing around one percent of the world's cultivated land. Their development is of immediate interest due to their occurrence in areas of prime agricultural land or near densely populated coastal communities. Asia and the Far East are known as locations with the highest occurrence of acid sulfate soils, followed by Africa. Countries found in tropical areas have been recognised as regions exhibiting major problem soils, with the area under acid sulfate soil influence reported to be approximately 7.5 million hectares in the tropics alone (Shamshuddin et al. 2004). High temperatures in the tropics and subtropics, particularly in areas with large amounts of tidal exchange, allow maximum pyrite accumulation, such as in the deposits adjacent to the South Alligator River, NT (Woodroffe et al. 1989).

Major international examples of acid sulfate soils to note occur in the Mekong River Delta in Vietnam, the Netherlands, Finland and other parts of Asia. The Pearl River delta in China, in contrast to the flood plains of coastal NSW, has a long history of land reclamation. Further, sedimentation rates have been much slower in NSW, with the generation of higher pyrite content in estuarine sediments in NSW coastal flood plains than the Pearl River delta (Lin et al. 1995). Water management, which often gives rise to problems, also differs between countries. In this case, the Pearl River delta has a bi-directional irrigation-drainage system, while the NSW coastal flood plains are drained by one-way flap gates, installed as part of a 'flood mitigation' programme (see Section 2.7; Lin et al. 1995). The Americas also show examples of problem areas arising from the presence of acid material. One prominent example with implications for current research is the analysis of dredged materials from the tidal Pocomoke Sound in Somerset County of the USA conducted by Demas et al. (2004). In this case, soil was deposited on a tidal marsh, and indications of acidity have

arisen as jarosite is present in soil, pH values are low and significant amounts of newly formed ironstone have been recorded at drainage water discharge points (Demas et al. 2004).

2.4 Case Studies in Australia

Each regional pattern found in different parts of the world may be determined by its unique sedimentary and geomorphological history (Dent and Pons 1995), thus it is often difficult to compile extensive data for worldwide occurrence of acid sulfate soils. In Australia, where acid sulfate soils have been a major development in lagoons and estuaries across the country since the last major sea level rise in the Holocene, scientists have estimated that there are in excess of 2 million hectares of acid sulfate soils containing approximately one billion tonnes of iron sulphides (Sammur et al. 2004). It has also been stated that there are over 260,000 ha of high risk areas, including about 150,000 ha under agricultural production (National Government 2011). ASS are found both inland and along coastlines across Australia (see Figure 2.1).

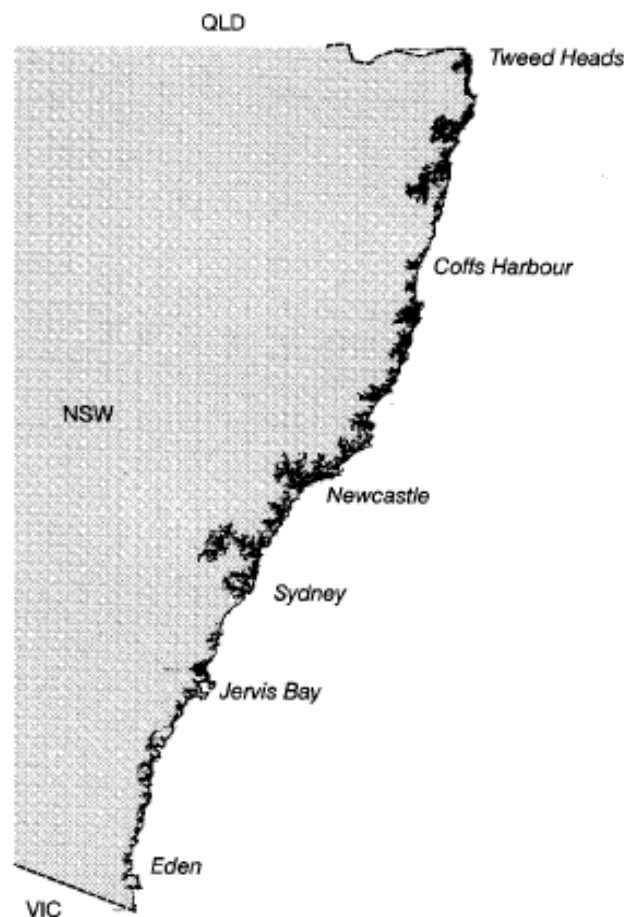


Figure 2.1: Distribution of coastal acid sulfate sediments in NSW. The Shoalhaven region is located between Sydney and Jervis Bay (Naylor et al. 1995; as used in White et al. 1997)

In eastern Australia, the tidal range is about 2 m and coastal rivers tend to have small catchments with low outflows, thus estuarine embayments are prime locations for sulphide deposits (White et al. 1997). Talua (1999 a-d, 2007) has published a number of documents identifying major priority regions for acid sulfate soil management in NSW. These include documents in relation to the catchment areas: Tweed, Brunswick, Richmond, Clarence, Coffs Harbour, Bellinger-Kalang, Nambucca, Macleay, Hastings and Manning (Tulau 1999b). In line with these documents, the NSW Government has also acknowledged the NSW coastal floodplains of the Tweed, Richmond, Clarence, Macleay, Hastings, Manning and Hunter Rivers as being the largest of the high risk areas in Australia (National Government 2011). These sites have all been subjected to flood mitigation drainage works.

The Clarence Catchment is one of Talau's identified priority areas and has been accredited with a catchment impact of very high for ASS, one of its major issues (Tulau 1999b). The Clarence river itself is the largest coastal river catchment in NSW at 22 700 km² (DLWC 1998; as reported in Talau 1999b) and underlying the associated floodplain downstream from Grafton is an extensive array of estuarine deposits, encompassing both actual and potential ASS.

The Tweed River and its upper tributaries drain the McPherson and Tweed Ranges, with the actual floodplain representing a typical drowned river valley with a generally low elevation and approximately 9700 ha of underlain high risk ASS (Tulau 1999c). Lin et al. (1995) revealed that the mean pyrite content of the pyritic layers is 1.6%. On the far north coast of NSW, at McCleods Creek, a tributary of the Tweed River, Smith et al. (2003) have indicated that while the degree to which land drainage has caused the acidity is unclear, the drainage systems do indeed provide the outlet for its increased transfer to estuaries. Acidity characteristics of McCleods Creek have also been analysed by Green et al. (2006), who found that the hydrolysis of dissolved metal species, particularly aluminium and iron, contributes to more than 70% of the total acidity. The Clothiers Creek catchment, immediately south to McCleods Creek also has many small field drains with a greater acid-producing potential (Green et al. 2006).

The Hastings River system has a catchment of 3600 km² with sediment being deposited annually. This area underwent a breakdown of sand barriers and dunes to form the river system that now connects with the lower Macleay system and overlies 21 737 ha of high risk ASS as part of the Hastings and Camden Haven systems (DCLM 1995; as reported in Talau 1999d).

In the area of the Tuckean Swamp, a tidal reach of the Richmond River, the estimated rate of sulfuric acid production from the floodplain is approximately 300 kg ha⁻¹ year⁻¹. At this location, like many others, drainage and flood mitigation works promote oxidation and the release of sulfuric acid and

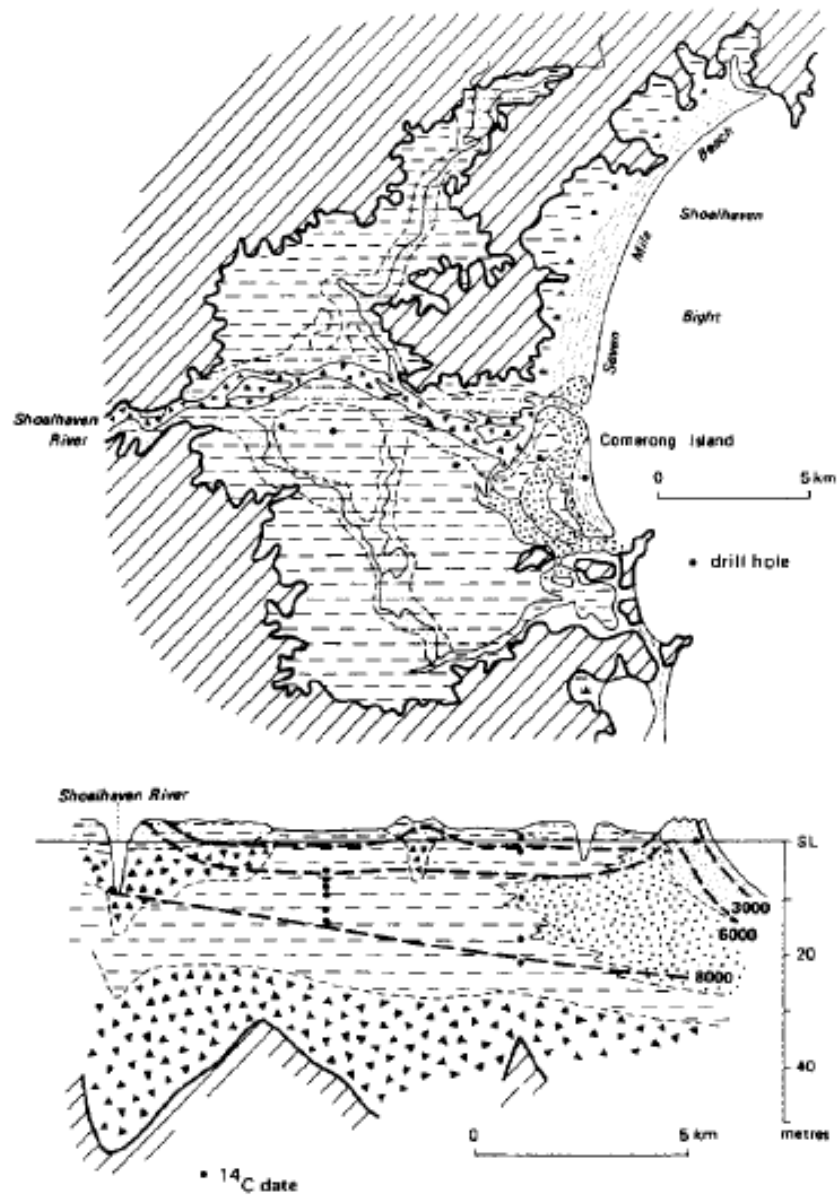
dissolved aluminium and iron into streams (Sammut et al. 1996). These areas along the coast of NSW all provide basis for comparison when assessing problems and management in similar situations at separate localities.

In terms of the Shoalhaven catchment, most of the land is underlain by brackish water sediments and soils containing naturally-occurring iron sulphide minerals. Sulphides are able to oxidise, producing sulfuric acid, with a drop in the watertable (S.C. Council 2011). This drop may be primarily attributed to drainage works.

2.5 Estuaries and Coastal Acid Sulfate Soils

The area studied for this project forms the Shoalhaven River Estuary. The evolution of such an estuary can be attributed to the “barrier estuary system”, which has been described by Roy and Thom (1985). In their synthesis of Holocene sea level and coastal and shelf stratigraphic data, they have been able to describe the formation of estuaries along southeast Australia and concluded that marine and estuary sedimentation has closely followed the pattern of sea level change. It was the Holocene sea level change that gave cause to the rise in deposition of sulfur-rich sediments, which is why many of the coastal estuaries along south east Australia do suffer the effects of acid sulfate soils. Other estuaries well known for problems with ASS such as the Tweed, Richmond and Macleay have also evolved as “barrier estuary systems” (Blunden 2000).

The coastal lagoon that may be seen as part of the Shoalhaven delta complex is characteristic of a barrier system as a sand barrier blocked the drowned river mouth. Previously, Comerong Island, the bay mouth barrier, enclosed a former barrier estuary and sedimentation of sands and muds infilled the lagoon, forming the extensive deltaic plain that we can see today (see Figure 2.2). The Shoalhaven River delta complex is now a mature system, in its final evolutionary stage, as except for a remnant of the former estuary at Crookhaven Inlet, infilling is now complete and the estuary is confined to a sinuous river channel bordered by levees (Thom and Roy 1985). These levees across the surface of the plain are interpreted to be a birdsfoot delta distributary complex (Umitsu et al. 2001).



Key to Lithofacies






-  Barrier and sand dunes
-  Estuary mouth and backbarrier sands
-  Estuarine and flood-plain muds
-  Levees
-  Fluvial delta and channel sands

Figure 2.2: Diagram showing the facies distribution in the Shoalhaven delta (Thom and Roy, 1985).

Other studies based on the sedimentation and formation of estuarine systems, have confirmed Holocene sea level depositional theories in estuaries similar to the Shoalhaven. Lin and Melville (1993) stated that pyrite is able to accumulate in early stages where there is an intertidal environment corresponding to a relatively open estuary entrance in their study of the Clarence system, while Woodroffe et al. (1989) described macrotidal estuaries, such as the South Alligator River of the Northern Territory, as being typically set within extensive Holocene sedimentary plains which indicate the infilling of pre-existing basins and valleys that were flooded by Holocene sea-level rise.

Following reconstruction of the environmental change that has occurred in the Shoalhaven area by use of radiocarbon dating, and detailed stratigraphy, macrofossil and microfossil analysis, Umitsu et al. (2001) have described the estuary formation as one that consisted of a transition from brackish conditions to freshwater alluvial sedimentation. A transition from marine to freshwater diatoms within core material supports the concept of continued sedimentation under freshwater conditions after the exclusion of tidal influence from the plains (Umitsu et al. 2001).

2.6 Problems associated with ASS

If left undisturbed, coastal ASS are harmless, however disturbance by excavation or drainage exposes sulfidic compounds in the soil to air, which results in the formation of sulfuric acid in large quantities (Fitzpatrick et al. 1998). Pyritic material that is excavated is oxidised a lot faster, and produces a much lower pH than the same sort of material in situ (Dent 1986). When excavated material is left on the sides of the drains, the pyritic material will quickly acidify and leach acid water as well as nutrients back into the drain (Robertson et al. 1998). Seepage and runoff waters from soils forming in sulphide-bearing dredge materials can have dramatic and lasting effects on the quality of water if placed adjacent to open water or drains and do not have adequate containment (Demas et al. 2004).

Disturbance of ASS for flood mitigation, urban development and agricultural production has acidified large areas of coastal catchments across the nation with significant environmental, social and economic impacts (Fitzpatrick et al. 1998). In general, acid sulfate soils become an issue when oxidation products are transported from the soil profile into the nearby streams and estuaries, potentially severely affecting the ecology, biodiversity, economic development and aesthetics of all adjacent waterways (Green et al. 2006). Issues with acid sulfate soils were initially recognised in 1987 with a link between acid sulfate soils and a history of water quality problems and fish kills in particular areas in coastal NSW (Tulau 2007). These fish kills are recognised as an immediate and

recognisable response to many acidification events. However, there are also a number of other direct and indirect impacts that are less obvious but more significant (Sammut et al. 1995). Acid water disrupts the ability of fish populations to recover and affects the habitat of all aquatic life with the eventual precipitation of iron oxyhydroxides smothering streambeds and creating a life threatening low pH (Sammut et al. 2004). Many varieties of vegetation are also affected by acid waters as many species in estuarine environments are unable to tolerate such a low pH. The re-colonization of native species is commonly prohibited, and resultant abandoned spoil dumps from dredging may remain bare for years before they become colonized by invasive species later (Ohimain et al. 2004). Thus, the acidification of estuarine tributaries is a major threat to the recreational, commercial and conservation value of aquatic ecosystems (Sammut et al. 1995). These observable problems are produced as a result of elements, such as iron and aluminium, being produced in toxic quantities. Silica and other compounds dissolved from ASS by acid may also result in algal blooms (Tulau 1999b). Additionally, some pyrite crystals may be contaminated with toxic heavy metals, such as nickel, copper or lead, which can together with acidity pollute the surrounding areas when pyrite eventually oxidises and disintegrates (Shamshuddin et al. 2004).

Due to the increasing population density of coastal communities in Australia, acid sulfate soils are progressively becoming a cause of problems affecting construction and urbanisation as the acidity that is released has the potential to produce extremely aggressive soil conditions which give rise to corrosion of concrete and other construction material leading to subsequent high construction and maintenance costs (Atkinson 2000). The use of land as a form of income through agricultural production, such as cattle or sugar cane, is also associated with ASS problems. Drainage of agricultural land is often the cause of acid soil and water problems in not only Australia, but at locations around the world where crops are grown and pastures are used for a range of agricultural purposes since not all plants can tolerate high acid concentrations. Animal productivity due to decreases in pasture quality and uptake of aluminium and iron by grazing animals may also potentially occur (EPA 2007).

As well as those impacts previously discussed, the presence of acid sulfate soil materials often produces an offensive odour due to the extensive amounts of sulphides in the soil (EPA 2007) and a cloudy blue colour (see Figure 2.3). Thus acid sulfate soils also affect the natural amenity and aesthetics of the environment by its unbecoming effects on natural or manmade waterways.



Figure 2.3: Photograph of P3D6 (6) displaying the blue colour that may potentially be produced by the presence of acid sulfate soils (taken 10 July).

2.7 The Use of Flood Mitigation Drains

Heavy rainfall events often result in flooding of agriculturally important land as plant requirements are exceeded and soil becomes saturated. Pastures suffer the longer this water is present. Therefore, it is essential for landowners to have a carefully designed drainage system in place to ensure the long-term productivity of the land and continued health of the associated waterways (Robertson et al. 1998).

The NSW Government has had a recorded involvement in flood mitigation and drainage used in the ‘reclamation’ of dry land from at least the 1890’s, and has assisted in draining large areas of NSW coastal floodplains under the provisions of the *Water and Drainage Act 1902* (NSW) from the early 1900’s with projects beginning on the Tweed coast, Byron, Clarence and Richmond areas, as well as in other regions by as early as 1907 (National Government 2011). Major construction of drainage and flood mitigation works commenced in the 1960’s (Tulau 1999a). A commonly used flood mitigation technique in coastal areas of Australia, like the Shoalhaven (a NSW coastal catchment recognised as a flood prone location), during the late 1960’s, was the installation of one-way floodgates on flood mitigation drains (Indraratna et al. 2005). Following the introduction of this technique, a system of flood mitigation channels, flood gates (see Figure 2.4) and bridges was constructed on the Shoalhaven River floodplain in the early 1970’s to assist in the control of floodwaters and tidal inundation of the surrounding land, much of which is used for farming.



Figure 2.4: Photograph of flood gate P10G1 on the Crookhaven River (taken 10 August 2012).

The role of land drainage in causing problems with acid sulfate soils is frequently misunderstood according to Melville and White (2007). Many areas of valuable drought reserve have been drained and ruined for grazing or any other agricultural purpose because the issues with acid sulfate soils were not understood (Robertson et al. 1998). However, Dent (1986) identified that the formation of acid sulfate soils is directly related to the formation of pyrite in a waterlogged environment and subsequently, the oxidation of this pyrite following natural or artificial drainage. The pyritic layer is stable while submerged under the watertable in a natural estuarine floodplain but becomes oxidised when exposed following drainage and subsequent lowering of the watertable (Morgan 2006). Thus, it has been recognised that it is drainage, much like what has occurred in the Shoalhaven catchment area, which gives rise to the exacerbated problems with acid sulfate soils. Flood mitigation and drainage schemes with one-way tidal flap-gates to prevent tidal ingress have greatly increased the rates of outflow of acidic water from estuary floodplains with well-developed natural levees (Melville and White 2007). Also, with subsequent routine maintenance of the drains, sulfidic material is commonly being scraped up along with cleared sediment. When this material is left on the bank, as it often is, it will acidify and leach acid water as well as nutrients back into the drain (S.C. Council 2011), polluting the waterways.

Many of the problems related to acid sulfate soils are caused by historical drainage. The greatest challenge now is to manage existing drains, floodgates and other associated structures, and also to facilitate the remediation of previously drained areas (Tulau 1999a).

2.8 Methods for testing Acidity

There have been an ever-expanding number of studies centred upon acid sulfate soils, their characteristics and remediation. The common feature among these is the need for some indication or measurement of acidity or oxidisable content as well as information pertaining to specific mineral constituents. Thus, a wide range of methods for testing the acidity of these types of soils may be discussed (see Appendix 4).

2.9 Global Management of ASS

Across the world, specific locations have been exposed to the problems associated with ASS, and subsequently there have been a range of alternative approaches developed to address their management. In countries such as the USA, Spain and China, high levels of acid sulfate soils have been addressed in different ways giving rise to the justification that not all cases can be remediated or treated in the same way.

In the mid-Atlantic region of the USA, the Stafford Regional airport, Virginia, suffered major acid rock drainage problems following excavation of sulfidic materials for construction purposes. In this particular instance, the site was primarily treated with lime-stabilised bio-solids, as well as straw-mulch, and acid- and salt-tolerant legumes and grasses, which resulted in a fully revegetated site (>90% cover) later that same year (Orndorff et al. 2008). There has also been increasing interest in utilising industrial residues for remediation purposes. Lin et al. (2004) conducted investigations into the acid neutralising capacity and potential beneficial uses of two different bauxite residues (red mud). Results indicated that the acid neutralising capacity is greater in red mud disposed of using a dry stacking method at the Pingguo Alumina Refinery in China as opposed to in the red mud disposed of by a wet method using seawater at the Queensland Alumina Ltd Refinery in Australia. Experiments conducted by Lin et al. (2004) also revealed that red mud may be superior to lime for treating potential acid sulfate soils, which contain sulphide minerals that could take an extended amount of time to oxidise and release soluble acid.

To add to these overseas cases and the occurrence of acid sulfate soils in regions other than coastal areas, Gilbert et al. (2003) researched and evaluated the use of municipal compost/limestone/iron mixtures as filling material for permeable reactive barriers (PRB) used for in-situ acid mine drainage treatment after comparing the alternative approach of metal precipitation by bacterially in-situ-generated sulphides to current techniques involving ex-situ chemical treatment which commonly uses alkaline agents to promote metal precipitation. This study made apparent the fact that not all methods may be used in all ASS environments, and the development of large-scale biotechnologies

such as PRB is inseparable from the supply and cost of raw materials, mostly wastes from other activities such as agriculture.

2.10 Management in Australia and the Shoalhaven

Although previously recognised as an environmental issue, serious research in Australia and NSW was not conducted on acid sulfate soil until major fish kills occurred in the 1980's in a number of NSW coastal rivers. Most of the attempts that have been made over time to address impacts in agricultural areas have revolved around floodgate management and modifications, and strategies to contain acid in the soil profile (Tulau and Henderson year unknown). Since problems and inhibitions have become apparent with historical resolutions, several techniques have been researched and developed that either prevent pyrite oxidation or remediate the resultant acidic drain-water or remediate the acidic groundwater (Indraratna et al. 2005).

In the Shoalhaven region and surrounding areas there have been a number of studies carried out on experimental procedures used to address the remediation or prevention of acidic soil and water in the drains. These have included procedures pertaining to the installation of weirs (Indraratna et al. 2005; Golab and Indraratna 2009; see Figure 2.5) and the placement of concrete slabs in drainage areas of the Manildra property to act as permeable barriers to acidic waters (Regmi et al. 2009; Indraratna et al. 2011).

Golab and Indraratna (2009) detailed what they described as four distinct remediation strategies that have been developed to tackle the issue of acidification by ASS in the area of the Broughton Creek floodplain. These four strategies encompass the major strategies that are described and applied in many further experimental or research papers. The first of these is the use of simple V-notch weirs that aim to raise water tables thus keeping pyrite submerged (see Figure 2.5). Indraratna et al. (2005) considered this method to prevent the oxidation of pyrite and found that following installation of weirs, rates of discharge of acidic oxidation products from the groundwater to the drain were reduced, but quality of groundwater and soil were not substantially improved. At a Maloney's drain study site, a location found within a small tidal tributary of the Clarence river estuary, Johnston et al. (2004b) similarly demonstrated that a constructed weir can be an effective way to reduce acid flux where the primary hydrological path for acid is through groundwater seepage. However, within that study it was also noted that the use of a weir may not actually prevent the continuation of sulphide oxidation (Johnston et al. 2004b). Indraratna et al. (2005) also investigated another of Golab and Indraratna's described remediation strategies. Golab and Indraratna (2009) stated that modified two way floodgates are able to be used by allowing the tidal

inflow of water into drains, therefore allowing for the buffering of acidity before water enters the river systems and the raising of watertables surrounding drains. Indraratna et al. (2005) recorded an improvement in mean drain water quality after floodgate modifications were made. The third distinct strategy involves the use of lateral impermeable lime barriers designed to prevent oxidation of pyrite by halting the downward movement of oxygen into the soil and also neutralising the acidity in the groundwater (Golab and Indraratna 2009). The final remediation strategy described by Golab and Indraratna (2009) which has been gaining recognition of late is the use of permeable reactive barriers that passively intercept the groundwater flow and neutralise the acidity. In recent years, permeable reactive barriers filled with waste concrete have received increased attention as an innovative, cost-effective technology used for the passive in situ clean-up of groundwater contamination (Regmi et al. 2009). Following this statement, Indraratna et al. (2011) were able to obtain conformational results by demonstrating the use of a pilot permeable reactive barrier that showed that the selection of recycled concrete performed well by neutralising large volumes of acidity and removing Al and Fe from solution without leaching harmful ions into the groundwater. Prior to this work, Indraratna and Glamore (2004) also applied a 2-stage flood estimation and water quality decision support tool to the Broughton Creek floodplain, near Berry, NSW which aimed to modify floodgates in order to restore tidal flushing, which ultimately resulted in the presentation of a model that may be applied to similar sites across Australia to predict the water quality and flood estimation within low-lying flood mitigation drains.



Figure 2.5: Photograph taken of a weir installed within drain P6D8a that has become overgrown with drain vegetation (taken 10 July 2012).

Another remediation technique described in the literature is that of the use of some form of barrier involving lime. Indraratna et al. (2006) found that an optimal mixture of lime, fly ash and water to form a slurry was effective in the installation of a horizontal alkaline barrier above the pyritic layer to stop infiltration of oxygen and treat acidity. Lime-fly ash barriers have been deemed effective in remediating acid sulfate soils in regions where floodgates and weirs are not a viable option, such as the land affected by ASS near Berry, NSW, Australia, and as opposed to floodgates which treat products after discharge into drains, the lime-fly ash barrier treats acid sulfate soils and subsequent environmental problems prior to them occurring (Banasiak 2004).

In other areas of Australia, there are also further cases of management options that have been explored. In relation to affected water, Green et al. (2008) conducted a study using a closed tank reactor filled with limestone aggregates which was constructed adjacent to an outlet drain from a 100 hectare sugar cane farm on the Tweed river estuary, a sub catchment of tidal McLeod's Creek far north coastal NSW. This method was developed as a means to treat acidic drainage water using the principles of oxic and anoxic limestone drainage systems to increase alkalinity produced from limestone dissolution (Green et al. 2008). Current research centred on long term remediation of the Tweed estuary aims to explore the possibility of restoring natural tidal exchange as a means to exploit natural processes to effectively remediate acidified coastal environments like the Clarence and Richmond estuaries (Australian Research Council 2011 - 2013).

Rather than treating or undergoing remediation programs for managing acid sulfate materials, there have been noted cases in Australia where dredge material has been disposed of in an alternative way. Clark and McConchie (2004) explored the process of sediment disposal sub-aerially, as well as changes to sulfur species distribution, degree of pyritisation and degree of sulfidisation, basing their research on the mixed near-shore and in-water dredge spoil paddocks at the Port of Brisbane Authority's reclamation paddocks at Fisherman Islands. The disposal method analysed imparts to dredge spoil a strong grain-size separation as a result of spoil being pumped in at the western end of the paddock and excess water discharged through weir boxes along the eastern edge. Sediments exposed to this process undergo subsequent diagenesis with resulting sulphide production (Clark and McConchie 2004). In Western Australia, south of Perth at the Peel Inlet, Hegge and Shute (2005) described marine disposal in conjunction with water quality monitoring the most suitable option for disposing of material derived from maintenance dredging of the channels. While this material did not indicate actual acidity, all test sites exhibited significant potential acidity and exceeded the Queensland action criteria for total sulfur (Hegge and Shute 2005), thus it becomes evident that the potential soils may not be obvious and must also be disposed of in an appropriate manner.

2.11 The Use of Agricultural Lime for neutralisation

In order to manage the production and presence of acidic sulfate soils in coastal environments, some form of neutralisation method is required to ensure that the pH of soil does not remain at low, toxic levels. It has been found that 1 ton of pyrite yields 1.6 ton of pure sulfuric acid (Melville and White 2007).

When neutralising soil, it is essential to provide adequate neutralising material to neutralise all acid that may be produced and to bring the pH of the soil to above 5.5 (Ahern 1998a). The final pH of the soil, nevertheless, depends not only on the amount of pyrite but also the buffering capacity of the soil (Bloomfield and Coulter 1974). Therefore there are a number of factors such as soil characteristics, including buffering capacity, that need to be taken into account when assessing the level of neutralisation required for different materials. Acidity can evidently be neutralised and corrected by liming due to the fact that it is a basic material, and acid sulfate soils have been successfully reclaimed in Europe where lime is cheap relative to the value of land (Bloomfield and Coulter 1974). Around the same time this reclamation finding was made, after measuring the rates at which pyrite oxidised in undisturbed cores of limed and un-limed soil, it was concluded that oxidation is in fact inhibited by liming (Trafford et al. 1973). Thus, liming of soils, particularly spoil mounds, and drain waters was one of the first strategies used to address the effects of ASS (Tulau 2007). However, while liming has long been recognised as a means to combat problems of rising acidity, there have also long been conflicting views on its effectiveness and amounts required for different materials. The use of liming has been described as generally limited and strategic only, such as to assist scald vegetation and treating drain spoil (Tulau 2007). In this case, we are only using lime for treatment of dredged material, thus its use may be justified and deemed effective.

The use of lime has been described along with bicarbonate in sea water as a commonly used neutralising agent (Atkinson 2000; Tulau 2007). Marine waters have a neutralising capacity up to 2 moles of H^+ per cubic metre of water (Melville and White 2007); however, while seawater neutralisation is possible only in lower estuaries, neutralisation with lime is described as a high cost alternative which has strategic options only (Atkinson 2000). In cases where liming rates have been calculated based on the amount of pyrite, or sulfates in the soil, or the amount of oxidation that occurs, quantities deemed effective have been variously estimated at anything from 4 to about 100 tons of $CaCO_3$ per hectare, however there is a dearth of critical field experiments for determining the optimum amounts (Bloomfield and Coulter 1974; see Section 2.8). Following this finding, Bloomfield and Coulter (1974) stated that calculations of lime requirements based on the pH of acid sulfate soils shows the need for enormous and generally quite uneconomic quantities. Melville and White's

(2007) findings agree with this statement, as they acknowledged that even if it were physically possible to apply the 3:1 lime:acid ratio required to neutralise existing acidity, it is indeed economically impractical. This ratio was also declared necessary by Dent (1986), with the description of one part by mass of pyrite sulfur being neutralised by 3 parts of calcium carbonate. In areas where large amounts of land are being treated, it is possible to neutralise sulfuric acid with agricultural lime, however again, it is very costly for land that is badly affected (Sammut et al. 2004). With neutralisation, the total cost of farming is also increased. However, a return on investment may also be expected with improved pastures.

Problems that occur with liming and its effectiveness arise from limited penetration of material and the predominant discharge from subsoils and groundwater (Tulau 2007). In addition, soils that may still have reserves of pyrite require large amounts of lime and it must be incorporated through rooting (Dent 1986). However, liming still may be an effective option for selected circumstances. Dent (1986) also stated that in old ASS where oxidation of pyrite is complete, a significant crop response to quite small applications of lime and fertiliser may be possible, while Talau (2007) has described instances where liming of drain banks at the point of groundwater discharge has demonstrated beneficial results, with reported increases of > 3 pH units as well as the fact that liming can be effective where subsurface cuts are required.

In terms of actually applying sufficient amounts of lime to soil, response to lime and fertiliser depends on the fertility of the soil and also the presence of natural calcium carbonate. In the absence of naturally-occurring calcium carbonate, total reclamation of acid sulfate soils will involve the processes of drainage, leaching of acid and soluble salts, and the incorporation of lime and fertiliser to remedy the actual acidity and nutrient deficiencies (Dent 1986). Dent (1986) has provided a valuable resource for introducing the production of limestone requirements as he describes the oxidisable sulfur content (usually percentage of dry mass), vertical distribution, apparent density of the soil and required rooting depth as factors that should be taken into account when applying 3.1 kg of pure CaCO_3 to neutralise every 1 kg of oxidisable sulfur. This also fits in with the 3:1 lime to acid ratio that was previously described. However, he has also claimed that there is an excellent response to nitrogen and phosphate in combination with lime applications at much lower than the full lime requirement (Dent 1986).

While liming is able to raise pH of dredged material, it does not target other problems that may arise with acid sulfate soils, thus further precautions or methods are required for problems of greater scope.

Quantities of lime to be used in the case of the Shoalhaven floodplain and its dredged drain material, have been described in the Shoalhaven City Council routine maintenance of flood mitigation drainage structures REF document (September 2011) in accordance with ASS management guidelines (Ahern et al. 1998a) and Acid Sulfate Soils Drainage Guidelines (Robertson et al. 1998). Ahern et al. (1998a) have produced a table that gives an indication or an estimation of the total quantity of lime involved if the total volume or mass of disturbed ASS is known and relevant soil analysis has been performed. The Shoalhaven City Council has indicated that lime shall be applied at the rate specified in a 'Look up table' produced by Rayment et al. (2001) for an oxidised field pH of 2.10. However, even before this preliminary rate is employed soil characterisation is necessary to categorize soils as clay, silt or sand. In order to modify these rates, sediment sampling and laboratory testing of pH will occur as part of this and further studies.

Additionally, in management plans which involve liming, an engineering safety factor of at least 1.5 – 2 times the theoretical lime requirements is deemed necessary to allow for the slow reactivity of lime and non-homogenous mixing in the field (Ahern et al. 1998).

While agricultural lime has been previously used in Australia as an appropriate means to neutralise acid sulfate material and has been deemed effective, there are known alternative ways to neutralise soils. For example, in Spain, Vidal et al. (2006) tested an acid soil with various calcareous amendments including limestone, dolomite, gypsum and sugar foam waste to compare the liming efficiency and effects of each material. This study found that sugar foam and dolomite were the most alkalizing treatments based on leachate parameters, with the sugar foam being the material with the highest soil liming efficiency due to the highest pH values it produced.

2.12 National Management Guidelines

Acid sulfate soils have been found across a great deal of Australia. There have been a number of documents that have been produced in order to manage and monitor the disturbance of these soils. As well as the National Strategy for the Management of Coastal Acid Sulfate Soils, prepared by the National Working Party on Acid Sulfate Soils (2000), there are also detailed guidelines that have been produced by and for separate states and territories.

In NSW in particular, where cases of acid sulfate soils have been found in every coastal estuary and embayment between the Victorian and Queensland borders (Stone et al. 1998), the most comprehensive document used for management and assessment is the Acid Sulfate Soil Manual, published by the NSW Acid Sulfate Soil Management Advisory Committee (formed in 1994 to coordinate government response) in August, 1998. This complete manual forms part of an 'all of

Government' approach to the management of acid sulfate soils in New South Wales (Stone et al. 1998). The manual consists of individual documents including those related to assessment guidelines, laboratory methods guidelines and drainage guidelines, as well as other types of guidelines for additional procedures. To accompany the manual, copies of ASS risks maps and ASS planning maps are also available for use. This general manual and its accompanying documents are to be used for management of ASS state-wide. However, similar documents from other jurisdictions, such as the Guidelines for sampling and analysis of Lowland ASS in Queensland (Ahern et al. 1998) are very useful sources for additional management information.

The NSW ASS manual has been utilised for this project to ensure that suggested management is in accordance with state guidelines and requirements.

3. Materials and Methods

3.1 Site Description

3.1.1 Introduction

This study was conducted in the Shoalhaven local council area. Flood mitigation drains installed in the area as a flood precaution formed the basis for fieldwork and are located throughout the whole Shoalhaven River estuary as identified by the council. Actual sites where samples were collected were chosen based on the nature of complaints in the area and accessibility.

3.1.2 Location and description

The Shoalhaven River is located on the south coast of NSW, Australia, approximately 150 km (2 hours) south of Sydney. The Shoalhaven catchment is approximately 300 km long extending from Braidwood, and travelling north easterly to where it meets the Pacific Ocean east of Nowra. The majority of the upper catchment is found in national park areas, with land uses including wool and cattle production and is managed by the Sydney Catchment Authority (Ocean Watch year unknown). The Shoalhaven River estuary situated on the floodplain of the catchment represents a much smaller area which encompasses the Shoalhaven River and its tributaries. The catchment area drained by the Shoalhaven River has an area of approximately 9260 km² (Umitsu et al. 2001) while the mature, barrier estuary has an area of approximately 32 km² and an average depth of 2.9 m (DEH 2012). An extensive floodplain extends on both the south and north side of the Shoalhaven River (Blunden 2000).

3.1.3 Soils and Geology

In terms of the soil landscape of the broad Shoalhaven area, all sub-areas show severe limitations in terms of acidity as part of the whole fluvial landscape. The Shoalhaven locality consists of a level to undulating active floodplain with small levees, minor depressions and backwater swamps on the coastal Plain, with minimal relief and slope (Hazelton 1992). Due to residential and mainly grazing on pastures as the primary forms of land use, natural vegetation has almost all been cleared with remaining scattered decorative paperbark, swamp oak (casuarinas), Illawarra flame tree on terraces and a range of weeds and reeds in swamps and drains. Hazelton (1992) has also described the floodplain as exhibiting a complex soil pattern consisting of levees, lower terraces, upper terraces and the actual floodplain, subject to various types of erosion during flooding. The soils found in the Shoalhaven floodplain locality include hardsetting, dark sandy loam (topsoil), weakly pedal clay loam (subsoil), massive sandy clay (subsoil) and moderately pedal light medium clay, all with a pH

between 4 and 5, confirming that the landscape has limitations in terms of its extensive actual and potential acid sulfate soils (Hazelton 1992).

The catchment is found above the Palaeozoic Lachlan Fold Belt, which comprises Ordovician metasediments, Siluro-Devonian volcanics and Devonian granites (Umitsu et al. 2001). The geology consists of alluvium, including forms of gravel, sand, silt and clay derived primarily from sandstone and shale overlying the buried estuarine sediments derived from the coastal environment (Hazelton 1992). The unconsolidated sediments of the floodplain are underlain by Berry Siltstone and Nowra Sandstone (Blunden 2000), which are characteristic Permo-Triassic sandstones and siltstones of the southern Sydney Basin (Umitsu et al. 2001).

3.1.4 Climate

The Shoalhaven Council local Government area within which this project was conducted is classified as a temperate climatic zone that is subject to a warm summer and cold winter (BOM updated 2012). The average annual rainfall since 2000, based on data from the Nowra air station is 854 mm/year with the highest average recorded in February. Mean temperatures range between 6.6°C and 27.5°C over the course of the year (BOM updated 2012).

3.1.5 Land Use

The Shoalhaven river estuary supports cattle industries, conservation reserves, urban areas, commercial fishing and recreational use as well as scenic and indigenous significant areas (Umwelt 2006). While agriculture plays a large role in the area, the overall Shoalhaven region is an urbanised environment with a growing population.

3.1.6 Study Sites

As of 30th June 2005, the flood mitigation system consisted of 50 flood mitigation drains with a total length of 48.5 km within the Shoalhaven floodplain in the localities of Worrigee Swamp, Jorams Creek, Bolong, Numbaa, Berry / Far Meadow, Brundee, Pyree, Comonderry / Coolangatta, Saltwater Creek and Nowra (S.C. Council 2011). For the purposes of this study, samples were collected from 17 of the total 50 drains with focus based around the Far Meadow and Comonderry areas as these are the areas with the highest level of land occupier complaints and maintenance requirements (see Figure 3.1).

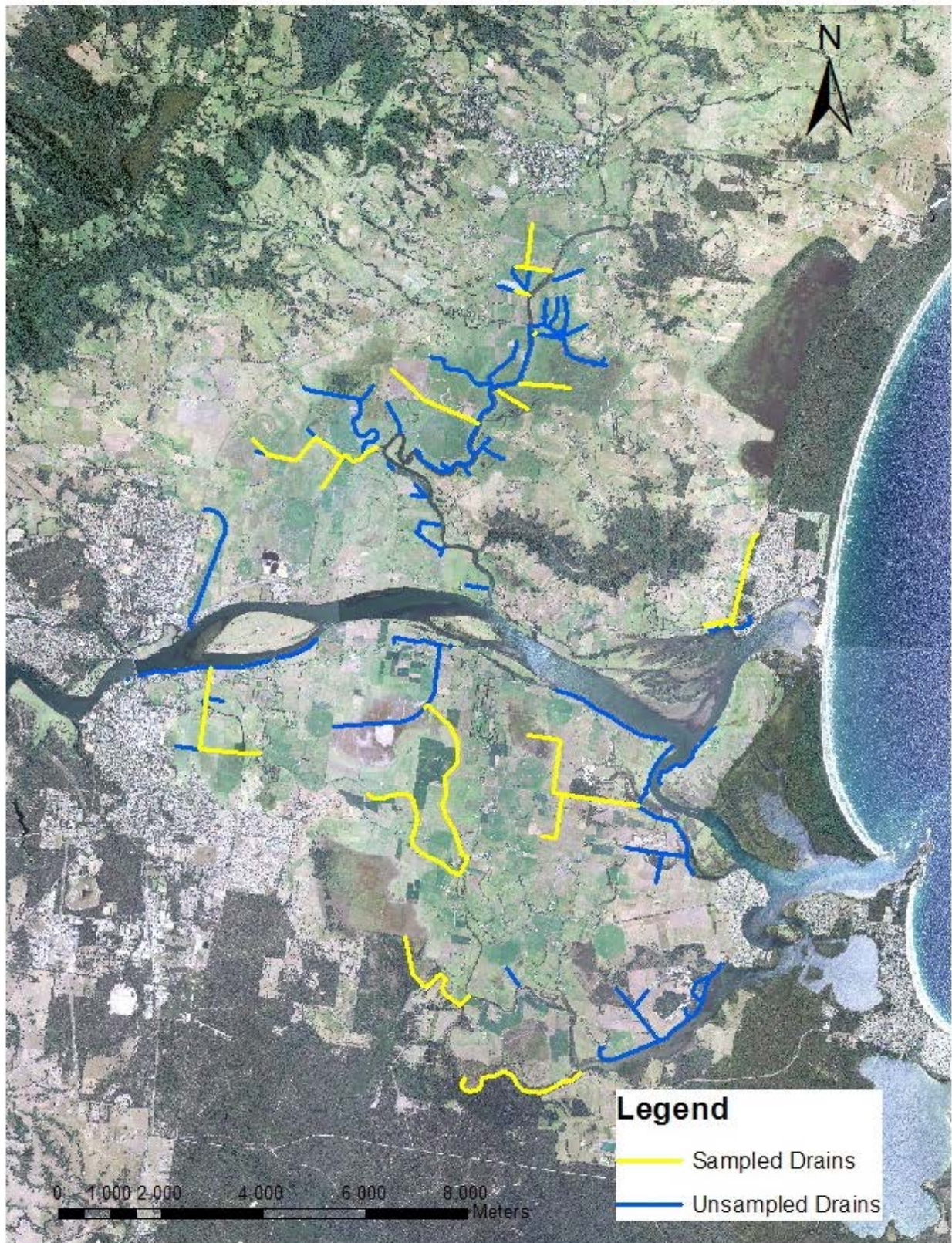


Figure 3.1: Map displaying the entire region that forms the area of study. The 17 drains from which samples were collected, as well as those drains that were not visited, have been highlighted (Data used © Shetland City Council).

3.1.7 Flora and Fauna

In the area where samples were collected, work was primarily conducted in grassed, paddocked areas or on creek banks. There was agricultural stock close to many of the drains (mainly cattle). Drains differed in the amount of vegetation they had growing within and around the drain. For example, some had a lot of reeds and weeds in the drain, and some bigger drains had large trees growing alongside them (see Figure 3.2).

Vegetation present at study sites includes bulrush/cumbungi and common reeds (*Phragmites*) as well as other macrophytes.



Figure 3.2: Photographs showing different types of vegetation that were observed in the field and the extent of overgrowth that has entered the drains (picture one is from P6D8 (2) and picture two is from P6D7, both taken 10 July 2012).

The area that was studied for purposes of the Shoalhaven city council maintenance activities has also been identified as a habitat for the threatened species Green and Golden Bell Frog (*Litoria aurea*). The whole of the drainage system is registered as key fish habitat by the Department of Primary Industries.

3.2 Field procedures

3.2.1 Initial Site Visit

Field work started with an initial site visit that allowed an introduction to the site and enabled an understanding of the observable problem with the drains which are located within the Shoalhaven catchment to be developed. On this first visit to the site, major drains and easily accessible southern

drains were visited. The problems with overgrown vegetation were observed and the site logistics were noted in order to prepare for sampling.

3.2.2 Location of field work

While conducting field work, particular areas where samples were taken were determined by prioritising drains where landholder complaints had been made to the council. These complaints centred around the loss of cattle that has been experienced due to cattle movement and subsequent bogging in weed that has overgrown the drains, as well as overflow of water into paddocks that has occurred due to blockages and lack of water flow. The routine maintenance that has been deemed necessary and gives rise to the need for this study, has been classified as including activities that are unlikely to have any significant impact on threatened species like the Green and Golden Bell Frog.

Due to the requirement for Council to urgently respond to landholder complaints and concerns, the Far Meadow and Comonderry areas of the Shoalhaven catchment have been identified as key sites for this study. These sites correspond to the high density of drains that are located in the northern most part of the greater study area. While these areas will be of highest priority due to the severity of acid sulfate soil problems that are evident, drains found on the southern side of the catchment were also sampled to allow comparisons. A total of 65 samples were collected from 17 different drains (see Figure 3.3).

Sites that required access to privately owned land were accessed following contact with landholders through Council contacts.

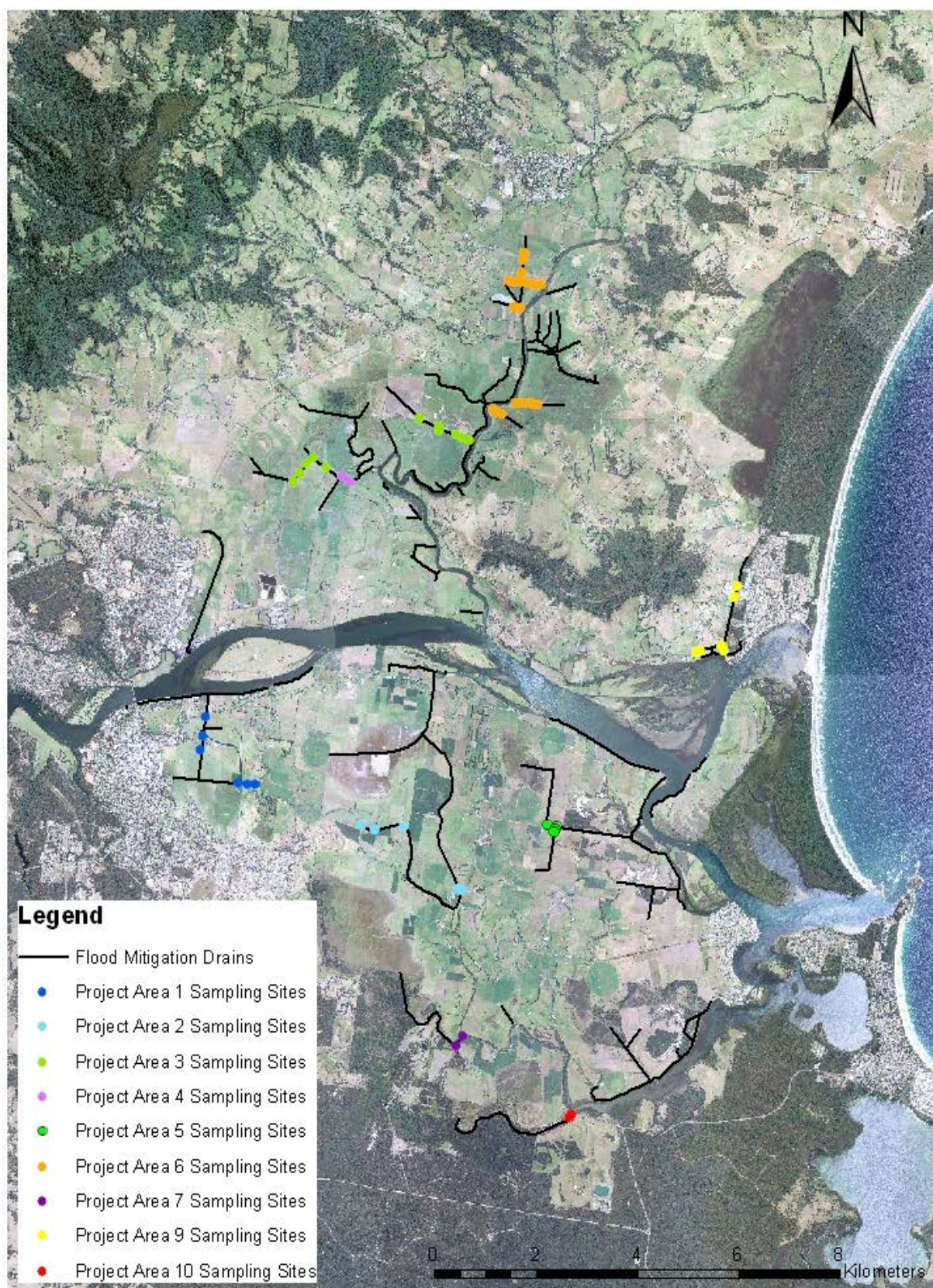


Figure 3.3: Map displaying all locations at which samples were collected. Sites are differentiated based on the project area within which they are found (Aerial photo and drain data © Shalhaven City Council).

3.2.3 Soil Sampling

Soil sampling was conducted over 3 days (see Table 1 for dates and drains sampled) with the same method being carried out for each drain. Beginning from one end of the drain the sampling team moved along the drain, walking along the banks. Samples were taken at intervals along the drain. These intervals were not uniform and depended on accessibility and safety of the drain, as well as the individual drain characteristics (i.e. if high levels of acidity were observed due to the physical features of the drain or it was a high complaint drain, then more samples were taken).



Figure 3.4: Photograph taken showing sampling technique at P6D3, sampling location 3 (taken 10 July 2012).

Samples were taken by use of a drill pole pushed as far into the bottom sediments as possible (see Figure 3.4). Samples were taken as close as possible to the centre of the drain. Once material was enclosed in the pole, the lever was pulled up and the pole removed from the drain. A small labelled sample bag was placed over the end of the pole and the lever released in order to empty the content of the pole into the bag. Any excess water was drained from the bag. Samples from each separate drain were grouped together and all samples were returned to the University where they were placed into a cold room for storage, following the completion of each sampling day.

Table 1: Days of sampling (Day 1: 10 July 2012, Day 2: 23 July 2012, Day 3: 10 August 2012) upon which each drain was visited and the number of samples collected from each separate drain (please note: a very small number of samples were not analysed due to limited amounts of viable material).

Sampling Day	Drain	Number of samples
1	P6D4	4
1	P6D3	7
1	P6D8	8
1	P6D8a	5
1	P6D7	3
1	P3D6	6
2	P3D1	5
2	P4D1	2
2	P9D2	2
2	P9D1	4
2	P1D1	6
3	P2G1	3
3	P7D1	2
3	P10D1	2
3	P2D2	2
3	P5D1	2
3	P5D2	2

3.3 Laboratory Procedures

Samples were kept within their sample bags in a cold room at the University of Wollongong until they were required.

3.3.1 Grain Size Analysis

Following the first day of sampling, samples were taken into the Sedimentology laboratory. Within this laboratory, a very small amount of sample (more if sand) was placed into small, labelled, plastic sample jars. These diluted samples were then individually sifted to remove any large organic

material, placed into a beaker full of water and run through a Mastersizer machine in order to determine grain size.

Grain size was analysed in order to classify each sample as predominantly clay, silt or sand, as liming requirements differ based on the type of soil. For each sample, three analyses were taken as well as an average that gave the percentages of clay, silt and sand in each sample.

Relevant data from each sample was kept in a datasheet on the Mastersizer computer before it was exported to Microsoft Excel and graphs were produced displaying the frequency percentage by volume for the range of different particle diameters (microns) of each sample. These were then able to be used for comparison of grain size in different areas.

3.3.2 Mineral Analysis – XRD and XRF

Following the oven drying (60°C) in labelled aluminium pie cases, samples were crushed using a Tema rock crushing machine. Each individual sample was placed into the Tema, and the machine was run for approximately 10 – 15 seconds until the sample resembled fine talcum powder. Small labelled sample bags were used to store crushed samples. Between each use of the Tema, the machine was cleaned using wet paper towel to remove any residue from the last sample. If any samples appeared to contain high levels of clay and residue proved difficult to remove, cleaning sand was crushed in order to clean the Tema. The paint brush used to transfer material between the Tema and sample bags via thin paper was also cleaned using compressed air between each use to avoid contamination between samples.

Following crushing, approximately 0.5 grams of each sample was processed through an X-ray - diffraction machine (XRD) to test for minerals present.

In order to carry out trace element analysis using X-ray fluorescence (XRF), pressed pellets were prepared and utilised. About 5.0 – 5.5 grams of powdered sample was measured in a paper cup and mixed with 10 – 11 drops of PVA solution (added as isolated drops) using a wooden stirrer, ensuring all large lumps were eliminated. The mixed sample was placed into an Al cup which was subsequently placed into the press cavity with the plunger lowered slowly to 2500 psi. Following pressing, the Al cup was removed and placed sample side up into a Perspex tray. Full Perspex trays were placed into an oven at 70°C for a minimum of 2 hours to dry the samples. Between each sample, the press cavity was cleaned using ethyl alcohol and paper towel to avoid any contamination between samples. Following drying, the samples were weighed (using tared Al cup) and weights

recorded on the cups. Samples were then placed back into the oven Al side up for storage until they could be placed into the XRF machine for analysis.

3.3.3 Hydrogen Peroxide Field Oxidation Test

The method used in order to measure pH of oxidised material removed from the Shoalhaven flood mitigation drains has been modified from the field peroxide pH test outlined in ASSMAC assessment guidelines (Ahern et al. 1998a) and the potential acidity method described by Blunden (2000). Testing was executed within laboratories of the School of Earth and Environmental Sciences at the University of Wollongong.

Prior to beginning experiments, pH of the 30 % hydrogen peroxide was tested by placing a suitable amount of the solution into a beaker. Adjustment of the hydrogen peroxide was conducted by adding a few drops of 0.1M sodium hydroxide if necessary in order to adjust pH to 4.5 – 5.5. To begin analysis, approximately 10 grams of each sample was placed into small centrifuge tubes. To this, 20 mL of 1M potassium chloride was added, along with 5 mL of the hydrogen peroxide 30% solution. This mixture was then shaken straight away, again after an hour and then left over night to fully react. Following reaction overnight, the tubes were given a small shake to ensure the reaction had gone to completion and left for approximately an hour to allow sediment to re-settle. The pH of all solutions were then tested and recorded.

In order to provide controls for the method, blanks were also prepared. For these blanks, the same procedure was followed, omitting the addition of sediment material. The pH values of these blank solutions were also tested the day following preparation.

3.3.4 Computer Analysis of Results

Following XRD analysis, all samples were corrected to the appropriate 2 theta spacings (26.66 for quartz) using Traces software before conducting Siroquant analysis. Siroquant Analysis involved creating a template with all expected major minerals to be found in the samples. This was altered based on initial results for each new sample. For each sample, background values were subtracted and analysis conducted until minimum chi-squared values were obtained. Results were then copied into excel for each successive sample. Microsoft excel tools were used to compare the spread of material found within samples from different drains and entire project areas.

From all trace element data that was obtained using XRF, further analysis was conducted on the levels of sulfur, chlorine, bromine, copper, lead and zinc found in all samples. Means were calculated and results compared between drains using tools found in Microsoft Excel.

3.3.5 Mapping

GIS techniques were used to produce a map of all drains in the Shoalhaven study area. Identification of the drains at which sampling was conducted was also performed using GIS mapping.

At each sampling location, a GPS was used to record the grid point location at which sediment was extracted. A sampling map was subsequently produced on an aerial photograph which showed the individual points at which samples were collected.

3.3.6 Liming Calculations

The calculation of lime required to neutralise material was carried out in 3 different ways based on the input data.

Following XRD, calculation was able to be carried out using the amount of pyrite found in each sample. The equations pertaining to the oxidation of pyrite and neutralisation of acid using carbonate in the form of limestone was utilised to obtain the molar application ratio of 1:2 pyrite: carbonate. Subsequently, the weight of limestone required to neutralise the acid produced from 1 tonne or 1 metre cubed of extracted material was calculated for each individual sample.

Following the analysis of trace elements using XRF technologies, calculations were carried out for determining the lime requirement based on the amount of elemental sulfur present. The sulfur values were utilised by predicting the potential amount of pyrite that could be produced, and thus the amount of acid that could be produced and the neutralisation that would be necessary. Once potential pyrite levels were determined, calculations could be conducted as with those from XRD analysis.

By obtaining the pH following oxidation of material within removed sediment for each of the samples, required neutralisation values were obtained by using the look-up table produced by Rayment et al. (2001) and contained in the S.C Council REF document (2011), which provides liming rates based on specific oxidised pH values.

4. Results

4.1 Introduction

This chapter aims to convey the major results and findings from this study. Results derived from analysis of grain size distribution, used to classify sediment, have been included as well as specific trace element concentrations from XRF analysis. Pyrite concentrations for each sample have been used to describe differences between project areas, while the oxidation test results are also used to display the range of pH values across sample locations. Using all this data as indications of acidity extent, lime application rates have been calculated using a number of different methods. Comparison between separate lime rates derived from the different acidity analyses have also been correlated and compared in terms of their uniformity.

4.2 Grain Size (Mastersizer data)

The grain size distribution in most samples ranges from approximately 0.5 micron to 1000 microns (see grain size data in Appendices 2 and 3). A few samples had a much smaller range with grain size ranging between approximately 0.5 microns to 225 microns (eg. P6D8 6; see Figure 4.1) to other distributions, with upper most sizes reaching around 2000 microns (P9D1 4; see Figure 4.1).

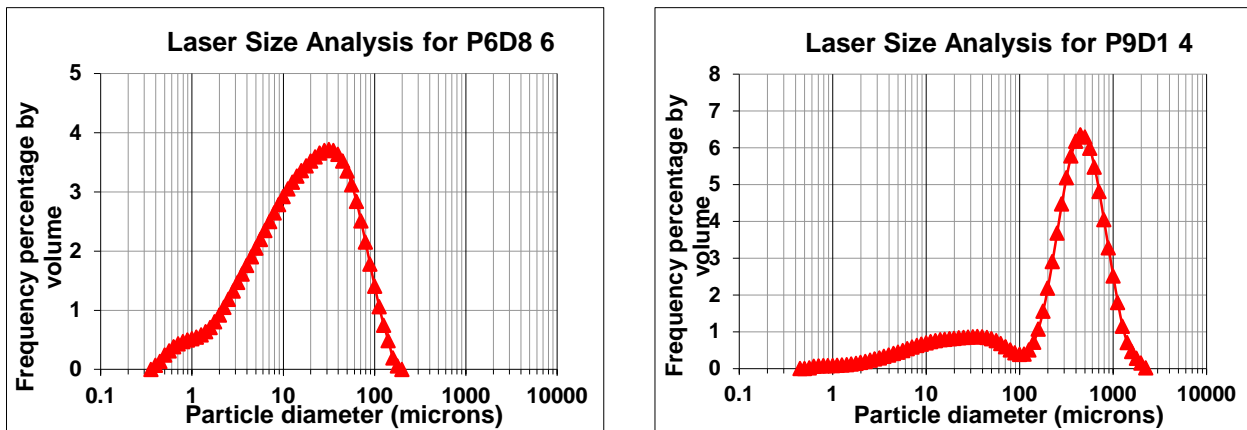


Figure 4.1: Grain size distribution for samples P6D8 (6) and P9D1 (4) with the frequency percentage by volume for different particle diameters (microns) shown.

The dominant grain size that was found in the samples was silt (3.9 – 63 μm). Even though some samples exhibited clay like textures in the field, no samples had clay as the highest grain size percentage. Using the USD soil classification scheme, all samples were classified based on levels of sand, silt and clay. Almost all samples were classified as silt loam, corresponding with a medium soil/sediment grain size. Due to the fact that a single liming requirement is desired for each project

area, area classifications have been based on the dominant or average classification of the drains in the area (see Table 2 for classifications for each area). These data should be treated with caution as due to the nature of sampling, differences between the exact sampling procedure attributed to exact locations and depths of extracted sediment within the same drains / areas may cause variation in the results.

Table 2: Soil classification for each project area based on average percentages of clay, silt and sand, and mean particle size found in each sample (ie. Most samples were silty loam, equal to medium sized grains).

Project Area	Mean % sand	Mean % silt	Mean % clay <4µm	Mean particle size (microns)	Mean Graphical Sorting (Std. Dev.)	Soil Classification
1 - Worigee Swamp	34.36	54.58	11.06	33.86	2.15	Medium
2 - Terara Swamp	30.01	60.47	9.52	31.17	2.12	Medium
3 - Joram's Creek	17.78	54.10	14.22	18.58	1.87	Medium
4 - Bolong Area	28.34	61.17	10.50	25.94	2.11	Medium
5 - Numbaa Area	59.92	34.64	5.43	89.48	1.95	Coarse
6 - Berry and Far Meadow	15.51	70.63	13.86	18.50	1.90	Medium
7 - Brundee Swamp	31.62	55.79	12.60	28.44	2.18	Medium
8 - Eelwine and Pyree areas	NO DATA					
9 - Comonderry - Coolanagatta area	39.74	38.55	8.07	92.57	2.31	Coarse
10 - Saltwater Creek	24.95	60.93	14.12	22.46	2.20	Medium

The areas that have been classified as containing coarse sediment (project areas 5 and 9) based on their higher levels of sand-sized material and greater mean particle size (see Table 2) are areas that are located at the eastern most side of the entire sampling region, closest to where the Shoalhaven River meets the ocean. These drains were also closer to, or part of, the widest or largest tributaries off the river. Thus they are closest to the source of sand for the area. Most samples from the east in these two areas contained at least 30 % sand.

All samples fell in to the categories of poorly sorted (σ_1 : 1.0 – 2.0) or even very poorly sorted (σ_1 : 2.0 – 4.0) following categorisation using standard deviation values, which are taken as a measure of the uniformity of grain size distribution. The smallest grain size distribution standard deviation across all samples is the one recorded for P5D2 (2) at 1.21 with the largest recorded for P6D8a (3) with a value of 2.78, thus indicating an average of poor sorting across the entire region with the samples containing sediment of many different particle sizes. This may be attributed to minimal water movement. The highest mean sorting value for project areas was calculated for the coarse material in the Comonderry – Coolangatta area at a value of 2.31 (see Table 2).

4.3 XRF (X-ray fluorescence) Trace Element Content

The results of the 61 samples analysed using X-Ray fluorescence trace element technology were compared to the NEPC (1999) National Environment Protection Council Guidelines and the Ontario contamination effects values (Fletcher et al. 2008) to determine whether any site is contaminated based on the levels of copper, lead and zinc. NEPC guidelines were also applied in analysing the levels of sulfur, indicative of an area of known acid sulfate soil existence. These guidelines and investigation levels aim to provide a national guiding principle for assessing possible contaminated land. The Schedule B document contains background levels, Health investigation levels (HILs) for areas such as recreation spaces and Interim Urban Ecological Levels (EILs), which were used for assessment in this study. The Ontario Ministry Guidelines SEL (severe effect level) values were applied to metal concentrations to determine if levels are high enough to be considered as detrimental to organisms and indicative of heavily contaminated sediment (Fletcher et al. 2008). The range of values in terms of different areas and elements were also analysed (see Table 3) to account for differences across the study area and identify possible sources of contamination.

Table 3: The highest and lowest concentration levels for each metal (copper, lead and zinc), the sampling locations at which they were found and the mean concentration (ppm) from all sites.

	Metals		
	copper	zinc	lead
Lowest concentration (ppm)	8.2	19	4.4
Sample number of lowest concentration	P5D2 2	P9D1 4	P9D1 3
Highest concentration (ppm)	52.7	192.5	30.5
Sample number of highest concentration	P6D8 3	P3D6 3	P1D1 1
Mean Concentration across all samples	25.7	123.9	15.6

4.3.1 Sulfur (S)

Of all elements that were detected during XRF analysis, sulfur generally showed the largest amounts on average for all drains. There was variation between samples from each individual drain as well as between different drains found in the same project area (see Table 4). The largest amount of sulfur for an individual sample was found in the Terara swamp area with a value of 113,600 ppm found in drain P2G1, at sample location 3 (see Figure 4.3). This large value gave rise to project area 2 having a much larger mean value than any other area, with the other drains having relatively similar averages (see Figure 4.2). Other drains with maximum values above the greater majority of drains included P3D6, P6D4 and P6D8, all of which have been identified as drains subject to complaints.

All of the samples (except for P1D1 1, with a value of 355.5 ppm) exceeded the NEPC (1999) interim urban EIL level of 600 mg/kg, however this is expected due to the nature of the acidic soil and the problems it has created.

Table 4: Maximum and minimum recorded values for sulfur (ppm) within each project area and drains with which these values correspond. Means for each project area are also included. Data are derived from XRF analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum concentration (ppm)	14060	113900	29160	36110	21190	28640	19720	26890	19280
Sample with maximum concentration	P1D1 (3)	P2G1 (3)	P3D6 (3)	P4D1 (2)	P5D1 (2)	P6D4 (2)	P7D1 (2)	P9D1 (2)	P10D1 (2)
Minimum concentration (%)	355.3	13260	3760	31090	7063	7218	12830	1329	8431
Sample with minimum concentration	P1D1 (1)	P2D2 (2)	P3D1 (3)	P4D1 (1)	P5D2 (2)	P6D8a (3)	P7D1 (1)	P9D1 (3)	P10D1 (1)
Mean concentration (ppm)	6730	51918	18312	33600	11813	19269	16275	11683	13855

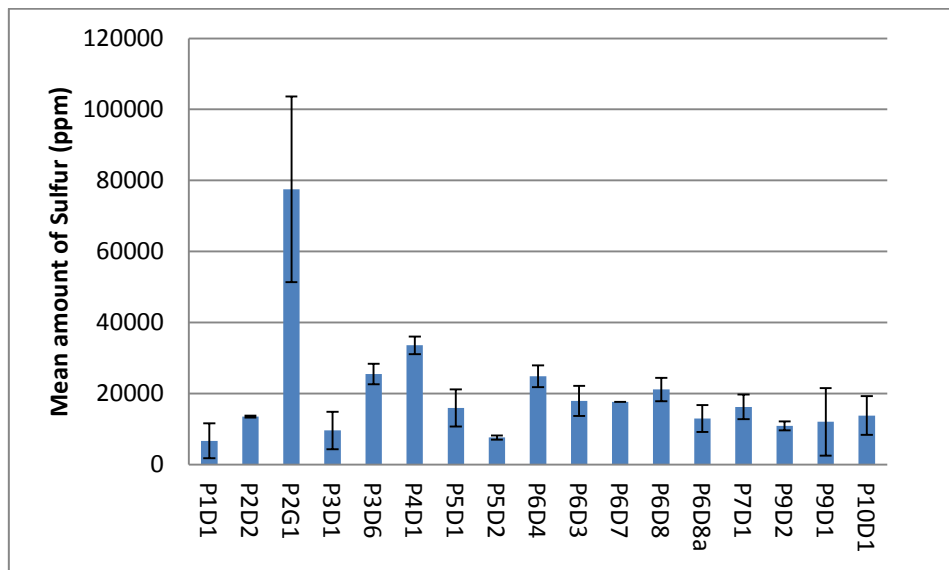


Figure 4.2: Graph showing the mean amount of sulfur (ppm) from each drain sampled (± 1 standard deviation). Data are derived from XRF analysis.

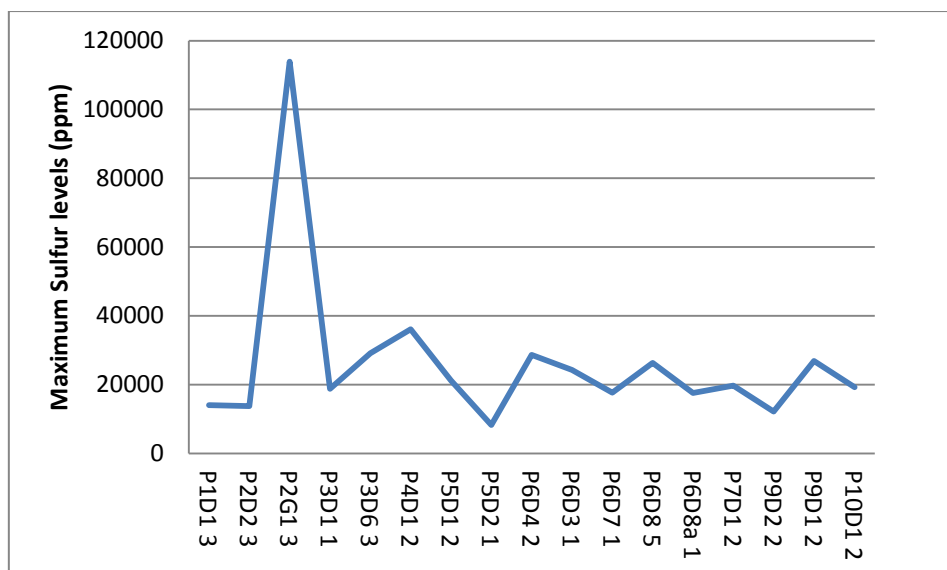


Figure 4.3: Graph showing the maximum amount of sulfur (ppm) that was recorded for each drain from which samples were collected. Data are derived from XRF analysis.

4.3.2 Chlorine (Cl)

The level of chlorine in each separate drain represents the level of salt (sodium chloride) throughout the different areas. It is expected that the level of chlorine alters between areas based on distance from the coast, and subsequent differing tidal influences. The smallest value recorded was 17.7 ppm, attributed to drain P9D1, location 3, which also resulted in project area 9 having the most significant range between values (see Table 5). The largest value recorded for chlorine was from the P6D4 drain, at sample site 4, at 35 190 ppm. The second largest maximum value was found at P7D1, sample site 1. Both of these high maximum drains found in the project areas of 6 and 7 are on the northern and southern most reaches of the study site, farthest from the Shoalhaven River, indicating a significant distance from a source of marine salt material, however it must be noted that the majority of drains in the P6 area have much lower maximum values, below most other drains (see Figure 4.4).

Table 5: Maximum and minimum recorded values for chlorine (ppm) within each project area and drains with which these values correspond. Means for each project area are also included. Data are derived from XRF analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum concentration (ppm)	2926	17020	10890	9166	8300	35190	25040	15440	9434
Sample with maximum concentration	P1D1 (3)	P2G1 (1)	P3D6 (6)	P4D1 (1)	P5D1 (2)	P6D4 (4)	P7D1 (1)	P9D2 (2)	P10D1 (2)
Minimum concentration (ppm)	388.5	3105	1048	3382	1099	254.4	8514	17.7	7470
Sample with minimum concentration	P1D1 (2)	P2G1 (2)	P3D1 (4)	P4D1 (2)	P5D2 (2)	P6D8a (3)	P7D1 (2)	P9D1 (3)	P10D1 (1)
Mean concentration (ppm)	1099	11584	5336	6274	4519	8782	16777	5116	8452

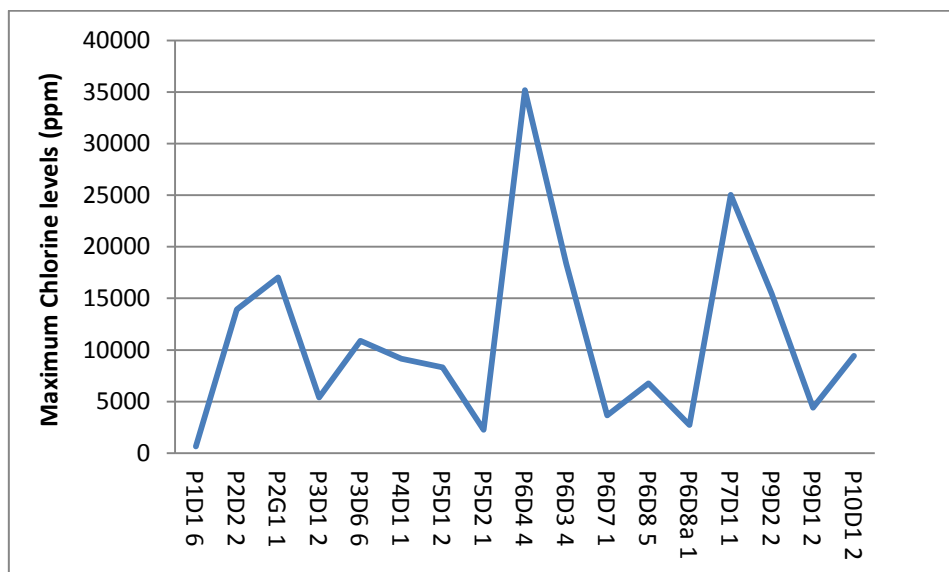


Figure 4.4: Graph showing the maximum recorded values of chlorine (ppm) for each drain. Data are derived from XRF analysis.

4.3.3 Bromine (Br)

Bromine was analysed in order to gain information on those dredged sediments with the highest level of organics and thus carbon. The largest maximum and resultant mean values were calculated for drain P2G1, which is also the drain with the highest level of recorded sulfur. Bromine values across all drains ranged between 5.3 ppm (P1D1 (2)) and 140.1 ppm (P2G1 (3)), a difference of 134.8 ppm (see Table 6).

Table 6: Maximum and minimum recorded values for bromine (ppm) within each project area and drains with which these values correspond. Means for each project area are also included. Data are derived from XRF analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum concentration (ppm)	11.8	140.1	51.9	33.2	84.4	58.2	55.6	59.2	67.4
Sample with maximum concentration	P1D1 (6)	P2G1 (3)	P3D6 (6)	P4D1 (1)	P5D1 (2)	P6D4 (2)	P7D1 (1)	P9D1 (2)	P10D1 (2)
Minimum concentration (ppm)	5.3	25.4	8.3	29.4	6.4	6.6	26	8	35
Sample with minimum concentration	P1D1 (2)	P2D2 (3)	P3D1 (3)	P4D1 (2)	P5D2 (2)	P6D8a (3)	P7D1 (2)	P9D1 (3)	P10D1 (1)
Mean concentration (ppm)	7.4	66.8	25.9	31.3	34.0	29.6	40.8	30.7	51.2

Drain P1D1 had both the smallest minimum value at only 5.3 ppm for location P1D1 (2), and the smallest mean at 7.4 ppm. While the mean for drain P5D2 also appears to be low similar to P1D1 (see Figure 4.5), once all drains in the area are taken into account, the mean for project area 5 increases generously (see Table 6), highlighting the immense difference between values of separate areas as well as separate drains.

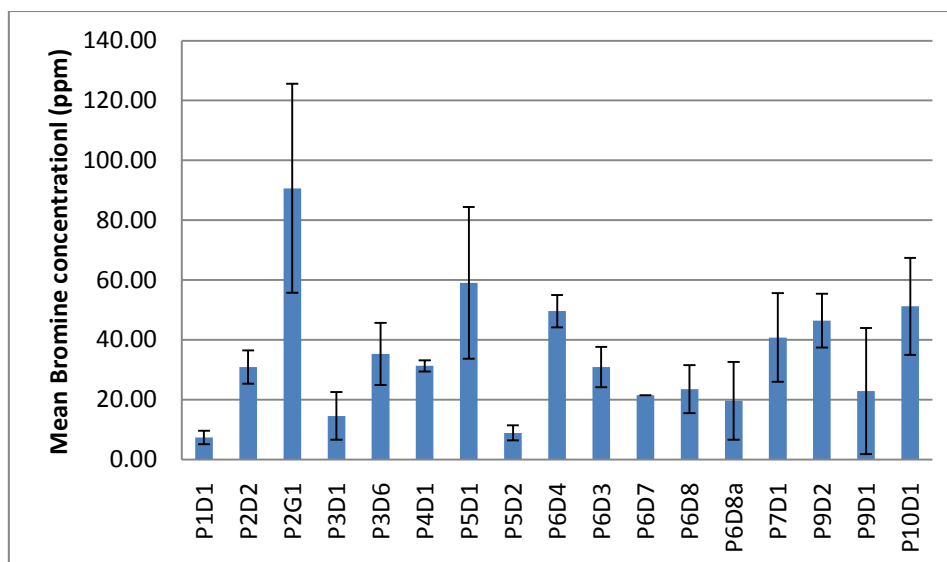


Figure 4.5: Graph displaying the mean concentration (± 1 standard deviation) of bromine (ppm) for each drain from which samples were collected. Data are derived from XRF analysis.

4.3.4 Copper (Cu)

The maximum and minimum concentrations of copper differed between each separate drain area studied. Values from across the entire region fall into the range of 8.8 ppm to 52.7 ppm (see Table 7).

Table 7: Maximum and minimum recorded values for copper (ppm) within each project area and drains with which these values correspond. Means for each project area are also included. Data are derived from XRF analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum Conc. (ppm)	32	26.9	38.3	30.1	8.2	52.7	20.2	29.7	18.6
Sample of Maximum conc.	P1D1 (1)	P2G1 (1)	P3D1 (4)	P4D1 (2)	P5D2 (2)	P6D8 (3)	P7D1 (1)	P9D2 (1)	P10D1 (1)
Minimum Conc. (ppm)	15.2	15	12.2	22.1	21.8	19.1	17.8	8.8	15.6
Sample of Minimum conc.	P1D1 (6)	P2D2 (2)	P3D1 (2)	P4D1 (1)	P5D1 (2)	P6D8a (3)	P7d1 (2)	P9D1 (3)	P10D1 (2)
Mean Conc. (ppm)	22.40	20.50	21.86	26.10	13.05	35.27	19.00	16.95	17.10

The highest copper concentration was found for sample 3 from drain P6D8 at a value of 52.7 ppm (equivalent to mg/kg). This locality is situated on the northern side of the Shoalhaven River, while the lowest maximum copper value (8.2 ppm from P5D2 (2)) is found on the southern side of the river. Following this finding, the mean values from all drains on the northern side of the river as well as all those on the southern side were calculated. The mean from all drains on the northern side (28.71 ± 10.66) also exceeds the southern drains mean at 19.02 (± 5.66). This may be attributed to the presence of underlying latite in the northern areas, as concentrations as high as 125 mg/kg may be found as background concentrations in Bumbo Latite (Carr 1984), found in surrounding areas. However with such a large standard deviation, caution must be used in applying reason to this finding. Apart from P6D8 (3), there are also 7 other samples in project area 6 that have greater values than the second largest area maximum of 38.3 ppm recorded at P3D1 (4) on land owned by the Manildra ethanol distillery, as well as a large proportion that come quite close to that value. The mean value for Project area 6 has been calculated at 35.27 ppm, above the average values for all other areas. In order to give cause to this value, it must be noted that project area 6 is situated closest to Berry, a small town in the Shoalhaven region (see Figure 4.6). This gives rise to the assumption that human activities in this town have caused elevated values of copper concentration in opposition to other project areas.

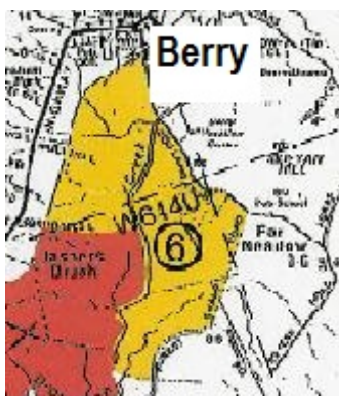


Figure 4.6: Map showing the location of Project Area 6, relative to the town of Berry. Cut out taken from Shoalhaven City Council Flood Mitigation Key Map, Drawn by P. Jennings, 4/9/02

The interim urban EIL value for copper is 100 mg/kg (NEPC, 1999), which is similar to the severe effects level of 110 ppm set by the Ontario Ministry (2008). Thus, any sample containing in excess of 100 mg/kg of copper would need to be managed appropriately.

Due to low copper values, there are no areas within those that were sampled that would need to be investigated in terms of copper contamination. All values fall within the NEPC background level range of 2 – 100 mg/kg (NEPC 1999).

4.3.5 Zinc (Zn)

Zinc concentrations in the catchment area range between 19 ppm for P9D1 (4) and 1016 ppm for P2G1 (3) (see Table 8). These concentrations also transfer to mean values with area 2 recording the largest by far at 500.5 ppm, which also demonstrates the very large range between values of the same project area. Project area 9 has the smallest mean at 47.27 ppm.

Table 8: Maximum and minimum recorded values for zinc concentrations (ppm) within each project area and drains with which these values correspond. Means for each project area are also included. Data are derived from XRF analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum Conc. (ppm)	130.6	1016	192.5	189.1	168.6	137.3	68.8	69.8	156.9
Sample with Maximum conc.	P1D1 (3)	P2G1 (3)	P3D6 (3)	P4D1 (1)	P5D1 (2)	P6D8a (1)	P7D1 (1)	P9D2 (2)	P10D1 (2)
Minimum Conc. (ppm)	46.8	39.2	48.4	185.5	26.4	41.9	67.7	19	156.8
Sample with Minimum conc.	P1D1 (5)	P2D2 (3)	P3D1 (5)	P4D1 (2)	P5D2 (2)	P6D8a (3)	P7D1 (2)	P9D1 (4)	P10D1 (1)
Mean Conc. (ppm)	86.90	500.48	94.93	187.3	98.88	86.44	68.25	47.27	156.85

The interim urban EIL value identified for zinc is set at 200 mg/kg (NEPC 1999). At 1016 ppm, the highest recorded value for zinc (see Table 8) is far above investigation guidelines set by NEPC and the associated background range of 10 – 300 mg/kg (NEPC 1999). It also greatly exceeds the value of 61 mg / kg calculated as possible background zinc concentration in the Bumbo Latite (Carr 1984). Using this value, the enrichment factor has been calculated at approximately 16.7, ruling out any ability to attribute elevated values to the underlying geology. This largest zinc concentration was found at the location also representing the highest level of sulfur concentration, P2G1 (3). Both other samples from P2G1 also recorded zinc values that dwarfed any values from other drains indicating a possible contaminated and problematic site. Following this finding, a significant relationship ($R^2 = 0.7416$) has

been found that highlights the positive relationship between zinc and sulfur concentrations indicating that areas with elevated sulfur concentrations will also exhibit large zinc values (see Figure 4.7)

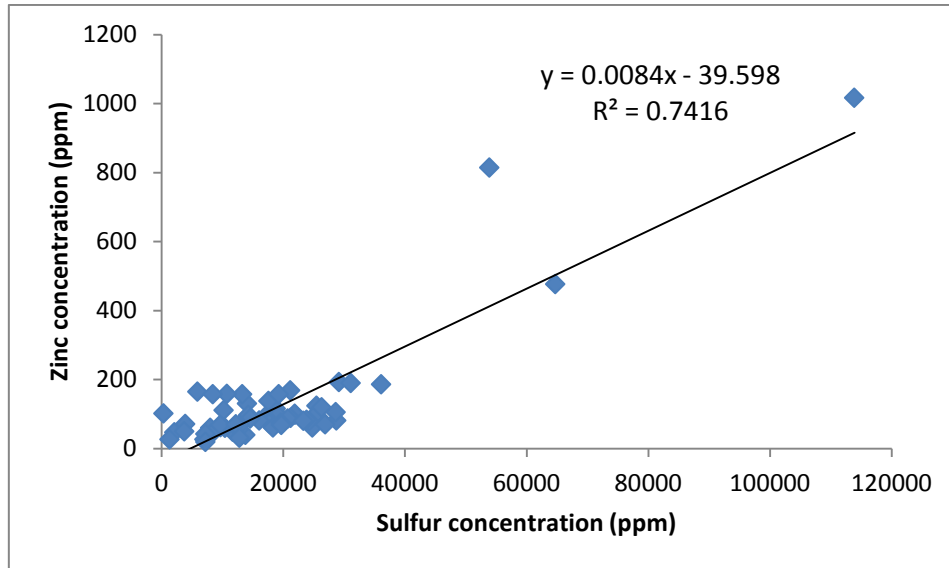


Figure 4.7: Relationship between sulfur and zinc concentrations (ppm) from all samples. Data are derived from XRF analysis.

Disregarding project area 2 results, the values obtained for zinc are low enough so that they should have no major effect on sedimentary organisms as all values are below the severe effects level of 820 ppm provided by the Ontario ministry (2008), however they are still above the lowest effect level set at 120 ppm, indicating only marginal pollution.

4.3.6 Lead (Pb)

The lead levels found within samples across the catchment range between 4.4 ppm and 30.5 ppm (see Table 9). The greatest value of 30.5 ppm was found in project area 1, the area with the highest mean value of 21.08 ppm. Project area 1 is within the town of Nowra, and thus a small amount of lead pollution may be related to human activities in the large town. However, with such a great spread of values (between 14.7 and 30.5 ppm) it is difficult to propose conclusive findings and relationships. Project area 5 has both the smallest maximum value at 12 ppm and mean value at 8.88 ppm, representing the area of minimum lead occurrence.

Table 9: Maximum and minimum recorded values for lead concentrations (ppm) within each project area and drains with which these values correspond. Mean values for each project area are also included. Data are derived from XRF analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum Conc. (ppm)	30.5	19.1	20.1	16.7	12	21.3	19.5	23.7	20.5
Sample with Maximum conc.	P1D1 (1)	P2G1 (1)	P3D1 (4)	P4D1 (1)	P5D1 (2)	P6D3 (7)	P7D1 (1)	P9D2 (1)	P10D1 (2)
Minimum Conc. (ppm)	14.7	13.8	13.5	15.2	5.1	10.5	13.3	4.4	16.1
Sample with Minimum conc.	P1D1 (6)	P2D2 (2)	P3D1 (2)	P4D1 (2)	P5D2 (2)	P6D8a (3)	P7D1 (2)	P9D1 (3)	P10D1 (1)
Mean Conc. (ppm)	21.08	15.66	15.40	15.95	8.88	16.22	16.40	11.38	18.30

This range of values is well below any guideline values identified for the cause of investigation. For this metal the background range reaches as high as 200 mg/kg (NEPC 1999) with a severe effects level of 250 ppm (Fletcher et al. 2008). Further, the NEPC interim urban EIL value is well above these at 600 mg/kg indicating that values that have been derived through this study show no reason for further investigation of lead contamination in flood mitigation waterways.

4.4 XRD (X-ray diffraction) Pyrite Content

XRD was used to analyse both the spread of common mineral phases within extracted sediment, as well as pyrite concentration as a basis for potential acid production (see Appendix 6 for full table of results). There was a great level of variance displayed for all phases, with some being found only in a select number of samples (see Figure 4.8). Sodium chloride was found in the smallest levels across almost all samples, with muscovite and albite showing the largest amount of variation between drains. The mean concentration of almost all phases, aside from these two phases, in addition to pyrite, fell below 10 %.

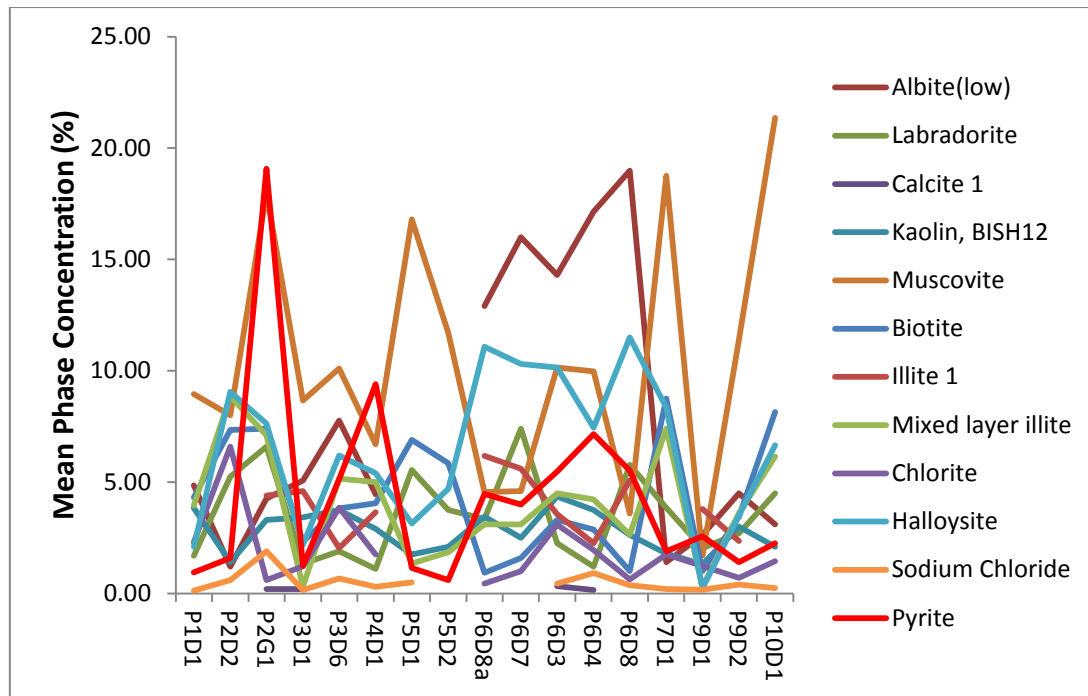


Figure 4.8: Mean concentrations (%) of each mineral phase detected (excluding Quartz), for each separate drain. Data is derived from XRD analysis.

The most meaningful results in terms of difference between drains and sites, exists for the concentrations (%) of quartz and pyrite (see Figure 4.9). The smallest quartz concentration (at 18.4 %) corresponds with the sample with the highest pyrite concentration (42.3 %), P2G1 (3), which exceeds all other mean pyrite concentrations by a substantial margin. The largest quartz concentration was recorded for drain P9D1, a drain characterised as high in coarse-grained sand material (see Section 4.2), composed primarily of quartz. Drains of the P5 area, another identified area of coarse-grained sand material, also exhibit large quartz concentrations. These two areas, as well as drain P3D1 all show elevated mean quartz concentrations with smaller mean pyrite concentrations than the other drains (see Figure 4.9). The relationship between mean pyrite and mean quartz concentrations is a slightly negative relationship ($R^2 = 0.4091$) indicating that there are generally smaller pyrite concentrations with a greater level of quartz, indicative of sand-based material (see Figure 4.10)

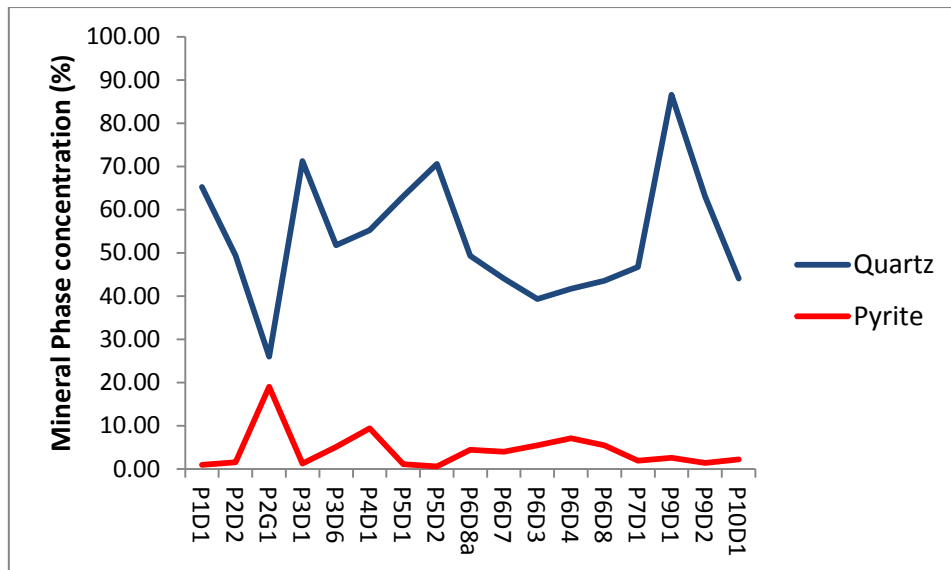


Figure 4.9: Mean concentrations of quartz and pyrite (%), for each separate drain.

Data are derived from XRD analysis.

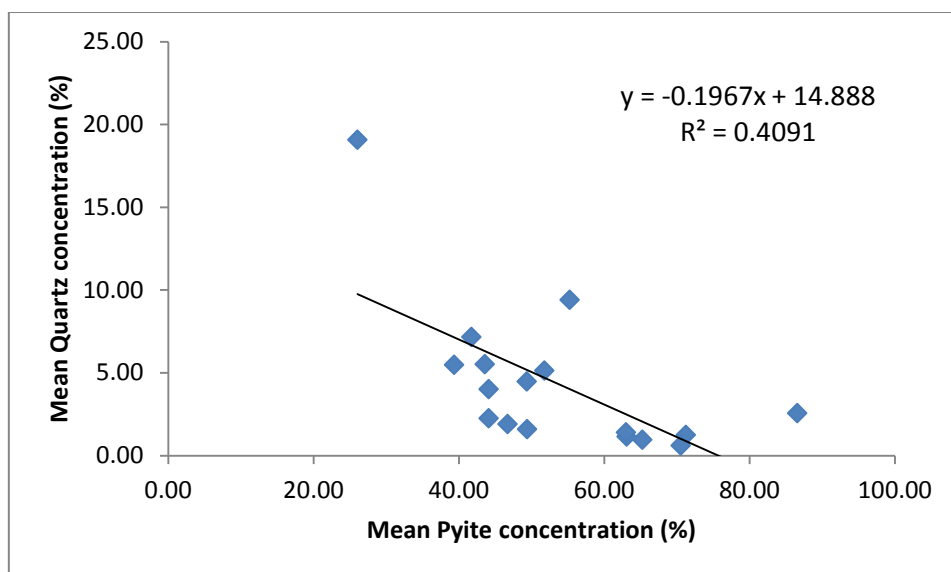


Figure 4.10: Relationship between mean pyrite and quartz concentrations (%) calculated for each separate drain. Data are derived from XRD analysis.

Pyrite concentrations in particular show great variability between drains (see Table 10). Across the entire sampled catchment area, values ranged between being non-existent at 0 % to 42.3 % for sample P2G1 (3). Drain P1D1, the large town drain, representative of project area 1, and areas 5 and 9 had the three smallest mean concentrations. Following the extremely large maximum value recorded for area 2, areas 4 and 6 also showed maximum pyrite concentrations greater than the rest of the catchment (see Figure 4.11).

Table 10: Maximum and minimum recorded values for pyrite concentration (%) within each project area and drains with which these values correspond. Mean values for each project area are also included. Data are derived from XRD analysis.

	Project Area								
	1	2	3	4	5	6	7	9	10
Maximum concentration (%)	3.5	42.3	6.3	13.1	1.8	8.5	2.2	5.2	3.6
Sample with maximum concentration	P1D1 (6)	P2G1 (3)	P3D6 (1)	P4D1 (2)	P5D1 (2)	P6D8a (1)	P7D1 (2)	P9D1 (2)	P10D1 (2)
Minimum concentration (%)	0	1.4	0.3	5.7	0.5	1.5	1.6	0	0.9
Sample with minimum concentration	P1D1 (2), (5)	P2D2 (2)	P3D1 (3)	P4D1 (1)	P5D1 (1)	P6D8a (3)	P7D1 (1)	P9D1 (3)	P10D1 (1)
Mean concentration (%)	1.03	12.08	3.36	9.4	0.88	5.54	1.9	1.75	2.25

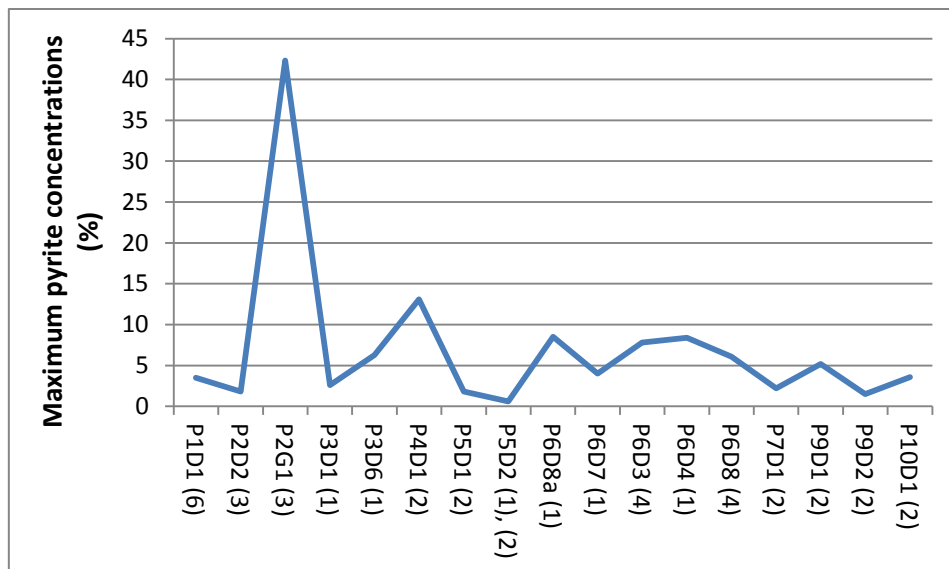


Figure 4.11: The maximum amount of pyrite (%) that was recorded for each drain from which samples were collected. Data are derived from XRD analysis.

4.5 Hydrogen Peroxide pH Results

Following oxidation of material in samples using the application of hydrogen peroxide, the resultant pH was recorded for each sample as well as blanks that were prepared (see Appendix 7 for list of pH values of all samples). The largest pH was attributed to sample P9D1 (3) with a value of 3.52 (see Table 11) indicating the location of lowest potential acidity across the whole region. However, as the associated project area has one of the smallest mean values, it is not practical to assume that this one value indicates lower levels of acidity for the whole drain or the whole project area. In addition, project area 9 also boasts the smallest recorded pH value of 1.51 and the largest standard deviation at 0.66, signifying that there is a great range in values even within the same project area and results need to be treated with caution. The smallest mean pH was recorded for area 2, with a value of 1.93. As all the recorded pH values are very small, accuracy is lost using standard measuring instruments.

Table 11: Minimum and maximum recorded pH values for each project area, and associated sample numbers from which these values were derived. The mean pH and accompanying standard deviation for each project area are also included. Data are derived from hydrogen peroxide oxidation test results.

Project area	Min pH	Min sample	Max pH	Min sample	Mean pH	Standard Deviation
1	2.09	P1D1 3	3.16	P1D1 1	2.52	0.42
2	1.62	P2G1 1	2.24	P2D2 3	1.93	0.20
3	1.58	P3D6 3	3.05	P3D1 4	2.22	0.42
4	2.04	P4D1 1	2.45	P4D1 2	2.25	0.21
5	2.3	P5D1 2	3.14	P5D1 2	2.61	0.34
6	1.74	P6D4 2	3.19	P6D8 5	2.19	0.42
7	1.96	P7D1 2	2.24	P7D1 1	2.10	0.14
9	1.51	P9D1 1	3.52	P9D1 3	2.08	0.66
10	1.88	P10D1 1	2.37	P10D1 2	2.13	0.24

Project area 5 had the largest minimum recorded pH values (see Figure 4.12), indicating the lowest amount of acidity present in samples. The greatest amount of variability between minimum pH values within the one area occurred for project area 6, with values between 1.74 and 2.29, a difference of 0.55.

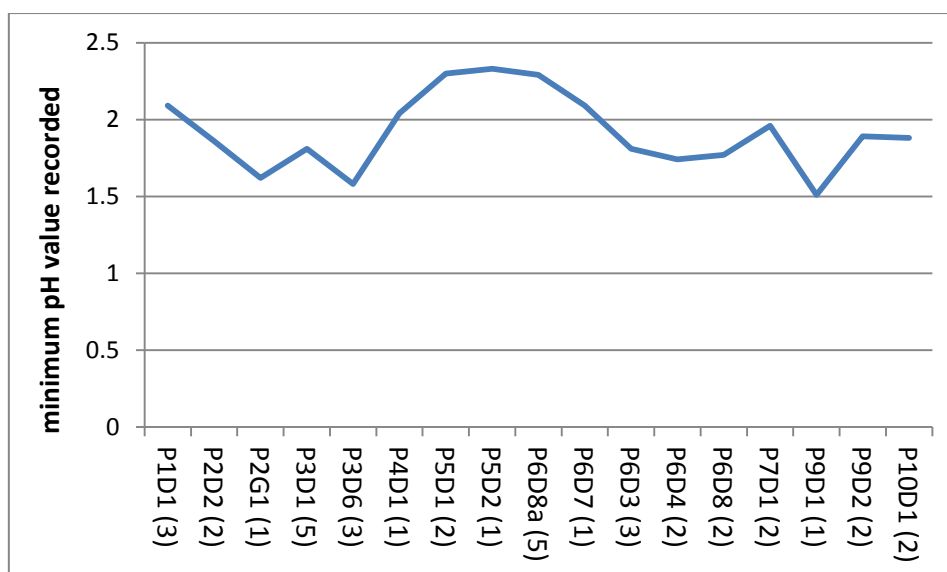


Figure 4.12: The minimum oxidised field pH that was recorded for each drain from which samples were collected. Data is derived from hydrogen peroxide field oxidation test.

4.6 Liming Requirement

The liming rate required to neutralise dredged sediment has been calculated for each drain and project area based on maximum indicators of acidity and mean values recorded following the use of the three methods of XRF, XRD and the field oxidation pH test. Using XRF and XRD requires material to be in a dried form and thus initial calculations following these two methods resulted in lime rates being presented in the form of kg/dry tonne. In order to calculate values that can be used in the field, values were also calculated in terms of kg/wet tonne and kg/m³. In order to do this, the average density of material was calculated by drying out a sample of average grain size distribution (sample P6D8 (7) was used) with a known weight in a container of known volume. Following drying, it was found that there was approximately half of the material left in terms of weight. Thus it was found that actual sediment makes up half of the weight of material removed from drains due to the water content and porosity of the sediment and the wet density of the material was approximately 1.2 tonne / m³. These values have been used for further calculations in the following sections.

4.6.1 Calculated from Sulfur concentration (XRF results)

The amount of calcite required to neutralise acidic material was calculated based on the amount of elemental sulfur found in each sample and thus the potential amount of pyrite that could be produced (see Appendix 9 for full table of calculated values). Values have been proposed based on

the worst case scenario for each area (see Table 12) and the mean sulfur concentrations for each project area sampled (see Table 13).

The values of lime range between 43.89 kg per dry tonne of dredged material in project area 1 to 355.53 kg per dry tonne in area 2 (without safety factor). The greatest liming requirement has been identified for project area 2 due to the large value of sulfur that was recorded for drain P2G1 (3) (see Section 4.3.1). The largest value, taking into account a required safety factor of 2 would require approximately 711.05 kg of limestone per every tonne of dry dredged material to be applied to dumped heaps. The weight of lime required has also been calculated in terms of kg per wet tonne (taken to be approximately half of a dry tonne) and per m³, using an average density value of 1.2 tonne/m³. These values equate to a range between 43.89 kg and 355.53 kg per tonne of wet dredged material, and 52.66 kg and 426.63 kg per m³ of wet dredged material, using the safety factor. The largest amounts of lime required are attributed to project areas 2, 3 and 4, as these are the areas with the greatest sulfur concentrations (see Section 4.3.1).

Table 12: Weight of limestone (assumed pure calcium carbonate) required to neutralise all acidic content in dredged material based on maximum S content and potential to produce pyrite. Weights have been calculated for tonne of dry material, per tonne of wet material and per m³ of wet material. Values are based on a worst case scenario for each project area determined from greatest S levels from drains contained within particular areas. Initial data are derived from XRF analysis.

Project Area	Drain / sample number	S content (ppm)	Weight of lime (kg) required per tonne of material	Weight of lime (kg) required per tonne of material (with safety factor of 2)	Weight of lime (kg) required per tonne of wet material (with safety factor of 2)	Weight of lime required per m ³ of wet material (with safety factor of 2)
1	P1D1 (3)	14060	43.89	87.77	43.89	52.66
2	P2G1 (3)	113900	355.53	711.05	355.53	426.63
3	P3D6 (3)	29160	91.02	182.04	91.02	109.22
4	P4D1 (2)	36110	112.71	225.43	112.71	135.26
5	P5D1 (2)	21190	66.14	132.28	66.14	79.37
6	P6D4 (2)	28640	89.40	178.79	89.40	107.28

7	P7D1 (2)	19720	61.55	123.11	61.55	73.86
8	NO DATA					
9	P9D1 (2)	26890	83.93	167.87	83.93	100.72
10	P10D1 (2)	19280	60.18	120.36	60.18	72.22

The mean concentration of sulfur has also been calculated for each project area with the accompanied weight of lime required (see Table 13). Similar to the use of maximum values, the greatest concentration is recorded for project area 2 at 51 918 ppm, which results in 162.06 kg of lime required for each wet tonne of material removed or 194.47 kg required for each m³ of material removed (including safety factors). Using mean values, the greatest requirements are recorded for areas 2, 4 and 6, closely followed by area 3. The smallest requirement is recorded for area 1, with 21 kg required for each wet tonne of material removed and 25.21 kg of lime required for each m³ of material removed in that area.

Table 13: Mean sulfur concentration (ppm) calculated for each project area sampled and the associated average values of lime required (with safety factor of 2) in terms of kilograms required per wet tonne and kilograms required per m³ of wet material.

Project Area	Mean Sulfur (ppm)	Weight lime required (kg) per wet tonne removed (with safety factor 2)	Weight lime required (kg) per m³ wet material removed (with safety factor 2)
1	6730	21.01	25.21
2	51918	162.06	194.47
3	18312	57.16	68.59
4	33600	104.88	125.85
5	11813	36.87	44.25
6	19269	60.15	72.18
7	16275	50.80	60.96
9	11683	36.47	43.76
10	13856	43.25	51.90

4.6.2 Calculated from pyrite concentration (XRD results)

Following analysis of XRD results, liming requirement was calculated for all samples based on the assumption that one mole of calcite will neutralise acidity produced from 0.5 equivalent moles of pyrite (see Appendix 10 for full list of values). Similar to those results described above, the greatest amount of lime required based on a worst case scenario was recorded for area 2, or more specifically, P2G1 (3), with 705.73 kg required per dry tonne of material (or per tonne of wet material (with a safety factor of 2)) and 846.88 kg per m³ of wet dredged material (see Table 14). Project area 4 has the second largest lime requirement at 218.56 kg per wet tonne of material, followed by area 6; however these values are substantially lower than those for area 2. Project area 5 has the smallest liming requirements with 30.03 kg per wet tonne of material and 36.04 kg per wet m³ of material (both with safety factor of 2). Project area 7 also has minimal lime requirements, followed by areas 1 and 10, all with values below the other project areas.

Table 14: Highest recorded pyrite concentrations for each project area and the associated calculated lime requirements in terms of application per tonne and per m³ of dredged material (based on sediment making up approximately half of raw material and density calculated as approximately 1.2 tonne/m³). Data are derived from XRD analysis.

Project Area	Sample with worst-case results	% pyrite	Weight of lime (kg) required per tonne of material	Weight lime required with safety factor of 2 (kg per tonne)	Weight lime required with safety factor of 2 (kg per wet tonne material)	Weight lime required with safety factor of 2 (kg per wet m ³)
1	P1D1 6	3.5	58.39	116.79	58.39	70.07
2	P2G1 3	42.3	705.73	1411.46	705.73	846.88
3	P3D6 1	6.3	105.11	210.22	105.11	126.13
4	P4D1 2	13.1	218.56	437.12	218.56	262.27
5	P5D1 2	1.8	30.03	60.06	30.03	36.04
6	P6D8a 1	8.5	141.81	283.63	141.81	170.18
7	P7D1 2	2.2	36.71	73.41	36.71	44.05
8	NO DATA					
9	P9D1 2	5.2	86.76	173.51	86.76	104.11
10	P10D1 2	3.6	60.06	120.12	60.06	72.07

Following the calculation of mean pyrite concentrations (%) for each project area and the accompanying liming rates, the greatest requirement is still attributed to area 2 with rates of 201.54 kg of lime for each wet tonne of material and 241.85 kg of lime for each m³ of material (with safety factors; see Table 15). These values are followed in decreasing value by areas 4 and 6, at approximately 75% and 45% respectively of the values recorded for area 2. Similar to what is described above, the smallest liming rate has been attributed to project area 5.

Table 15: Mean pyrite concentration (ppm) of each project area sampled and the associated average values required of weight lime required (with safety factor of 2) in terms of kilograms required per wet tonne and kilograms required per m³ of wet material.

Project Area	Mean Pyrite concentration (%)	Weight lime required with safety factor of 2 (kg per wet tonne material)	Weight lime required with safety factor of 2 (kg per wet m ³)
1	1.03	17.24	20.69
2	12.08	201.54	241.85
3	3.36	56.12	67.34
4	9.40	156.83	188.19
5	0.88	14.60	17.52
6	5.54	92.41	110.90
7	1.90	31.70	38.04
9	1.75	29.20	35.04
10	2.25	37.54	45.05

4.6.3 Calculated from Hydrogen Peroxide Test (pH results)

The look-up table provided by the Shoalhaven City Council (2011) to aid in easy calculation of lime rates was used for determining lime amounts for the recorded pH values (see Appendix 11 for full table of values). Due to the 'look-up table' only containing values for pH in increments of 0.2, there is a lack of accuracy attached to the use of this table. In order to produce lime values, two methods were used. First, a correlation graph was produced based on the relationship between pH and application rates in the table (see Figure 4.13). This graph shows that greater differences in lime

application rates occur when pH values are below 2-3, which indicates high levels of acidity. The associated equation to describe the relationship (with an R^2 value of 0.9684 for medium soil, and 0.9285 for coarse soil) was then applied to all recorded values to obtain lime rates. Further, values were also obtained by simply taking the value in the table associated with the pH closest to that recorded.

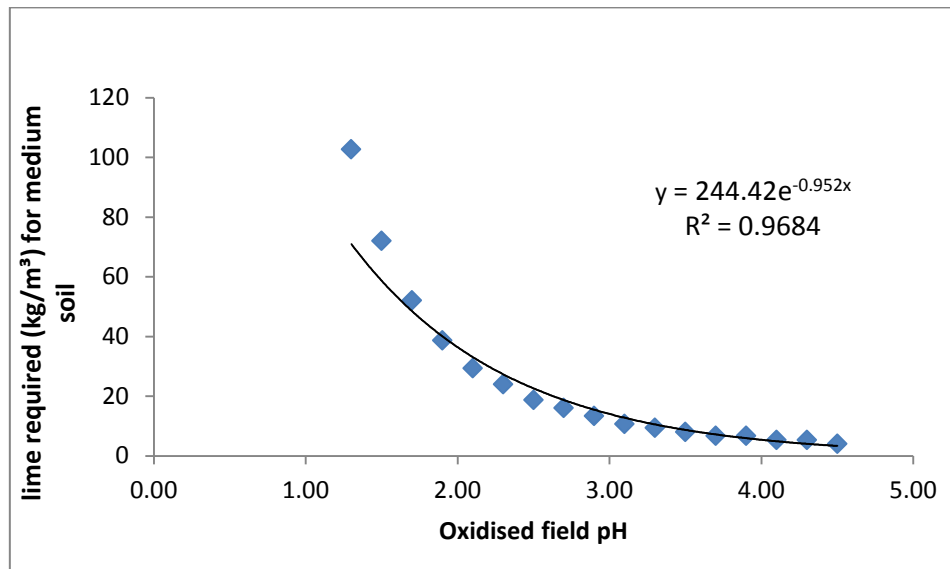


Figure 4.13: Scatter graph displaying the exponential relationship between values of lime required (with a safety factor of 2) based on oxidised pH values of medium-grained soil. All values are derived from a 'Look up table' (Rayment et al. 2001) contained in Shoalhaven City Council Routine Maintenance Review of Environmental Factors document (2011).

There was a significant relationship found between the values produced using the two separate methods ($R^2 = 0.9258$, Figure 4.14). In comparing these two sets of values it becomes apparent that using those associated values with a pH in the table closest to that recorded produces a stepped set of values with a number of samples sharing the same value, while if calculated based on statistical relationships, there is greater variation between similar pH values and their subsequent lime application rates.

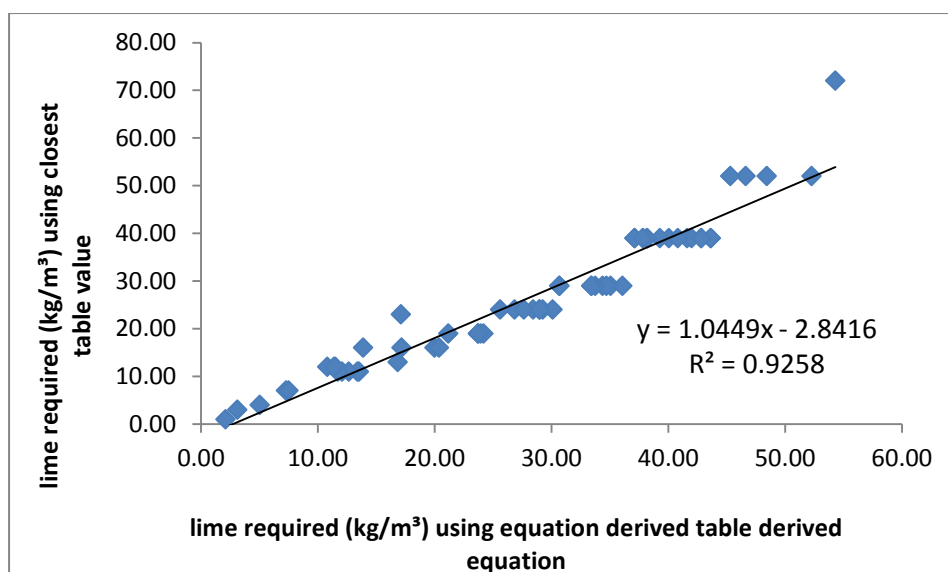


Figure 4.14: Scatter graph displaying the linear relationship between lime application rates calculated by using the equation calculated for the relationship of values in the ‘look-up table’ and values produced based on taking the applicable rate for the closest pH value included in the table.

Values calculated using a correlation equation range between 2.10 kg/m³ with a pH of 3.52 (sample P9D1 (3)) and 54.31 kg/m³ for a pH of 1.58 (sample P3D6 (3); see Table 16). Values calculated using rates associated with the closest pH value in the ‘look up table’ range between 1.00 kg/m³ for a pH of 3.52 (sample P9D1 (3)) and 72 kg/m³ for a pH of 1.58 (sample P3D6 (3); see table 17). These results confirm the positive relationship between calculated values of the separate methods as the highest and lowest application rates apply for the same samples (a full table of calculated values is included in Appendix 12). The reason that the greatest lime rate does not apply to the smallest pH value (1.51 for sample P9D1 (1)) is due to project areas 5 and 9 containing coarse material and thus values were calculated based on different lime requirements (as soil grain size increases, lime requirement decreases due to a reduced ability to react).

Project area 3 recorded the greatest lime requirements, with project area 2 closely following as expected (see Tables 16 and 17). Project areas 5 and 9 recorded the smallest lime requirements, which can be attributed to the use of different table values due to the coarse texture of the sediment in these areas. The greatest difference between values from the two separate calculation methods occurred for the maximum value for project area 3, with a difference of approximately 17.7 kg/m³.

Table 16: The maximum and minimum lime requirements, calculated as kg/m³ and kg/ton, and the associated pH value for each project area calculated by using the equation produced from a graph of Look-Up table values.

Project Area	Maximum lime Requirement (kg/m ³)	Maximum lime requirement (kg/wet tonne)	Associated pH for maximum lime requirement	Minimum lime requirement (kg/m ³)	Minimum lime requirement (kg/wet tonne)	Associated pH for minimum lime requirement
1	33.42	27.85	2.09	12.07	10.06	3.16
2	52.28	43.57	1.62	28.97	24.15	2.24
3	54.31	45.26	1.58	13.40	11.17	3.05
4	35.05	29.21	2.04	23.72	19.77	2.45
5	7.50	6.25	2.30	3.12	2.60	3.14
6	46.64	38.86	1.74	11.73	9.77	3.19
7	37.82	31.52	1.96	28.97	24.15	2.24
9	17.12	14.26	1.51	2.10	1.75	3.52
10	40.82	34.02	1.88	25.60	21.33	2.37

Table 17: The maximum and minimum lime requirements, calculated as kg/m³ and kg/ton, and the associated pH values for each project area calculated by taking the lime rate associated with the closest listed pH value in the Look-up table to the recorded value.

Project Area	Maximum lime Requirement (kg/m ³)	Maximum lime requirement (kg/wet tonne)	Associated pH for maximum lime requirement	Minimum lime requirement (kg/m ³)	Minimum lime requirement (kg/wet tonne)	Associated pH for minimum lime requirement
1	29.00	24.17	2.09, 2.18	11.00	9.17	3.04, 3.16
2	52.00	43.33	1.62	24.00	20.00	2.24
3	72.00	60.00	1.58	11.00	9.17	3.05
4	29.00	24.17	2.04	19.00	15.83	2.45
5	7.00	5.83	2.33, 2.30	3.00	2.50	3.14

6	52.00	43.33	1.77, 1.74	11.00	9.17	3.11, 3.19
7	39.00	32.50	1.96	24.00	20.00	2.24
9	23.00	19.17	1.51	1.00	0.83	3.52
10	40.82	32.50	1.88	24.00	20.00	2.37

In order to produce one table of results from pH measurements that could be used in lime application, the maximum value for each project area, taken from the method that produced the highest value has been tabulated to allow for errors in results and to increase the safety component (see Table 18).

Table 18: The maximum lime application rates applicable (worst-case scenario) based on the greatest values calculated from either of the two pH methods used. For practicality, decimal places have been removed.

Project Area	Maximum lime requirement (kg/m³)	Maximum lime requirement (kg/tonne of wet material)
1	33	28
2	52	44
3	72	60
4	35	29
5	8	6
6	52	43
7	39	33
9	23	19
10	41	34

The mean pH for each project area has also been calculated, along with subsequent liming rates, calculated in the same two ways as described above (see Table 19). The mean pH values range between 1.93 and 2.61. The smallest, most acidic pH is recorded for project area 2, with the only mean pH value below 2. This results in the largest lime requirements being 39.56 kg for each m³ of removed material (using correlation equation) and 32.97 kg of lime for each wet tonne of material removed (using correlation equation). The largest pH, and thus the smallest lime requirements was

recorded for project area 5 with 5.25 kg of lime required for each m³ of removed material and 4.38 kg of lime required for each wet tonne of material removed (both use value according to closest pH in look-up table).

Table 19: Mean pH of each project area sampled and associated lime requirements (with safety factor of 2) in terms of weight of lime (kg) required per tonne of wet material and per m³ of wet material using both values derived using the table – derived equation and values for the closest pH in the look up table found in the S.C.C. maintenance REF document.

Project area	Mean pH	kg/m ³ using equation (safety factor of 2)	kg/m ³ using value for closest pH in table (safety factor of 2)	kg/tonne using equation value (safety factor of 2)	kg/tonne using value for closest pH in table (safety factor of 2)
1	2.52	23.82	20.50	19.85	17.08
2	1.93	39.56	38.60	32.97	32.17
3	2.22	31.93	30.55	26.61	25.45
4	2.25	29.39	24.00	24.49	20.00
5	2.61	5.73	5.25	4.77	4.38
6	2.19	32.54	30.57	27.12	25.47
7	2.10	33.40	31.50	27.83	26.25
9	2.08	11.13	12.67	9.28	10.56
10	2.13	33.21	31.50	27.67	26.25

4.6.4 Comparison between calculation methods

Graphs were produced to show the correlation between liming values to be used for a worst case scenario calculated by use of the three separate methods described above in order to display uniformity of values. Unfortunately there was a great lack of correlation between the chosen methods in terms of actual values. Based on an average wet density of 1.2 tonne per m³, and sediment material making up approximately 50 % of wet dredged material, results can be compared in terms of weight and volume for all lime rates (see Tables 20 and 21). Due to the intense variability between results produced from separate methods, there are a select number of areas that have similar values across the three methods (see Tables 20 and 21).

Table 20: The maximum liming requirements for each project area using three separate methods to calculate values. Values represent kilograms of lime required per m³ of dredged material.

Project Area	Calculated from Oxidised field pH	Calculated from pyrite concentration (from XRD)	Calculated from sulfur concentration (from XRF)
1	33	70	53
2	52	847	427
3	72	126	109
4	35	262	135
5	8	36	79
6	52	170	107
7	39	44	74
9	23	104	101
10	41	72	72

There is no significant relationship between values calculated in kg/m^3 derived from pyrite concentrations and oxidised field pH, with an R^2 value of only 0.11 (see Figure 4.15). The smallest difference between calculated values occurs for area 7 with a difference of 5 kg/m^3 . Aside from this area, all values are larger using values derived from pyrite concentrations.

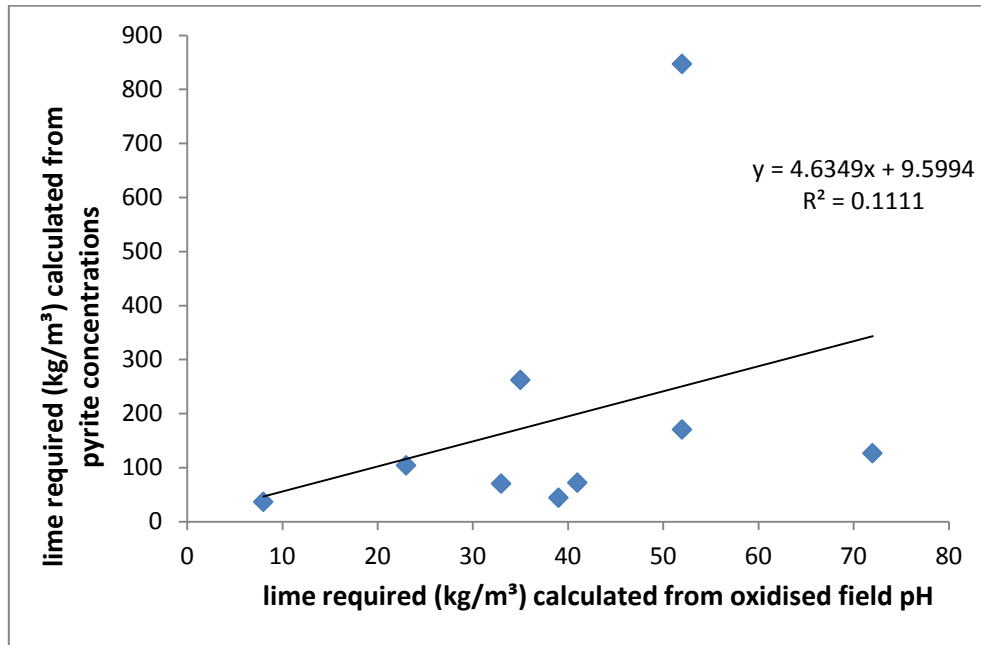


Figure 4.15: The relationship between maximum lime requirement values determined by use of pyrite concentrations derived from XRD analysis and oxidised field pH. All values are presented as kilograms of lime required per m^3 of dredged material, based on an average density of 1.2 tonne/ m^3 .

There is no significant relationship between values calculated in kg / m^3 derived from sulfur concentrations and oxidised field pH, with an R^2 value of only 0.0973 (see Figure 4.16). The smallest difference between calculated values of the two separate methods occurs for area 1, with a difference of 20 kg/m^3 . All values are higher using sulfur concentration as the basis for calculation.

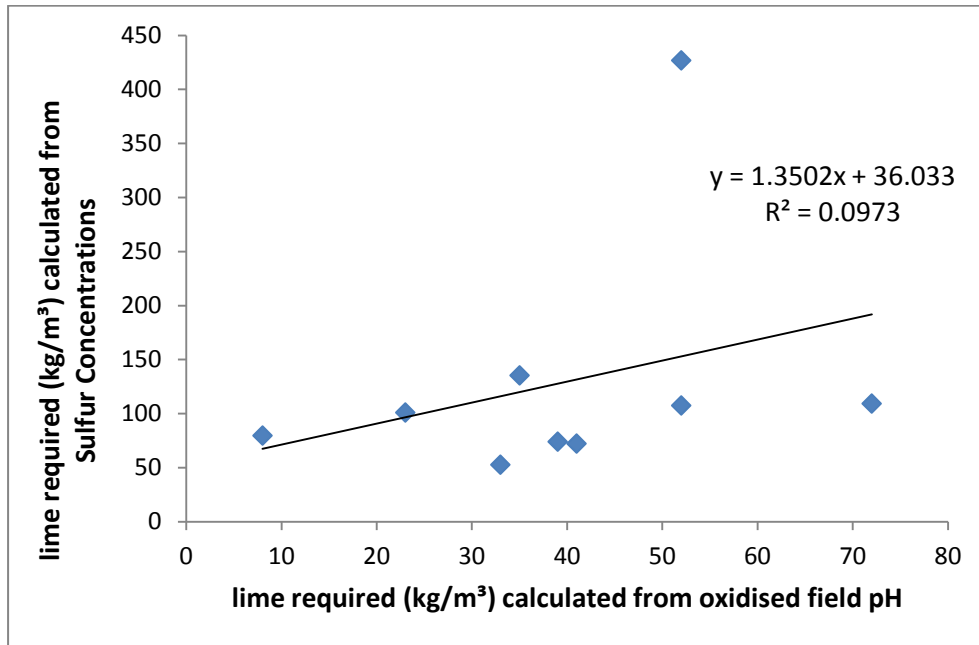


Figure 4.16: The relationship between maximum lime requirement values determined by use of oxidised field pH and sulfur concentrations derived from XRF analysis. All values are presented as kilograms of lime required per m^3 of dredged material, based on an average density of 1.2 tonne/m^3 .

There is a significant positive relationship between the values calculated in kg / m^3 derived from sulfur concentrations and pyrite concentrations, with an R^2 value of 0.9808 (see Figure 4.17). Once the point for area 2 is removed due to it being an outlier, the R^2 value is reduced to 0.7585, however this value still indicates a positive relationship. The most closely related values were obtained for areas 9 and 10, with the greatest difference between values being recorded for area 2 (although this area still has the largest rate for both methods), followed by areas 4 and 6.

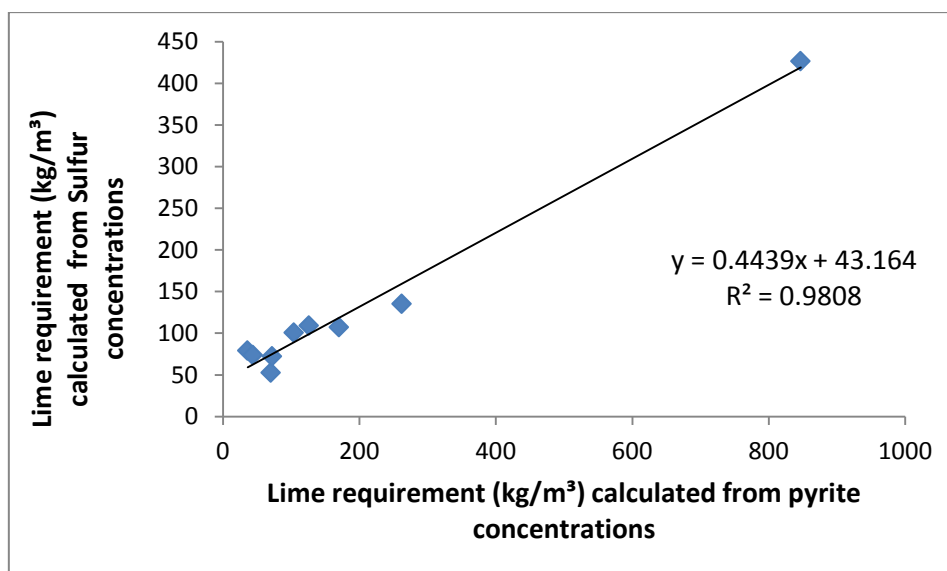


Figure 4.17: The relationship between maximum lime requirement values determined by use of pyrite concentrations derived from XRD analysis and sulfur concentrations derived from XRF analysis. All values are presented as kilograms of lime required per m^3 of dredged material, based on an average density of $1.2 \text{ tonne}/\text{m}^3$.

The differences between values produced as a result from the three separate methods are very similar when presented as kg / tonne of required material rather than as kg/m³ due to the values being altered using a uniform density value (see Table 21).

Table 21: The maximum liming requirements for each project area using three separate methods to calculate values. Values represent kilograms of lime required per tonne of dredged material.

Project Area	Calculated from Oxidised field pH	Calculated from pyrite concentration (from XRD)	Calculated from sulfur concentration (from XRF)
1	28	58	44
2	44	706	356
3	60	105	91
4	29	219	113
5	6	30	66
6	43	142	89
7	33	37	62
9	19	87	84
10	34	60	60

There is no significant relationship between values calculated in kg/tonne, derived from pyrite concentration and oxidised field pH, with an R^2 value of 0.1179 (see Figure 4.18). Area 2 exhibits the largest difference between values.

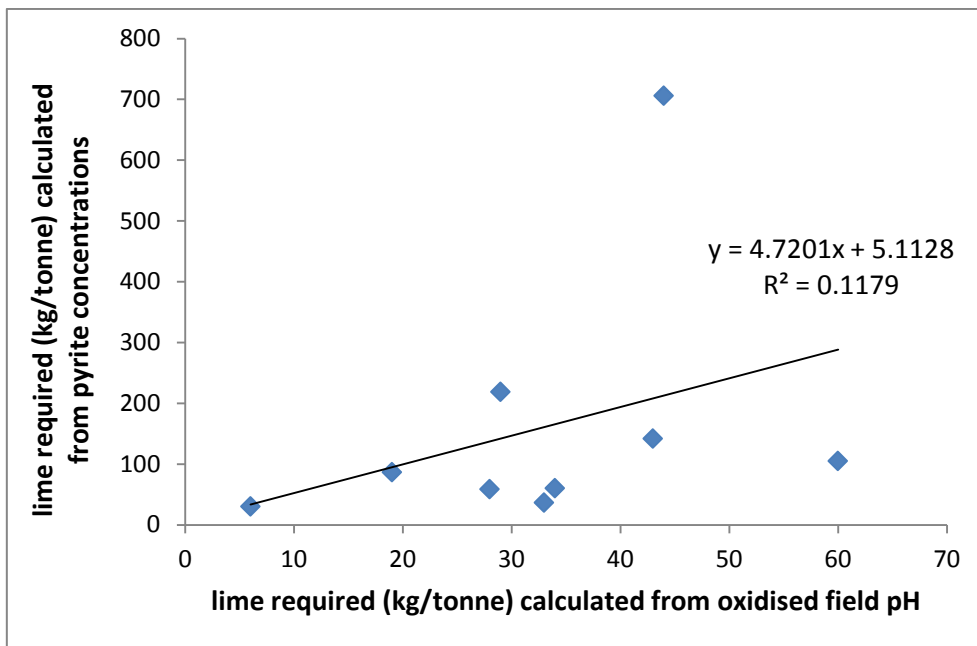


Figure 4.18: The relationship between maximum lime requirement values determined by use of oxidised field pH and pyrite concentrations derived from XRD analysis. All values are presented as kilograms of lime required per wet tonne of dredged material.

There is no significant relationship between values calculated in kg / tonne, derived from sulfur concentrations and oxidised field pH, with an R^2 value of 0.1034 (see Figure 4.19). The biggest difference between values also occurs in respect to project area 2.

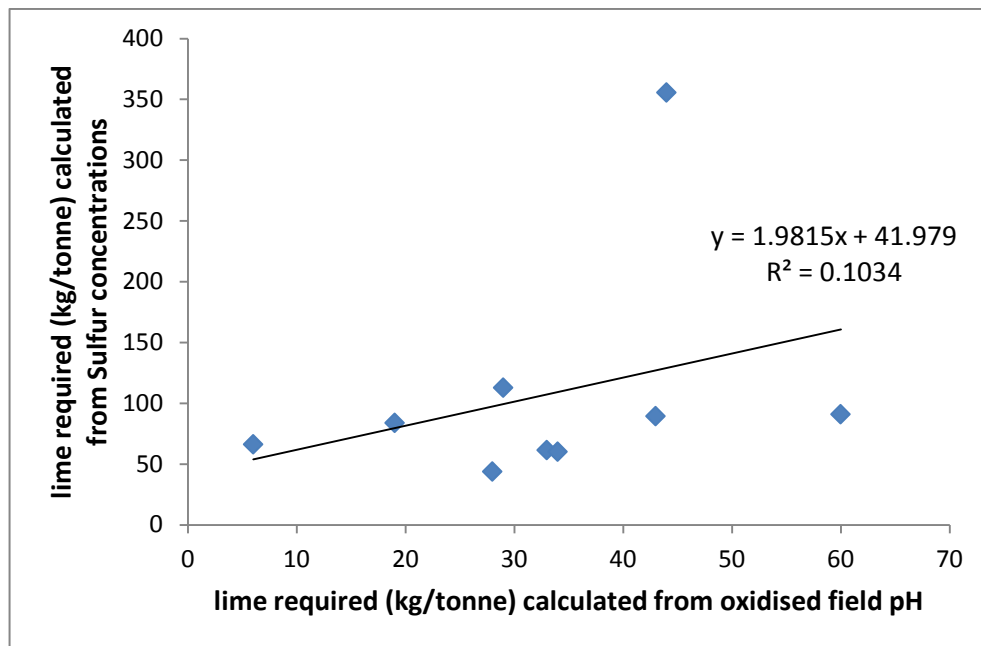


Figure 4.19: The relationship between maximum lime requirement values determined by use of oxidised field pH and sulfur concentrations derived from XRF analysis. All values are presented as kilograms of lime required per wet tonne of dredged material.

There is a significant positive relationship between values calculated in kg / tonne, derived from sulfur concentration and pyrite concentration, with an R^2 value of 0.9808 (see Figure 4.20), which is reduced to 0.7585 if the outlier for area 2 is removed. This indicates a level of correlation between values calculated using these two separate methods.

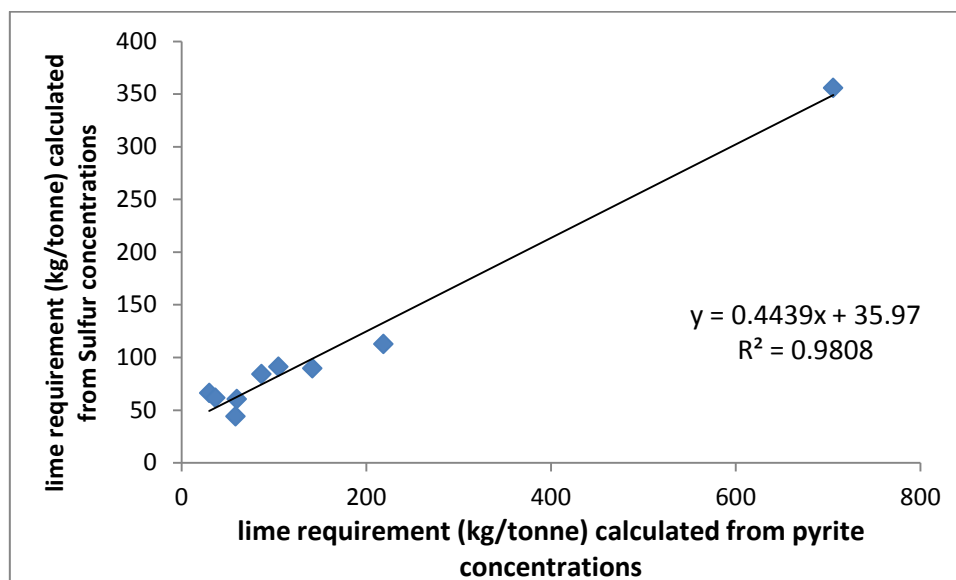


Figure 4.20: The relationship between maximum lime requirement values determined by use of pyrite concentrations derived from XRD analysis and sulfur concentrations derived from XRF analysis. All values are presented as kilograms of lime required per wet tonne of dredged material.

Due to the very large amounts of lime that have been proposed above, following the calculation of values for a worst case scenario and the implementation of a safety factor of 2, there would be a considerable cost involved to apply lime. Therefore, mean values for each project area have also been calculated following each method of determination (see Figure 4.21 and 4.22). In terms of comparison of these values and identification of highest values, the largest liming rate has been recorded for project area 2, with rates determined using XRD and XRF methods being much greater than those determined by pH testing. This area is followed by project area 4, the area recording the second largest rates. These two areas have the greatest difference in values between X-ray and pH methods. All those areas recording much smaller lime requirements have a closer relationship between values calculated using all 4 methods. The analysis of mean values has resulted in the same general trend exhibited by the use of maximum acidity values with the same areas being classed as low or high concern in terms of the amount of lime required. The use of means has also resulted in a greater correlation between methods, as the mean values projected by using pH testing are highest for project area 2, as they are by using XRD and XRF, signifying a common area of greatest

requirements. Using maximum values, pH testing indicates area 3 as being the area with highest acidity and lime requirements, rather than area 2.

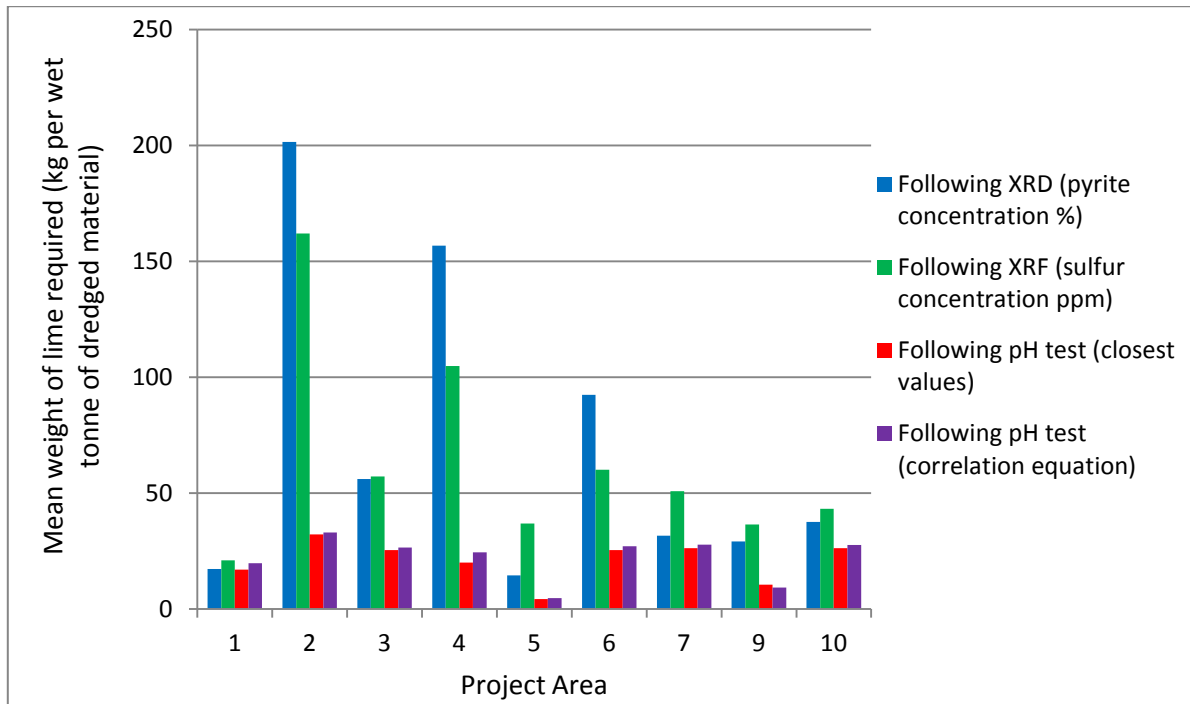


Figure 4.21: Mean weight of lime required for each project area (kilograms per wet tonne of dredge material) based on 4 separate methods of calculation.

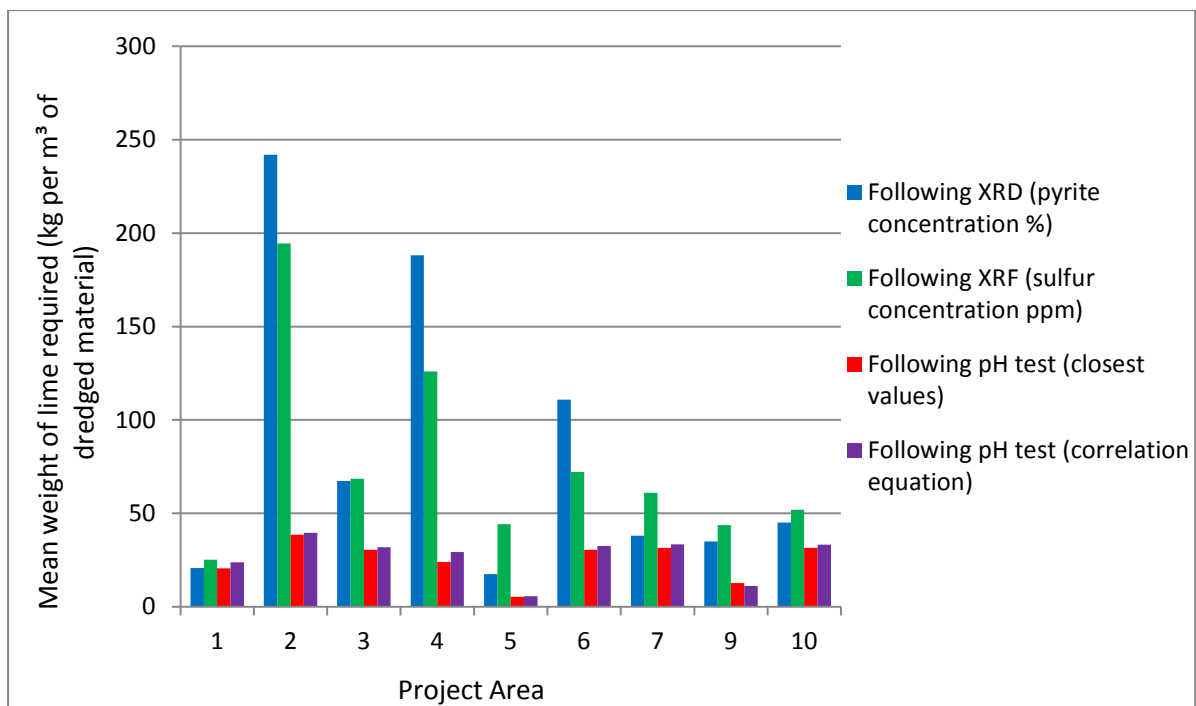


Figure 4.22: Mean weight of lime required for each project area (kilograms per m³ of dredged material) based on 4 separate methods of calculation.

5. Discussion

5.1 Introduction

The central aim of this thesis was to identify neutralisation rates required for the treatment of sediment material removed from flood mitigation drains known to be problem areas in terms of Acid Sulfate Soils within the Shoalhaven River estuarine area on the south coast of New South Wales. Throughout the study, a number of fundamentally different methods were used to propose liming rates required to neutralise any potential acidity. This thesis also strove to find any relationships between specific area location characteristics and levels of acidity and varying elements in the accompanying sediment. In terms of critiquing the methods used and testing for accuracy in results, correlation between results derived from separate methods was also examined. This study is one of very few that looks at approaches for the management of dredged material removed as a result of drain maintenance activities. The results have implications for the maintenance activities and resultant further actions pursued by the local Council initiated by landholder concern and also other areas facing similar issues. It also assists in the understanding of levels of acidity difference between locations of the same wider area. As previous studies of the Shoalhaven Acid Sulfate Soils have done, this thesis highlights the potential for further research into the dynamics of the soils and how they are managed.

5.2 Methods of determining potential acidity and lime application rates

For the purposes of this study, the method chosen to conduct analysis has implications for the results that have been derived. To reach a common end point in the form of an area specific amount of lime to counteract dredge spoil acidification, XRD was used to measure pyrite levels, XRF was used to measure sulfur levels and a hydrogen peroxide test was used to measure the pH of oxidised material. All methods that were used have some level of problems and inconsistency with accuracy, as well as applicability as described in the literature.

Without detailed laboratory analyses to confirm and support the results, no one method can be assumed to be more accurate than the others. XRD was the initial choice to assess the amount of potential oxidative material because it has been recognised across all literature that nearly all sulfur occurs as pyrite in acidic soils (Dent 1986). XRD as a method in itself is highly inaccurate when it comes down to the use of human knowledge and interpretation to determine phase components of material. In this study, difficulties were encountered in determining the correct number of major phases for each sample, as with small changes in components, there were often very large alterations in concentrations. While this is a major limitation of the XRD use and increases difficulty

in carrying out analysis, for this particular research, the pyrite concentrations did not vary in a large manner in comparison to other phases with subsequent testing. Thus, pyrite concentrations have been assumed to be accurate enough for these purposes.

Trace element analysis, while also a method of recognised low reliability, has pinpointed the areas of highest concern in terms of potential acid generation with sulfur concentrations displaying a great deal of variation across the catchment. This method of using X-ray fluorescence to determine total sulfur has proved to be a rapid method for the initial screening of a large number of samples (Bloomfield and Coulter 1974) and while it is unable to produce a set of accurate and conclusive values it is still very helpful in highlighting those potential problem areas. Due to correlation with pyrite concentrations derived from XRD, values are indicative of potential acidic reactions that could take place.

The use of an oxidation pH test was an essential part of this study as pH is one of the most simple, primary indications of the presence of either acidic or alkaline material. A rapid field test such as the one used enables prediction of the quantity of agricultural limestone required to neutralise drain spoil containing pyritic acidity (Rayment et al. 2001). Within the Shoalhaven City Council Review of Environmental Factors document, the 'look up table' intended for use as a means to determine lime application rates uses field oxidation pH as the measure to base applications on. The supplied table, produced and supported by validation from Rayment et al. (2001) can be used in conjunction with ASSMAC detailed field tests to specifically predict lime required for neutralisation based on the kilograms of lime to be mixed with each m³ of removed drain sediment (S.C. Council 2011). While this allows for easy use of oxidised pH, values that were recorded have been deemed appropriate for qualitative rather than quantitative analysis due to the decreases in accuracy associated with incredibly low pH values following oxidation. There is also a possibility that total potential acidity may vary at a certain pH, especially below pH 2.5 (Konsten et al. 1988). A lack of any major trends in values also confirms a limited analytical use with a lack of accuracy.

The ASSMAC guidelines state that the lower the pH drops, the presence of sulphides becomes increasingly positive (Ahern 1998a), thus the pH method is sufficient to grade areas in terms of which ones require more intensive treatments. The integration of this method with the more laboratory based method described by Blunden (2000) allowed an increase in applicability and accuracy as samples were left to digest overnight to ensure complete reaction and potassium chloride (KCl) was used to increase the amount of liquid in the sample. In terms of other useful indicators of sulfate presence, violent reactions could not be used as indicators as these are also fuelled by the presence of organic matter, present in many of the samples (see Appendix 8 for soil

notes), which also hinders the effectiveness of the field test method because results cannot be unambiguously related to the production of sulphuric acid derived from pyrite oxidation (Vegas-Vilarrúbia et al. 2008). This issue was not believed a major hindrance for pH values as actual pH values should not have differed greatly based on organic content and their removal from dredged material is quite difficult.

The correlation between lime requirements calculated from XRD and XRF derived acidity values is the most convincing when analysing the relationships between all maximum calculated values due to the more closely related way in which values were produced from these two methods. There is also a lack of any major observable trends in pH data, highlighting that calculations of the quantity and type of neutralising material to apply to ASS – affected areas should be based on acidity titrations or similar processes rather than pH as there may well be a lack of a relationship between the amount of acidic species and measurable pH (Green et al. 2006).

5.3 Indications of contamination and analysis of minor elements

High concentrations of sulfur were expected due to sulfur being a key component in the production of highly acid material. However, contamination in the form of other elements was not expected. Concentrations of lead, copper and zinc are useful indicators of contamination in an area. While most areas have recorded concentrations well below any kind of trigger level, differences between areas and location are still able to be used to gain an understanding of the distribution of such elements.

The area with the largest number of maximum copper concentrations is project area 6, found at the northern most point of the sampling region. Analysis of this finding uncovers a trend of falling copper values with increasing distance away from the township of Berry as well as smaller values overall on the southern side of the Shoalhaven river. With a large amount of human activity taking place in Berry, there is a greater chance of copper leaching into drains here rather than in areas of minimal human activity where there is no production or use of metallic materials. Concentrations of lead and zinc show no trends in their distribution or differences in value across the region. Most values fall well below any sort of trigger values, and thus can almost all be attributed to background values. However, there is an extremely large zinc level recorded for P2G1 (3) (value has been confirmed by re-testing), the same locality that also recorded the largest sulfur value by a substantial margin. Acidic conditions produced by high levels of sulfur often result in the dissolution of clays and other minerals and cause the release into waterways of metals such as iron, aluminium, manganese, copper and zinc (Green et al. 2006) which may settle and give cause to raised contamination levels in

the form of zinc. The Palaeozoic Lachlan Fold Belt, across which the Shoalhaven estuary stretches, is also a known source of elements such as zinc derived from volcanic and granitic rocks. The P2G1 drain has been identified as one that requires further research and management (see Section 5.5).

5.4 Analysis of acid levels in dredged sediment and subsequent liming rates

Based on the correlation between methods in terms of the range between acid levels and lime rates from highest to lowest, results may be interpreted by analysing the order of decreasing maximum lime requirement in terms of project areas (see Table 22). This allows some interpretation, in the most basic of terms, based on the locations subject to the highest level of potential acidity and relevant location characteristics that allows for increased attention to be paid to these areas. By investigating the distribution of acidity in the landscape, 'hotspots' can be identified and managers can then target these areas (Smith et al. 2003).

Table 22: Project areas listed in in order of decreasing lime requirement based on calculations using maximum acidity data from three separate methods.

	Sulfur content	pyrite content	pH
1	2	2	3
2	4	4	2
3	3	6	6
4	6	3	10
5	9	9	7
6	5	10	4
7	7	1	1
8	10	7	9
9	1	5	5

Results showed that using different methods produces a range of very different values. However, it has also been shown that while actual values differ, there is a certain level of correlation between

the orders in which project areas fall when described in terms of increasing or decreasing lime requirements necessary for neutralisation of material (see Table 22). While the results are riddled with inaccuracy and uncertainty, there is some confirmation that particular areas do actually exhibit higher concentrations or indications of potential acidity and require more intensive treatments, following correlation between all methods using both maximum acidity values and mean values for each project area. Using data derived from maximum sulfur content and pyrite content analyses, the first 5 ordered drains are the same and in almost the exact same order. Excluding area 2, an area of high concern (see Section 5.5), all areas that make up the top end of the table are areas of the northern side of the catchment, on the northern side of the Shoalhaven River. On the northern side of the estuary, mainly the areas of 3 and 6, drainage channels are much more densely clustered than any other location. If there are more drains, there is a greater chance of complaints which has been seen in this particular area, as well as an increased acidity level due to the larger amount of material that would have been disturbed in these areas, increasing the degree to which the area is affected by ASS leachate and increasing the interaction with acid in groundwater. Across this region, an active ASS layer is found approximately 1 m below the soil surface and all discharges occur into Broughton Creek, a left-bank tributary of the Shoalhaven River (Glamore and Indraratna 2004). The Broughton Creek floodplain, an entity in itself, has been the centre of a range of remediation studies due to it being an area of acknowledged problems (Glamore and Indraratna 2004; Indraratna et al. 2005).

Project area 1 values are found at the smaller end of the table for all methods used. This is expected as high lime requirements were not predicted for the P1D1 drain sampled due to its indicative features. This drain is found at the western most extent of the sample region, and branches directly off the Shoalhaven River, indicating that this drain may be subject to tidal movement which would allow for buffering of acidity by the carbonate / bicarbonate in seawater (Indraratna et al. 2005). P1D1 is also identified as the town drain for the town of Nowra, classified as Shoalhaven City Council land, and flows through city areas rather than purely agricultural land. This drain had some indication of flowing water and was the widest of all drains visited based on human judgement.

Project area 4 has the second largest lime rate values based on XRF and XRD analysis. This area, while being part of a project area found directly adjacent to the Shoalhaven River, has a very small number of drains with the potential to be sampled. The one drain in area 4 that was sampled is nestled in an area with a large number of area 3 drains, an area subject to landholder complaints and high liming requirements in comparison to other areas (see Table 22), along with project area 6. The P4D1 sample sites all fall along a natural section of the drain channel similar to the P2G1

samples (see Section 5.5). As noted during sampling, this drain requires very minimal, if any, maintenance efforts in terms of removal of vegetation.

Analysis of grain size and subsequent sediment texture classification along with the relationship between these, pyrite concentrations and resultant lime requirements supports differences between necessary lime rates as a result of the size of material particle size. In this study, project areas 5 and 9 were classified as being of a coarse-grained texture, an indication of a high energy environment. When using the 'Look-up table' they were both attributed with smaller lime requirements, placing them at the bottom of Table 22, even though a sample from area 9 recorded the smallest pH (indication of high acidity) overall. Areas 5 and 9 also had some of the highest quartz concentrations recorded; correlating with minimal pyrite concentrations indicating high levels of quartz sand based material can be associated with reduced amounts of pyrite and sulfur. This stems from the theory that fine-grained sediments should contain proportionally greater reactive surfaces than coarse-grained sediments (Rickard year unknown), increasing the potential for pyrite reactions to occur with more fine-grained material.

5.5 Elevated values of drain P2G1

As has been extensively discussed, project area 2 has been identified as a hot spot to be targeted in terms of management efforts due to the prominent potential acidity indicators recorded for the P2G1 drain.

In agreement with those results obtained using XRD, project area 2 has been identified as an area of highest potential acidity due to the large sulfur concentration obtained for drain P2G1 (see Figure 5.1). The possibility that this value, far above any others recorded, is simply an anomaly or result of poor use of analysis methods has been outlawed due to repetition of analysis, however due to inaccuracy associated with the methods used, further laboratory analysis is still deemed essential for complete confirmation. Following the calculation of mean lime rates for each area, area 2 has also been attributed with the largest lime requirement following all methods of calculation. Therefore, results of this study strongly suggest that the P2G1 drain, representative of project area 2, is a locality of prime concern. In comparison to almost all other drains that were sampled, P2G1 is a natural drain, rather than one constructed as part of the flood mitigation scheme. Therefore, it is not included in the 50 flood mitigation drains identified as assets by the Shoalhaven City Council (2011; see Appendix 1).



Figure 5.1: Photograph taken of P2G1, standing at sampling location 2 looking towards sample site 3 (taken 10 August 2012).

As previously established, project area 4 also has large calculated lime requirements, placing it second in the table of decreasing maximum lime requirements (see Table 22). The drain of project area 4 sampled, P4D1, also forms part of a naturally formed channel, indicating that there may actually be a link between the way in which drains are formed and the level of potential acidity.

Even though location 3 from this drain is the sample with the highest sulfur and pyrite concentrations, the other two samples collected from P2G1 also exhibit large amounts of sulfur content when compared to all other samples and drains. In addition, sample P2G1 (3) has the highest recorded sodium chloride concentration, with the second largest concentration being attributed to P2G1 (1) indicating that this drain may have had the largest amount of material derived from marine waters, the primary supplier of sulfate material, of all drains sampled. Project area 2 also had the second largest mean chlorine concentration recorded following the use of XRF, which gives another indication of saline waters being present in this area.

Natural flood channels are different to constructed flood mitigation structures as they have not been subject to the removal of large amounts of material in order to produce a drain through which water can flow. Natural drainage systems have remained in place and been in existence longer than constructed drains due to the movement of water along the channels that has resulted in larger amounts of erosion taking place, and thus subsequently smaller amounts of material being deposited, inhibiting the areas ability to build up with material. Because natural drains will have more natural flows of water and the fact that P2G1 appears to be slightly shallower than the other drains it may have been subject to a small amount of later stage accumulation of material.

This study has based most calculations on the presence of pyrite and sulfur in sediments. These are species that have not actually oxidised yet to produce sulfuric acid. Within this study, there is a possibility that sulfur has actually been oxidised to sulphate but not detected by X-ray technology. However, due to the lack of artificial disturbance, it would be expected that sources of acidic material in natural drains would still be overlain by alluvial sediment, rather than removed and allowed to oxidise, leaching acidic material back into drains. The samples from drain P2G1 have the highest sulfur and pyrite concentrations, indicating that natural drains may have a greater concentration of potential acidity. To test this theory, water samples should be collected and analysed for acid concentration.

In addition, sample site 3 of P2G1 also has the greatest concentration of bromine of all sample sites. Bromine is an indication of the amount of organic matter present. Therefore there may also be a strong possibility that decaying organic matter is actually initiating modern pyrite formation in these drains from the presence of sea water, as pyrite that causes problems pertaining to acidity often accumulates in saline sediments where there is a supply of decomposed organic matter (Dent 1986).

Drains P2G1 and P4D1 both have very minimal, if any, indications of necessary maintenance with no weeds growing in the waterways like many of the other drains. Thus, flow of water has not been interrupted in these drains. This may cause drains like these to be overlooked when maintenance is scheduled because they appear to be in fine form from an observational point of view. This may also be connected with the salinity levels (discussed above) of these drains as high levels of salt will inhibit the growth of plants (see Figure 5.1).

5.6 Applicability of lime application rates and effectiveness of current use

The Shoalhaven City Council Review of Environmental Factors document (2011) identifies that as part of their response to introduce safeguards, prior to the collection of sufficient samples over time, lime should be applied at a rate specified by the 'Look up table' (Rayment et al. 2001) used in this study for an oxidised field pH of 2.10. There is no explanation given in the document that aims to provide reason behind why this value has been chosen as a base value for the proposal of liming rates and without sufficient sample collection over a long period of time, there is little evidence to suggest this value is actually indicative of the environment within which works are to take place. The samples collected as part of this study provide an indication of the insufficiency of current application procedures, however they are unable to provide information to assist in the ongoing modification of liming rates. Of the 61 samples collected, 32 samples recorded a pH less than 2.10, implying that approximately half of locations visited would not be sufficiently neutralised using a

value derived from an assumed pH of 2.10. Of those 32 samples exhibiting pH values less than 2.10, 15 are from project area 6, an area targeted due to complaints. All of project area 9 locations, another area subject to landholder complaints, are also represented in this group, as well as all those samples collected from the P2G1 drain, a drain highlighted as being a major concern as part of this study. Thus, efficiency of ascribed lime rates is shadowed with doubt as to their potential effectiveness. However, there is an ASSMAC-recommended safety factor of 1.5 that is commonly used to account for all actual and potential acidity. For the purposes of this research, a safety factor of 2 has been implemented to provide additional precaution as lime is often slow to react and mixing between soil and lime is difficult. Due to such a large safety factor, there is adequate room for a general lack of accuracy in calculations of exact amounts. Yet, differences between drains still need to be analysed due to large variations in liming rates for only small changes in parameters such as pH. The use of field oxidation pH values as the basis for lime calculations remains the most inaccurate method for accurate proposal of values.

As has been duly noted, project area 2 has the greatest lime requirement based on sulfur and pyrite concentrations, while areas 1 and 5 have the smallest calculated lime requirement (see Sections 5.4 and 5.5). This is in stark contrast to what was expected as those areas that were targeted and sampled more intensively did not rate as the areas of highest concern in terms of acid material concentration. These areas were project areas 6, 3 and 9, which were all identified as being in the middle of the range in terms of environmental concern when classified based on values produced from all 3 methods (see Table 22). Consequently, there is a lack of a relationship between those drains that have been identified as a concern by landowners and the level of acidity that the drains are subject to. Further, this means that the amount of maintenance required is independent of the level of acidity.

The results suggest that there is limited conclusive data that identifies broad project areas as having distinctly different acidity levels and thus liming requirements. Project areas 2 and 4 show markedly higher maximum concentrations of both sulfur and pyrite than all other drains, which show relatively similar distributions of concentration. Areas 2 and 4 are found at a similar position in relation to the ocean opening; both are directly adjacent to the Shoalhaven River, yet on opposite sides. It must also be noted that those drains exhibiting the largest values are found within the part of their project area farthest from the river, ruling out any interaction from the major waterway and highlighting the fact that they are in extremely close proximity to other bordering project areas. Thus, the use of project areas as regions of rate differentiation may not be an adequate procedure for alteration of application rates. Not only are there extreme differences in concentration and pH

between drains in the same project area, there are also noticeable differences between samples collected from different points of the same drain. As part of the environmental management safeguards described in Section 2.4.1 of the Shoalhaven City Council maintenance document (2011), routine maintenance activities are to be undertaken in such a way that only a portion (less than 60% of the length) of individual channels are worked on in any one year. Therefore, it is needless to actually group samples into drains and drains into project areas when all locations are not going to be dredged and thus material limed at the same time. Liming values would be more accurate if they were calculated for material removed from a certain location where maintenance is actually required as close as possible to the time when maintenance involving dredging and removal of sediment is to occur.

The results that have been obtained, mainly from the use of XRD and XRF technologies, propose application rates that would require large quantities of agricultural lime material. While pyrite is the principal component of material that calculations are based on, there are other aspects that should be tested for with an increased amount of time and resources to complete analysis. The accuracy of results could be improved if other contributing factors were taken into account. Bloomfield and Coulter (1974) identified aluminium as the major exchangeable cation in very acid soils, with considerable amounts occurring in solution in water samples from oxidised pyritic muds. This major cation was also recognised by Dent (1986) who described aluminium as the principal exchangeable cation in ASS with activity inversely related to pH. Aluminium concentration has also been described as a major water quality issue of concern that aids in describing the extent to which a system is impacted by acid sulfate soils (Ahern 1998). It is an element that has a profound relationship to the acidity of sediment and associated waterways. Similar to iron, aluminium has the capacity to adversely affect marine ecosystems (Murphy et al. 2007). It also has the ability to hinder liming efforts, highlighting it as a component of ASS that should be taken into account when determining liming rates in the future, as the formation of precipitates, in particular oxy-hydroxides of aluminium can coat or armour the limestone surface obstructing direct contact with the acidic solution (Green et al. 2006).

The buffering capability of the soil is another issue to be taken into account (Bloomfield and Coulter 1974; Dent and Pons 1995), as well as rainfall and leaching capabilities which all affect neutralisation rates.

In the Shoalhaven estuary, dredging and other maintenance activities are to be undertaken by people trained in excavator use rather than extensive ASS management, thus lime application rates must be simple and straightforward to be applied to areas subject to varying levels of acidity. The

implementation of a system that has areas listed in decreasing order of acidity extent and concern level with accompanying amount of required lime should be easy enough for others to follow. The differences between the separate areas will alter the ease to which rates are altered when moving between the separate areas. Also, it is expected that only small areas of differing lime requirements would be subject to maintenance activities on any one day. In order to ease application, values also need to be rounded to closest whole values, another cause for loss in accuracy.

5.7 Complete Management of ASS affected areas

Successful management of ASS requires coordinated input across the spectrum of community, industry and governments (National Working Party 2000). In order to successfully ensure complete and effective management is achieved, landowners and the surrounding industrial community must work with the local Government to become involved with activities concerning the flood mitigation network. All people involved need to be educated and made aware of the impacts of disturbance. As noted in the literature review conducted as part of this study, there are a range of options for minimising impacts of ASS within actual drainage channels. These include the use of weirs, floodgates and neutralisation barriers. While these options may prove promising during trials (Indraratna et al. 2005), there have been limited long term studies of these installations. Also, while most options target material while it is still within the drain, there is noticeably less literature available which provides information on options for treating material once it is removed.

In this case, ASS found within drains of the Shoalhaven estuary are well-established, as are many more similar areas across the coast of Australia. They require intensive management if they are to be disturbed. In order to avoid other problems with surrounding land and livestock that are escalated with poorly maintained drainage, maintenance is essential. Thus, ASS disturbance in the area is often unavoidable. Research into best management practice for drain maintenance and water table management is crucial to fill critical knowledge gaps (National Working Party 2000). There is a great need for treatment technologies to be adapted and refined so that they may be adopted into routine practice, as currently there is a lack of affordable, simple and standardized methods for the treatment of sulfidic material, hindering the ability to meet the third and fourth principal objectives of the National strategy which aim to mitigate impacts when ASS disturbance is unavoidable and rehabilitate disturbed ASS and acid drainage (National Working Party 2000).

The neutralisation of sulfuric acid has been identified as possible using agricultural lime (Sammut et al. 2004) as oxidation is inhibited by liming (Bloomfield and Coulter 1974) however it has also been widely recognised that the use of lime is often economically impractical (Melville and White 2007)

and quite difficult to apply and dissolve in large amounts. Other options for the use of lime include its use in liming drains so acid produced in the drain walls is neutralised as it washes out as well as in the treatment of acid water (Sammut et al. 2004).

In order to manage the ASS of the Shoalhaven in a comprehensive and complete manner, simple but periodic procedures must be carried out along with the implementation and monitoring of specific management methods. The production of the REF document (2011) in response to planned maintenance activities including dredging highlights the fact that prior to this there has been limited full scale maintenance activities carried out. As current practice, the Shoalhaven City Council attempts to combat the overgrown vegetation within drainage channels using herbicides and chemicals. While this method is able to target problems in the short term, it is not sufficient to make up an entire remediation plan or to resolve problems raised by concerned landholders (see Figure 5.2). The eventual cost of this large scale irregular maintenance is often much higher due to the long term accumulation of material and bank erosion that may not be dealt with (Robertson et al. 1998). This accumulation of material may alter the original design of the drains and thus should be monitored and dealt with periodically to ensure drainage channels work as they should.



Figure 5.2: Photograph taken at P1D1 (3) displaying the close proximity of livestock to drains, and weeds that could be potentially mistaken as grass (to be treated with herbicides) (taken 23 July 2012).

The ASS drainage guidelines (Robertson et al. 1998) also recognise that material originally removed while digging the drains has remained dumped on banks and may continue to be a source of acidity,

leaching acid many years later. This type of material should also be identified and subsequently limed, as well as preferably capped or removed to reduce continuing impacts.

While it goes beyond the scope of this research, the management of acid sulfate soils requires the integration of many different assessment and management tools. Identification of the problem is the first step, followed by prevention including planning, remediation, education and research (Atkinson 2000). Remediation is the part of management addressed in this study; however it does not stand alone in the fight to tackle the ASS problem. As stated by Atkinson et al. (1999), it is apparent that there are limited strategies for dealing with acid in the environment. These include containment, neutralisation, dilution and transformation. For treating material that has been removed from its original environment, neutralisation using lime is the most appropriate strategy. As has been previously noted, there is a lack of extensive options for remediation and treatment of material outside of drainage channels on the Shoalhaven floodplain, in opposition to those targeting remediation within drains (Blunden 2000; Indraratna et al. 2005; Indraratna et al. 2006; Golab and Indraratna 2009; Indraratna et al. 2011). While there may be literature available on treating dry land tailings, these occur on mine sites where there is a reduced capacity to act in the best interests of the natural environment and formation of ASS has occurred via other mechanisms, thus there is a limited use for this type of research in its application to coastal environments (Fitzpatrick et al. 1998; Lin et al. 2004), due to caution required when applying industrial residues in coastal areas.

5.8 Additional causes for error in results and limitations of study

While this study has produced some interesting results, there were a number of methodical aspects of the study that have led to limitations in the precision of research and the degree to which conclusions may be drawn. Apart from result accuracy of the chosen methods, as described above, there were also a number of other causes for error in completeness that may be noted. These are hereby described.

In terms of the collection of samples, while all efforts were made to ensure the same method was used, not all were taken on the same day, or in the same weather conditions. Therefore, there would have been small differences. There was no uniformity in the manner in which samples were drawn, as some may have been closer to the bank etc. than others and samples were not all collected at the same depth causing major differences between samples in the amount of water or organic matter present, as well as the depth to which the sulfuric layer was actually sampled. Those with large amounts of water often lead to difficulties with analysis because of the limited amount of actual sediment that was available following drying. Samples that were taken from deeper levels

were often more firmer and difficult to remove from the sampling pole, hindering the ability to collect a representative sample. This procedural problem also contributes to the problem of being unable to determine whether each different sample represents a recent accumulation or an older part of the subsoil.

In terms of the number of samples and completeness of collection across areas, there were issues with time limiting the number of samples that could be analysed. Also, only small parts of some long drains were sampled and not every drain with complaints was actually sampled due to accessibility to land problems. As a result, occasionally there was reason to believe that some drains would have similar results to other drains in the area or there would be uniform results along a drain. However, as seen in results, this is not necessarily the case and the worst case scenarios that have been proposed may not be accurate as the specific locality with the highest acidity ratings may not have actually been sampled. Problems in interpreting mean values also arise from these issues. Yet following from this, a safety factor of 2 has been used in the proposal of lime rates, removing the need for a high degree of accuracy because any excess acid to be neutralised should be accounted for with a doubling of the lime amount. However, it must be noted that this also increases the cost of liming by double.

Finally, in terms of the transport and laboratory work associated with the collected samples, issues such as oxidation prior to analysis and changes in pH over time had the potential to affect results. Also, as with any laboratory analysis of a large number of samples, small amounts of contamination may have occurred due to remnants of previous samples remaining on or within equipment.

6. Conclusions and Recommendations

6.1 Conclusions

The primary aim of this study was to analyse differing levels of acidity and subsequent liming rates required for complete neutralisation of dredged material for flood mitigation drains and wider project areas of the Shoalhaven River estuary region. The use of agricultural lime was examined in order to assist with remediation following maintenance works of the drains part of a flood mitigation scheme in the area. Previous studies of management options in ASS areas were also discussed in order to gain a holistic view of the approach to tackle problems pertaining to coastal ASS environments. This study has presented the project areas in terms of their relative liming requirements and identified reasons for possible variance in values across the region. The study directed attention to drain P2G1 as a naturally formed drain with elevated sulfur and pyrite concentrations, key factors in potential and actual acidity. Issues with zinc contamination were also found pertaining to this drain. Characteristics including grain size and distance from the Shoalhaven River have also been described as reasons behind locational differences in acidity and consequential lime rates. The extent to which values produced from separate methods correlate with each other has also been used as a base upon which to discuss the reliability and accuracy of results using these methods. The comparative values that have been presented in this study emphasise the need for extensive management to be carried out involving additional analysis measures to be introduced to accompany maintenance works and additional management options to be used in the target of identified 'hot spot' locations.

6.2 Recommendations for Management

The discussion of remediation options, integrated with results of this study which has characterised areas in terms of acid neutralisation necessary following maintenance, provides the foundations for additional management recommendations, as follows:

- P2G1 has been identified as a drain of heightened acidity. This drain is not recognised in the 2011 S.C.C. Review of Environmental Factors maintenance document as an asset of the flood mitigation scheme due to the fact that it is a natural, rather than constructed drain. Therefore, drains in addition to those identified by the flood mitigation scheme also need to be monitored and entered into management documents to ensure they are targeted in the same manner as the constructed drainage channels.

- Not all drains need to have removal of sediment undertaken, thus I would recommend that drains are classified not solely on location, but rather the type and level of maintenance that needs to be carried out, as more intensive maintenance may result in the removal of deeper sediments and in greater amounts.
- Following classification of the degree of required maintenance, a document should be prepared that provides details on which drains should be dredged first and how often maintenance activities are to be carried out. A program needs to be developed to ensure periodic monitoring and regular maintenance works rather than sporadic large scale activities.
- As part of the listed safeguards (S.C. Council 2011), regular laboratory testing of pH should be accompanied by further analysis of acid material concentrations such as sulfur in order to produce a fuller picture of acidity derived from acid sulfate soils.
- No more than 60% of a drain is to be dredged within the same year, thus areas / locations that are to be subject to maintenance works within a specific year should be sampled and analysed in terms of sulfate / pyrite concentrations in the same way each year. Laboratory analysis would be the most optimum method for uniform analysis.
- Scalds, persistently bare areas of land associated with pyrite oxidation (Hughes et al. 2004) in the area should be identified and efforts made for their revegetation.

6.3 Recommendations for Future Studies

Carrying on from findings of this study, recommendations for future research directions include the following:

- To confirm results and obtain higher levels of accuracy, more detailed laboratory analysis should be carried out, especially for those drains that recorded unusually high or outlier results from any of the three methods.
- Investigation into the confirmed neutralisation of large amounts of material as maintenance is actually carried out should be conducted to assess whether liming rates applied are sufficient enough for treatment purposes. Effectiveness of different project area applications should also be explored.
- To assess differences over time, a study similar to this one could be conducted over an extended time period, including varying weather, climatic and tidal conditions in an

attempt to assess reasons for difference in acidity levels. Samples would need to be collected at exactly the same locations at each time of collection.

- Effects on the surrounding environment following dumping of dredged material could potentially be a source of future study.
- Research into the occurrence of elevated zinc concentrations in the area could be conducted.

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Appendix 1: Asset Table of flood mitigation drain system

Project no.	Project name	Plan Reference Number	Relevant Drains	Asset ID	Drain Length (m)	Sampled?	Complaints?
1	Worigee Swamp	521.01	P1D1a	43353	160		
			P1D1b	43354	40		
			P1D1c	48991	230		
			P1D1	43330	2760	Yes	
2	Terara Swamp	522.01	P2D1	43309	3160		
			P2D2	43367	3760	Yes	
			P2D3	43368	1000		
3	Joram's Creek	523.01	P3D1a	43369	230		
			P3D1b	43356	230		
			P3D9a	43357	280		
			P3D2	43311	1150		
			P3D3	43312	400		
			P3D4	43313	690		
			P3D8	43314	1120		Yes
			P3D9	43315	450		
			P3D10	43316	95		
			P3D1	43334	2300	Yes	
			P3D5	43335	265		
			P3D6	43336	2000	Yes	Yes
			P3D7	43337	1530		Yes
4	Bolong Area	524.01	P4D1	43338	755	Yes	
			P4D2	43339	2700		
			P4D3	43340	250		
			P4D3a	43370	380		
			P4D4	43371	170		
5	Numbaa Area	525.01 and .02	P5D3	43372	1035		
			P5D1	43317	3400	Yes	
			P5D2	43318	1500	Yes	
			P5D3a	43360	655		
6	Berry and Far Meadow	526.01	P6D8a	43361	480	Yes	Yes

			P6D5a	48994	300		
			P6D9	49171	100		
			P6D1	43319	635		
			P6D5	43320	690		
			P6D6	43321	150		
			P6D7	43322	290	Yes	
			P6D2	43341	520		
			P6D3	43342	1035	Yes	Yes
			P6D4	43343	730	Yes	Yes
			P6D8	43344	770	Yes	Yes
7	Brundee Swamp	527.01	P7D1	43325	2600	Yes	
8	Eelwine and Pyree Areas	530.01	P8D2a	43323	370		
			P8D3	43324	370		
			P8D1	43345	100		
			P8D2	43346	1220		
9	Comonderry - Coolangatta Area	532.02 and .03	P9D2a	43374	120		Yes
			P9D2	43308	620	Yes	Yes
			P9D1	43331	1800	Yes	
10	Saltwater Creek	529.01	P10D1 (creek)	43348	2900	Yes	
11	Comerong Island	502.02					
12	Nowra, Scenic Drive	3212.01	P12D1	48298	15		

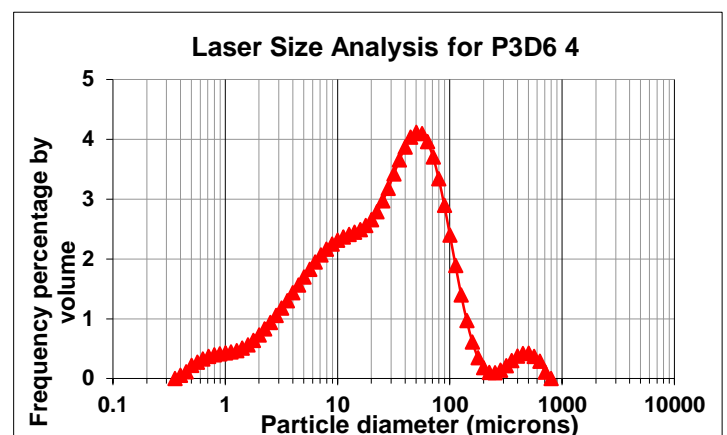
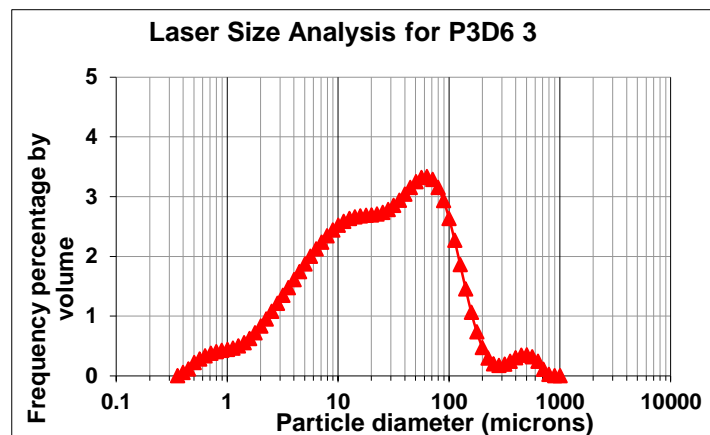
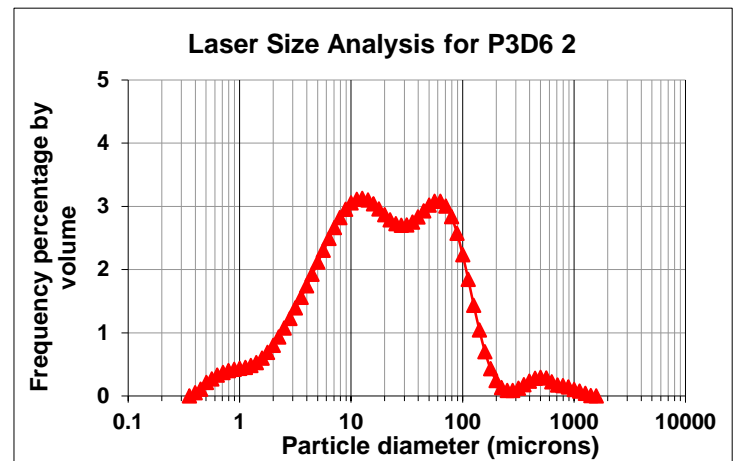
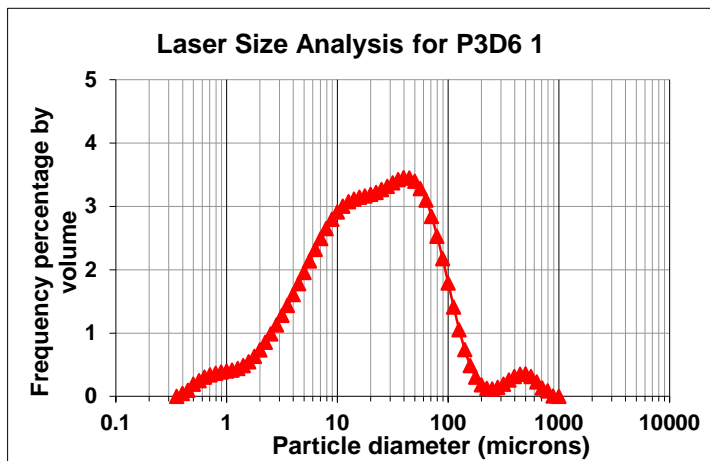
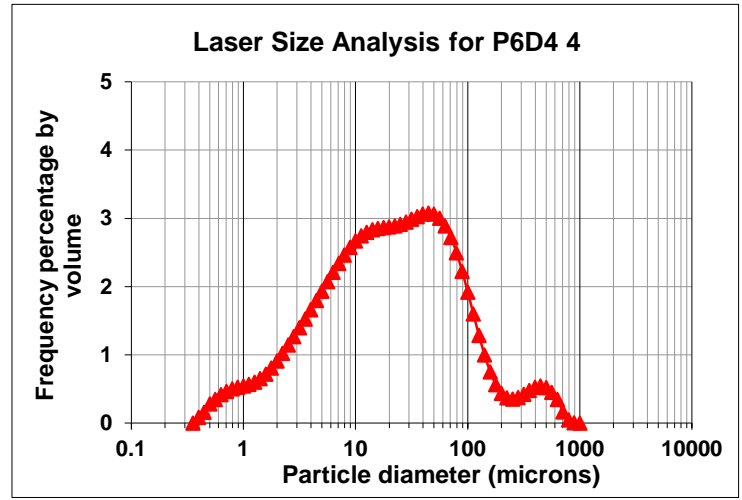
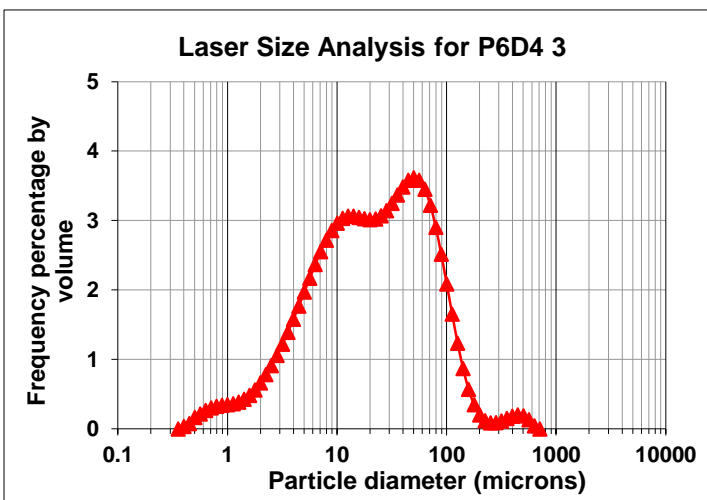
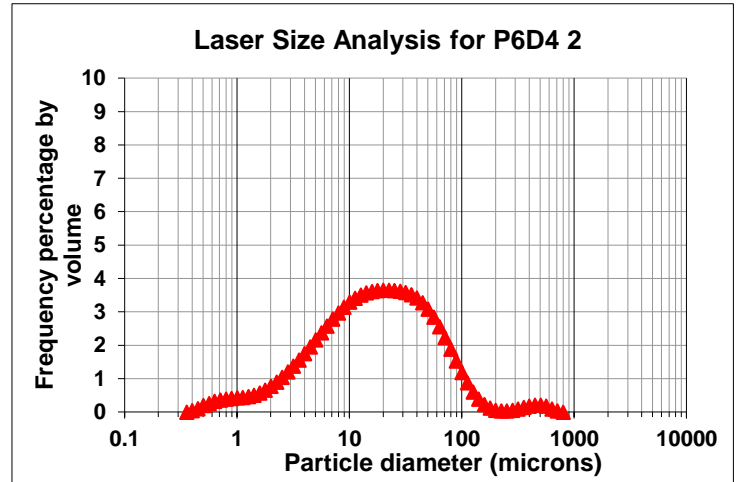
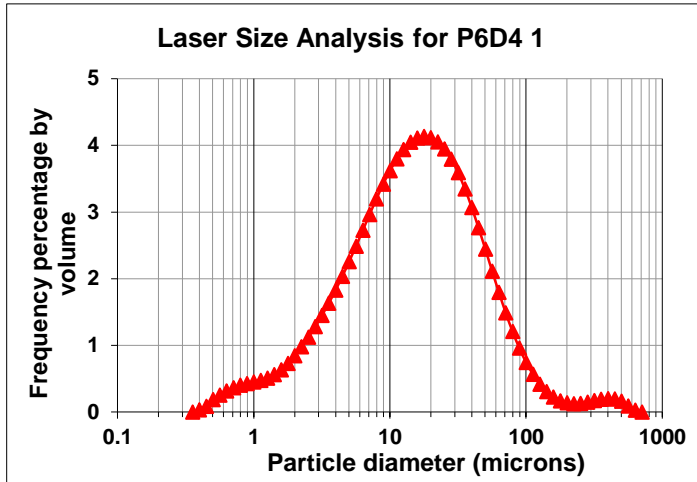
Appendix 2: Grain size Distribution Data (from Mastersizer)

Sample Name	Sand %	Silt %	Clay <4um %	Clay <2um %	D [4, 3] - Volume weighted mean	Mode 1 (microns)	Mode 2 (microns)	Mode 3 (microns)	Mean (microns)	Mean (phi)	Std Dev (phi)	Gskew (phi)	Kurtosis (phi)
P6D4 1	7.73	77.67	14.6	6.27	27.036	16.948	376.26	0	13.74	6.19	1.66	0.1	1.04
P6D4 2	10.45	75.74	13.81	5.93	30.394	20.759	443.89	0	15.46	6.01	1.72	0.11	0.97
P6D4 3	17.04	71.03	11.94	4.96	36.668	47.798	12.74	444.07	18.96	5.72	1.79	0.12	0.89
P6D4 4	19.67	64.71	15.62	7.57	48.255	42.642	425.09	0	18.08	5.79	2.11	0.08	0.99
P3D6 1	16.21	70.85	12.93	5.61	40.678	39.711	452.41	0	18.19	5.78	1.84	0.11	0.94
P3D6 2	19	66.95	14.06	6.11	44.496	11.712	56.66	481.75	17.9	5.8	1.94	0.05	0.89
P3D6 3	22.77	63.18	14.05	6.34	46.485	58.288	460.04	0	20.18	5.63	2.01	0.14	0.89
P3D6 4	20.68	66.64	12.68	5.92	46.096	49.192	452.73	0	21.25	5.56	1.9	0.25	0.93
P3D6 5	17.11	69.52	13.37	5.88	39.066	49.248	12.38	429.16	18.36	5.77	1.85	0.14	0.9
P3D6 6	10.89	76.55	12.56	5.01	27.97	16.938	0	0	15.62	6	1.67	0.06	1.02
P6D8a 1	19.28	71.83	8.9	3.8	53.137	21.181	469.77	0	22.01	5.51	1.86	-0.02	1.14
P6D8a 2	11.54	71.88	16.58	7.88	37.172	18.498	414.05	0	14.37	6.12	1.9	0.09	1.07
P6D8a 3	33.47	54.58	11.96	5.76	132.776	34.759	456.09	0	39.37	4.67	2.78	-0.07	0.89
P6D8a 4	19.39	75.81	4.79	1.77	54.733	23.013	285.27	0	25.45	5.3	1.67	-0.1	1.22
P6D8a 5	6.46	72.79	20.74	10.46	21.958	21.926	0	0	11.75	6.41	1.85	0.18	0.97
P6D8 1	23.28	73.33	3.39	1.12	66.133	21.943	0	0	29.71	5.07	1.75	-0.19	1.17
P6D8 2	33.62	53.91	12.46	6	64.586	93.387	0	0	27.43	5.19	2.23	0.14	0.89
P6D8 3	8.23	72.65	19.12	9.29	24.787	21.873	0	0	12.66	6.3	1.85	0.15	0.98
P6D8 4	6.03	77.28	16.69	7.57	22.033	22.956	0	0	13.23	6.24	1.7	0.18	0.98
P6D8 5	21.31	71.6	7.08	2.91	61.308	18.821	0	0	24.45	5.35	1.92	-0.15	1.18
P6D8 6	10.48	73.82	15.69	7.26	26.496	30.049	0	0	15.25	6.04	1.79	0.18	0.95
P6D8 7	11.57	73.41	15.02	6.82	33.893	26.896	438.54	0	15.59	6	1.81	0.14	0.98
P6D8 8	20.26	64.43	15.31	7.57	48.046	36.354	383.73	0	18.82	5.73	2.12	0.11	1.01
P6D7 1	18.24	65.88	15.88	7.89	44.351	20.039	0	0	17.33	5.85	2.12	0.04	1.07
P6D7 2	17.86	75.41	6.74	2.73	48.15	24.078	406.89	0	22.93	5.45	1.67	-0.01	1.12
P6D7 3	18.5	74.05	7.46	3.21	53.022	24.171	396.74	0.87	23.24	5.43	1.79	-0.03	1.25
P6D3 1	21.06	65.42	13.53	6.07	41.53	14.236	0	0	19.19	5.7	2	0.04	0.93
P6D3 2	17.86	66.37	15.77	7.6	35.79	47.43	12.38	0	17.22	5.86	2	0.12	0.92
P6D3 3	16.28	67.29	16.42	7.77	38.417	13.375	329.96	0	15.88	5.98	2.02	0.04	0.98

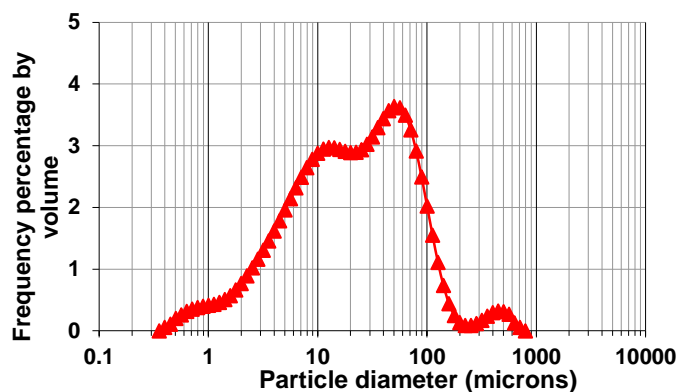
Sample Name	Sand %	Silt %	Clay <4um %	Clay <2um %	D [4, 3] - Volume weighted mean	Mode 1 (microns)	Mode 2 (microns)	Mode 3 (microns)	Mean (microns)	Mean (phi)	Std Dev (phi)	Gskew (phi)	Kurtosis (phi)
P6D3 4	2.65	78.37	18.99	7.81	15.828	10.842	0	0	9.89	6.66	1.52	0.08	1.06
P6D3 5	5.7	75.84	18.46	8.52	20.447	12.641	0	0	11.92	6.39	1.73	0.11	0.99
P6D3 6	14.55	67.77	17.68	8.29	38.844	11.802	0	0	14.54	6.1	2.06	0.01	1.05
P6D3 7	6.24	74.04	19.72	9.06	22.333	11.062	0	0	11.15	6.49	1.76	0.07	1.02
P9D2 1	28.4	56.14	15.46	7.35	79.644	13.205	376.35	0	24.13	5.37	2.55	-0.08	0.95
P9D2 2	41.34	47.46	11.2	4.81	105.47	106.96	11.76	348.67	37	4.76	2.51	0.06	0.81
P4D1 1	30.59	55.8	13.62	6.28	56.181	77.213	14.75	0	24.21	5.37	2.19	0.13	0.87
P4D1 2	26.08	66.53	7.38	2.81	69.885	23.8	402.19	0	27.66	5.18	2.02	-0.08	1.09
P1D1 1	3.24	73.02	23.74	11.72	16.233	11.053	0	0	9.04	6.79	1.73	0.12	1.06
P1D1 2	36.5	54.84	8.66	3.83	97.537	18.865	313.91	0	36.88	4.76	2.36	-0.06	0.88
P1D1 3	50.16	42.38	7.47	3.24	101.124	128.758	20.16	0	47.6	4.39	2.18	0.29	0.87
P1D1 4	38.91	53.32	7.77	3.56	78.895	140.317	24.15	0	36.32	4.78	2.09	0.08	0.86
P1D1 5	33.03	54.9	12.07	5.49	74.87	31.146	0	0	28.68	5.12	2.33	0.05	0.91
P1D1 6	44.34	49.02	6.64	2.71	104.205	119.025	23.65	0	44.66	4.48	2.2	0.09	0.87
P9D1 1	59.14	32.8	8.07	3.79	181.304	342.789	14.12	0	71.94	3.8	2.56	0.36	0.8
P9D1 2	30.08	61.46	8.46	3.59	79.643	29.276	440.23	0	30.39	5.04	2.16	-0.03	1.05
P9D1 3	81.44	16.1	2.46	0.98	311.914	354.142	40.57	0	189.29	2.4	1.9	0.56	1.7
P9D1 4	79.88	17.34	2.78	1.11	393.08	433.884	33.68	0	202.67	2.3	2.16	0.57	1.65
P3D1 1	30.23	60.02	9.74	3.73	82.454	15.96	308.9	0	29.84	5.07	2.34	-0.15	0.9
P3D1 2	38.04	49.67	12.29	5.41	86.905	88.102	12.22	0	31.24	5	2.42	0.08	0.86
P3D1 3	31.75	53.81	14.44	6.34	105.872	13.71	381.91	0	30.01	5.06	2.74	-0.17	0.78
P3D1 4	23.45	60.68	15.87	6.51	55.66	11.609	399.7	0	19.19	5.7	2.24	-0.03	0.94
P3D1 5	34.94	46.31	18.75	10.63	76.934	76.563	10.77	0	24.39	5.36	2.67	0.15	0.87
P2G1 1	24.45	66.91	8.64	3.64	67.253	24.826	381.36	0	26	5.27	2.05	-0.05	1.14
P2G1 2	16.55	74.22	9.23	3.42	43.062	20.908	403.26	0	19.97	5.65	1.74	0	1.06
P2G1 3	18.61	73.47	7.91	3.41	47.929	33.145	398.57	0	23.74	5.4	1.7	0.11	1.12
P7D1 1	17.18	68.13	14.69	6.79	45.485	15.056	424.58	0	17.22	5.86	2.03	0.03	1.04
P7D1 2	46.06	43.44	10.5	5.02	94.709	112.203	0	0	39.65	4.66	2.33	0.27	0.88
P10D1 1	31.51	56.84	11.64	4.99	77.986	45.208	401	0	28.14	5.15	2.31	0.05	0.97

Sample Name	Sand %	Silt %	Clay <4um %	Clay <2um %	D [4, 3] - Volume weighted mean	Mode 1 (microns)	Mode 2 (microns)	Mode 3 (microns)	Mean (microns)	Mean (phi)	Std Dev (phi)	Gskew (phi)	Kurtosis (phi)
P10D1 2	18.39	65.01	16.59	7.53	41.977	13.791	29.31	0	16.77	5.9	2.08	0.04	0.95
P2D2 2	49.25	42.23	8.52	3.76	127.049	253.32	40.38	0	50.64	4.3	2.43	0.19	0.79
P2D2 3	41.19	45.51	13.31	5.72	114.903	284.579	10.15	0	35.5	4.82	2.66	0.01	0.7
P5D1 1	51.19	40.83	7.97	3.83	123.611	202.39	30.57	0	53.18	4.23	2.35	0.25	0.83
P5D1 2	39.58	55.1	5.32	2.21	89.231	36.737	0	0	41.88	4.58	2.01	0.04	0.95
P5D2 1	60.45	32.76	6.78	2.91	130.726	188.988	22.04	0	64.56	3.95	2.23	0.5	0.82
P5D2 2	88.47	9.87	1.66	0.5	216.257	220.723	23.53	0	198.28	2.33	1.21	0.37	2.21

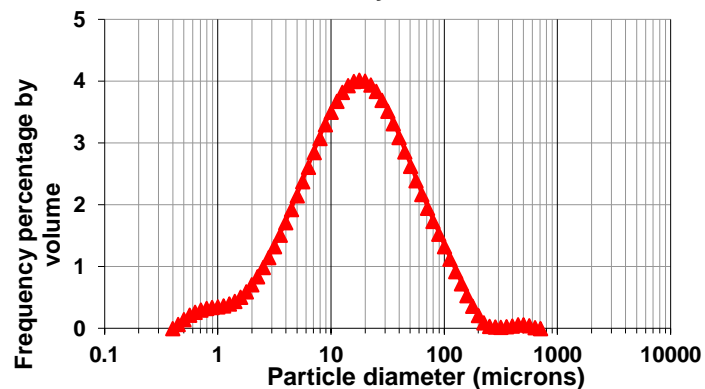
Appendix 3: Grain Size Distribution Graphs



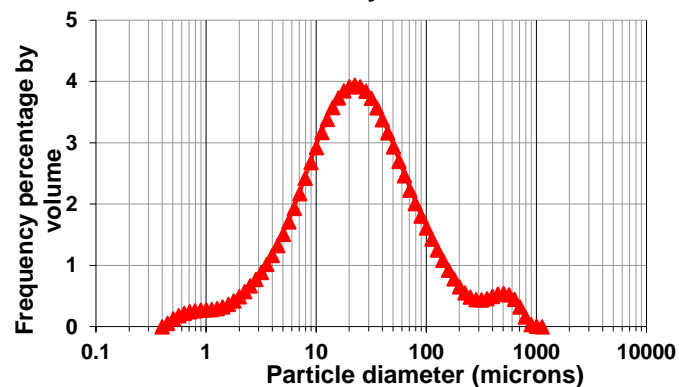
Laser Size Analysis for P3D6 5



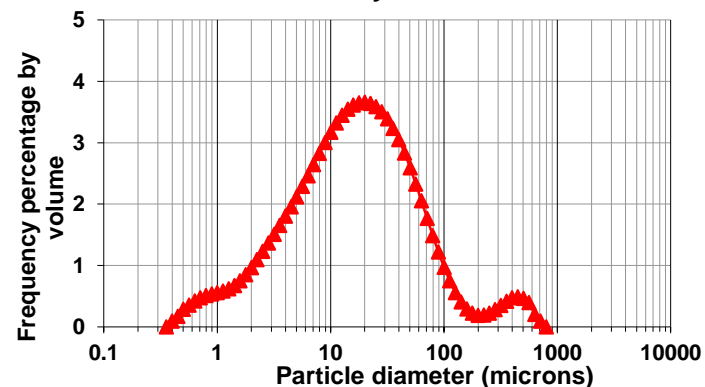
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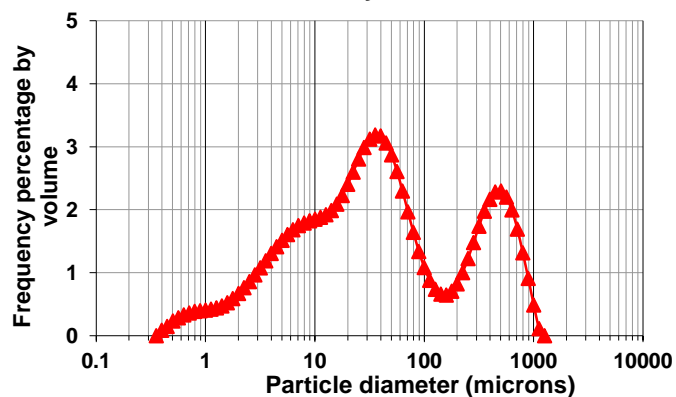
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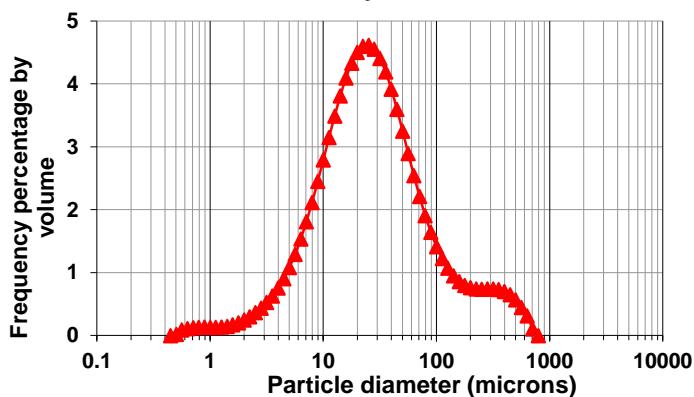
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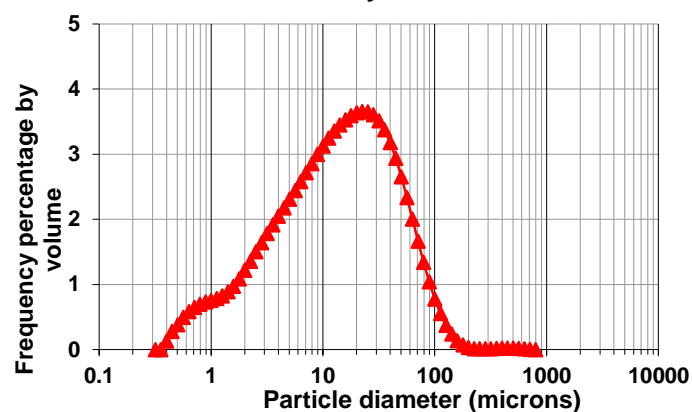
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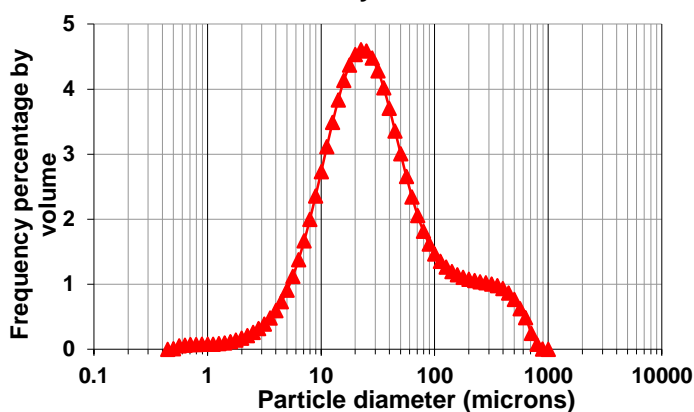
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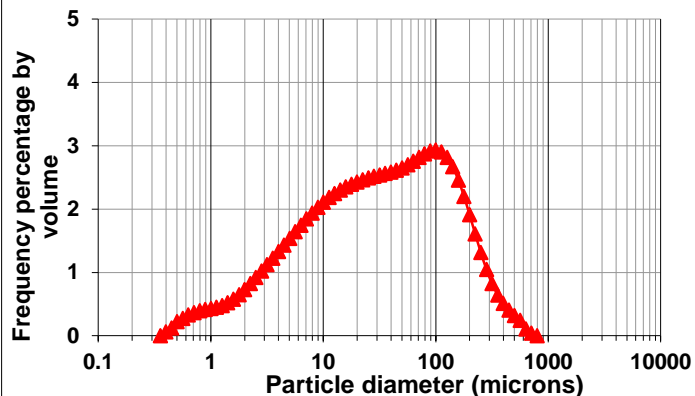
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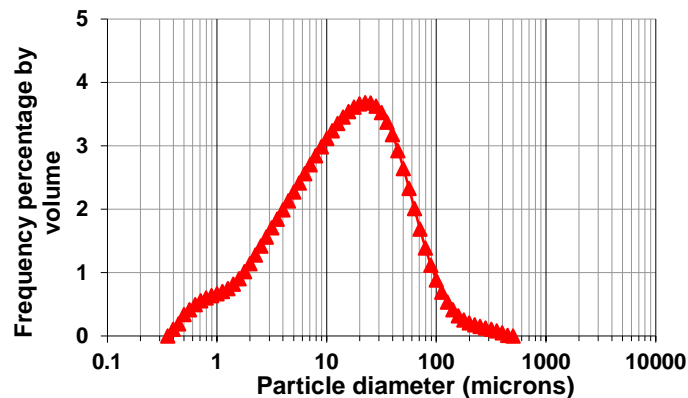
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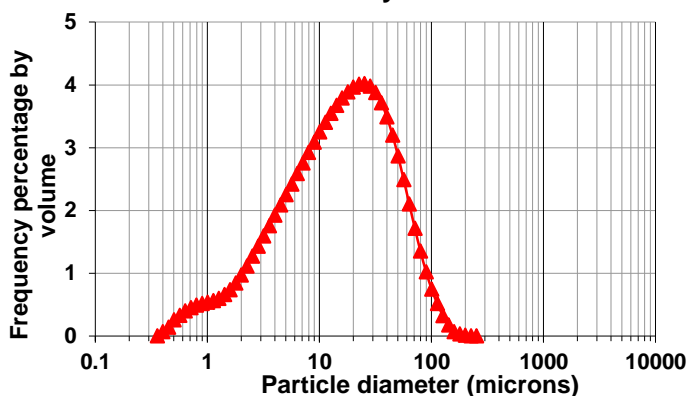
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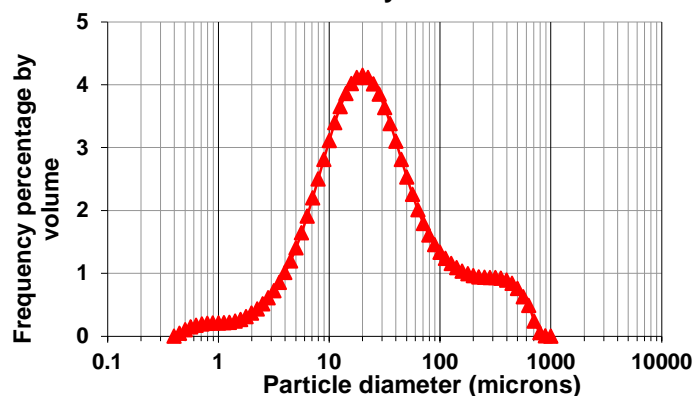
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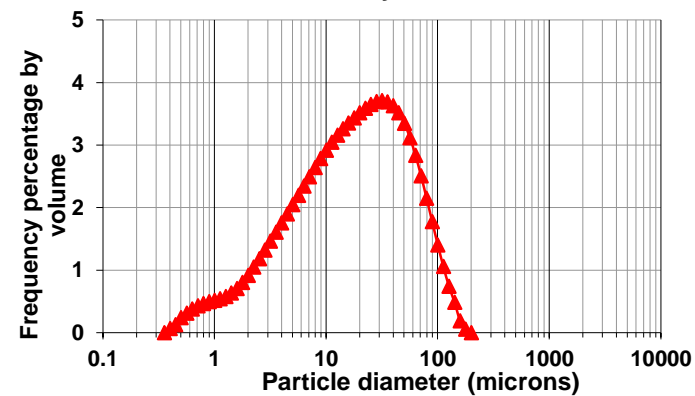
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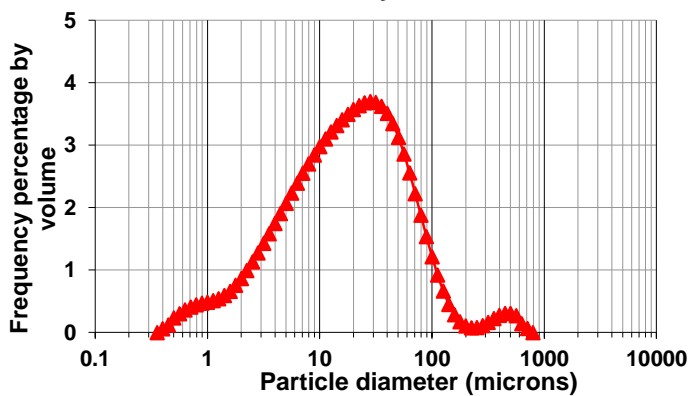
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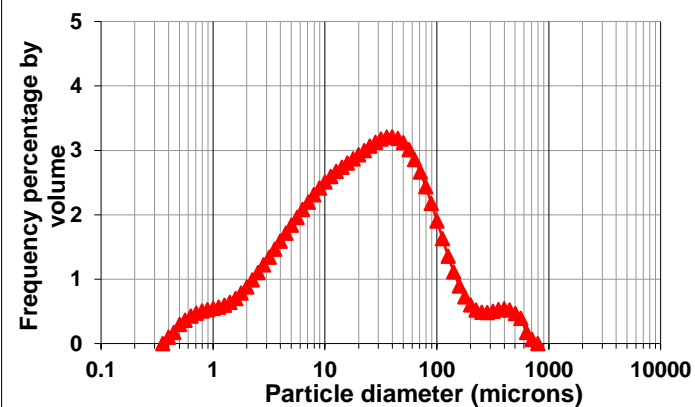
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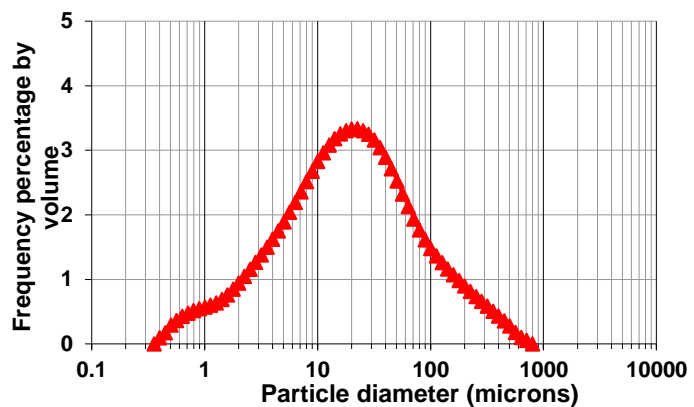
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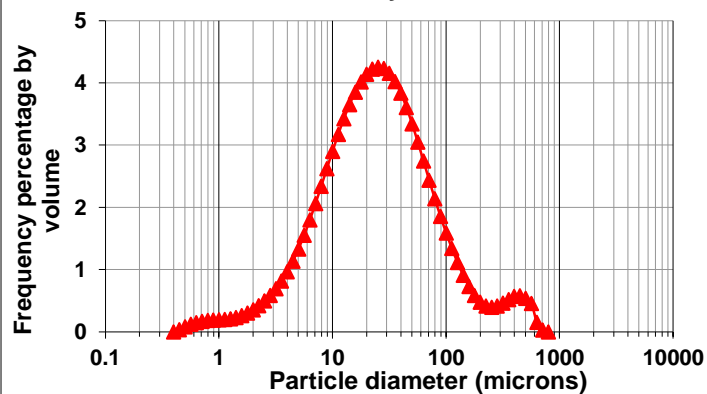
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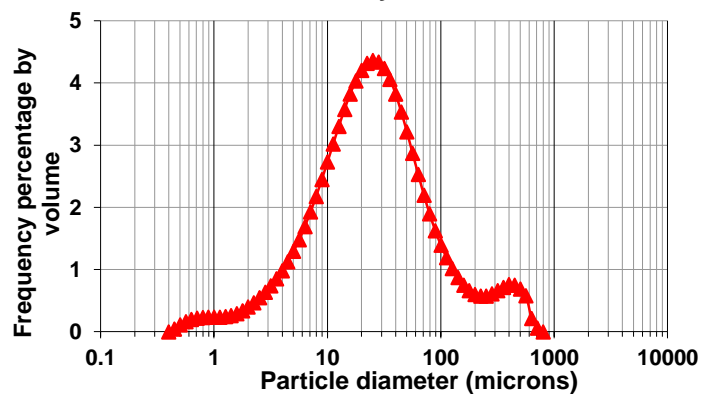
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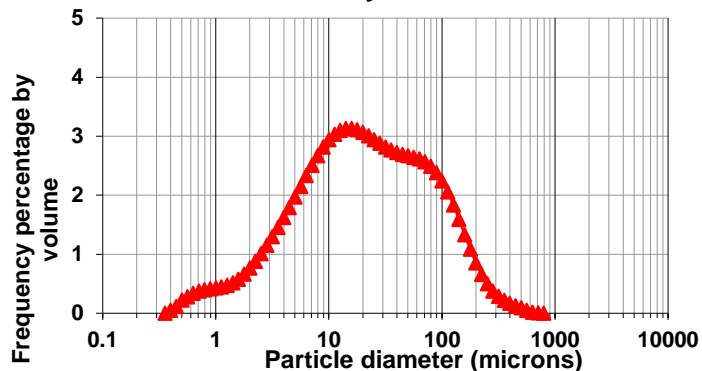
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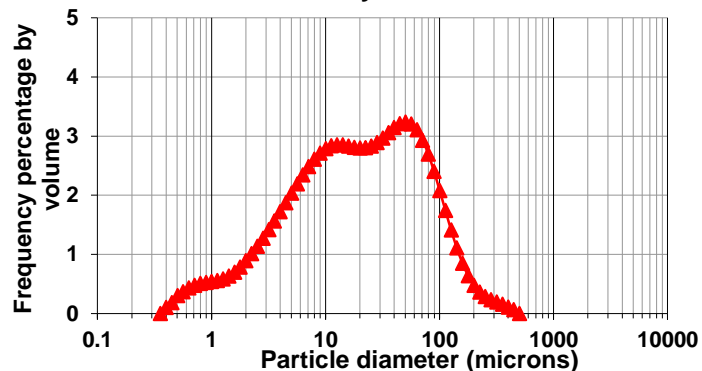
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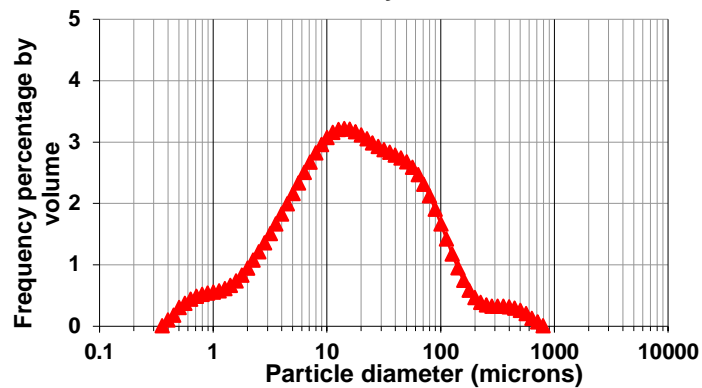
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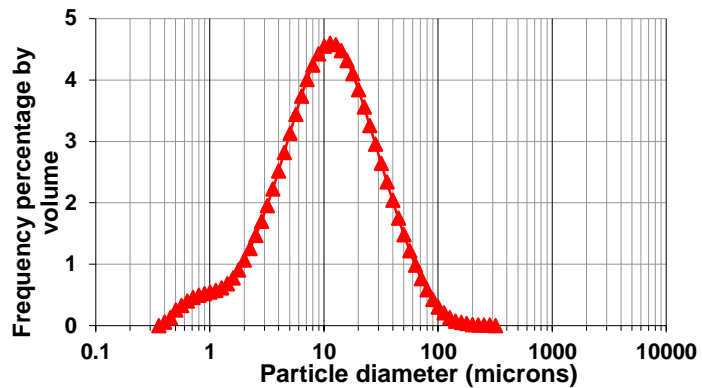
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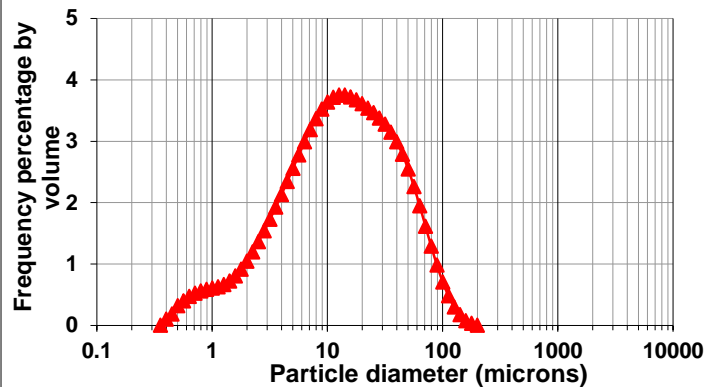
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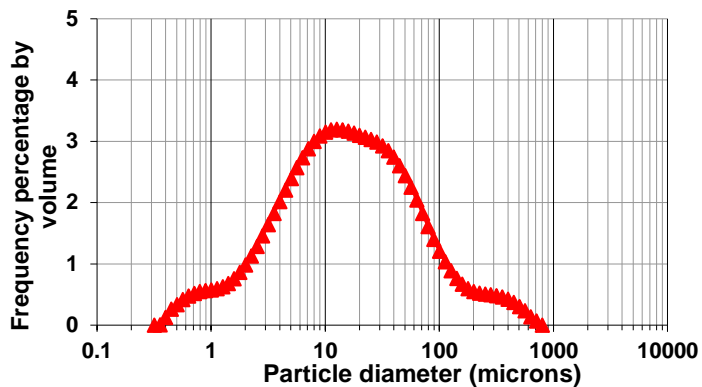
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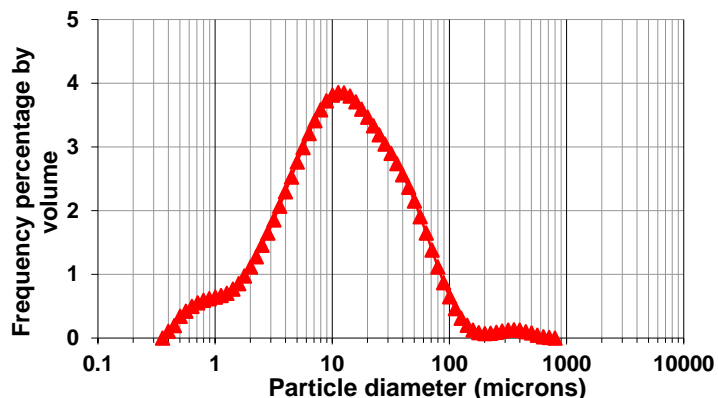
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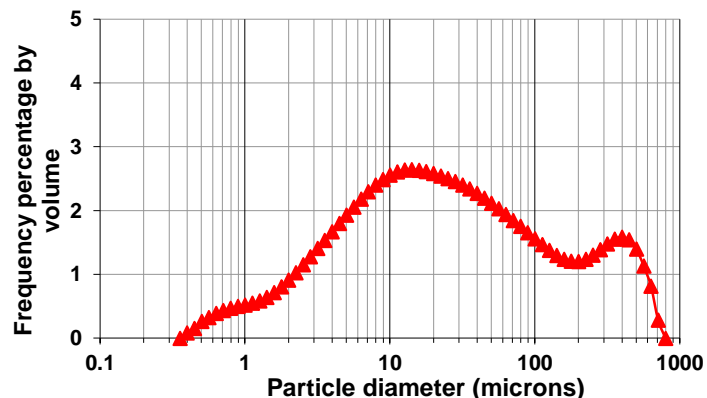
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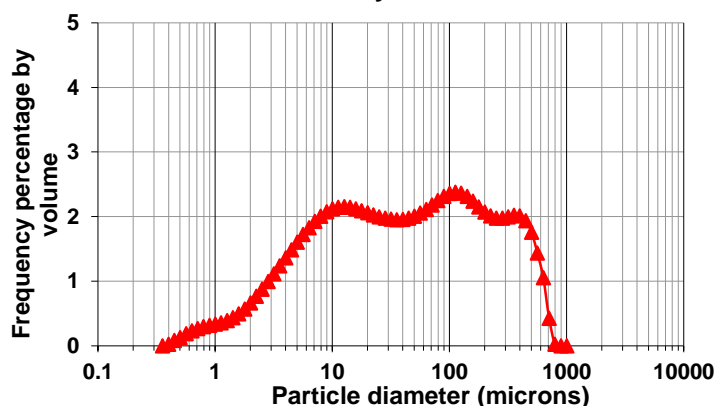
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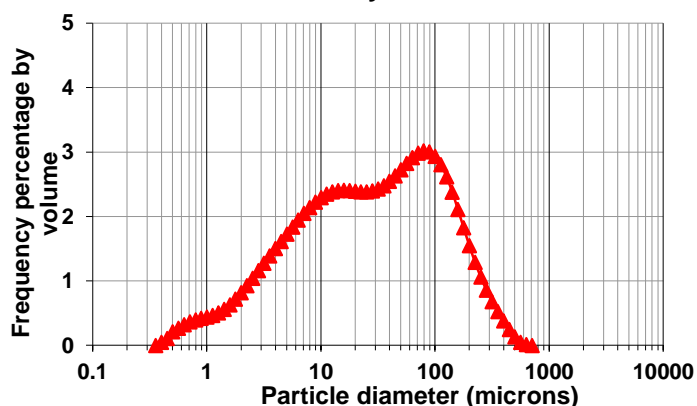
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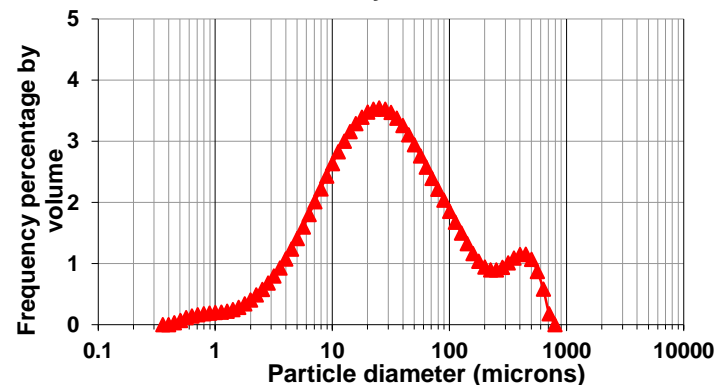
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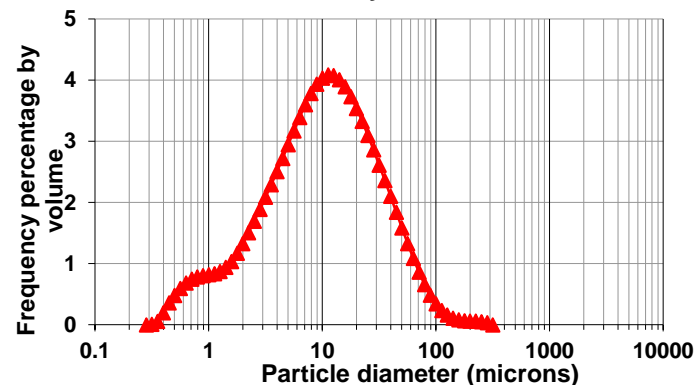
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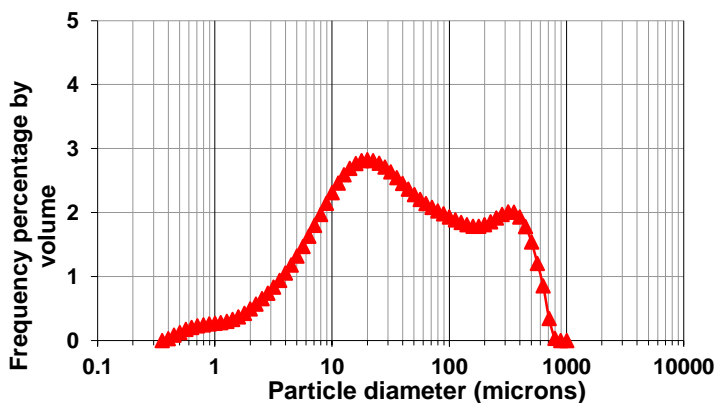
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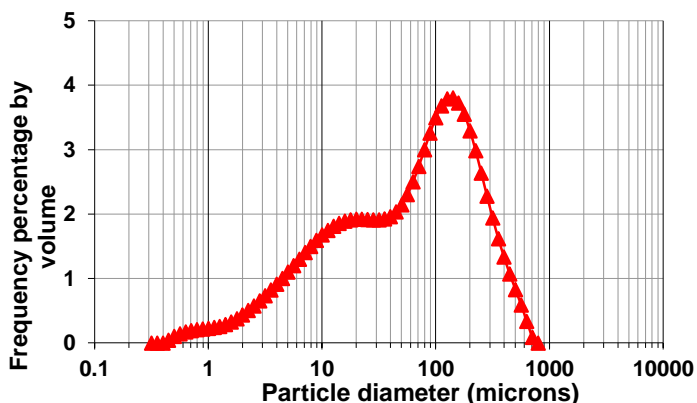
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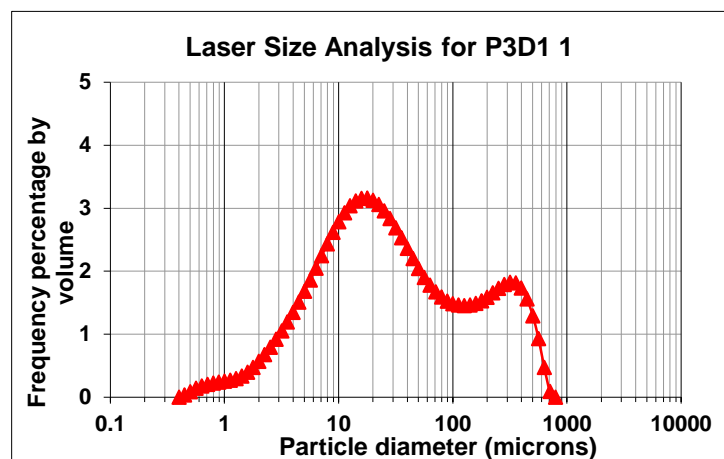
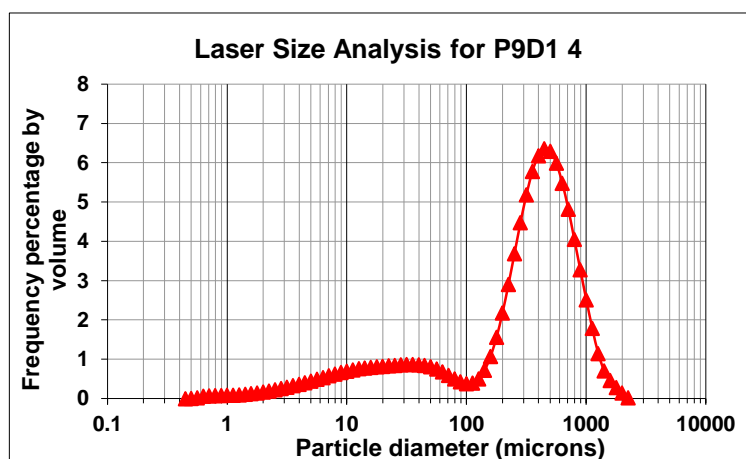
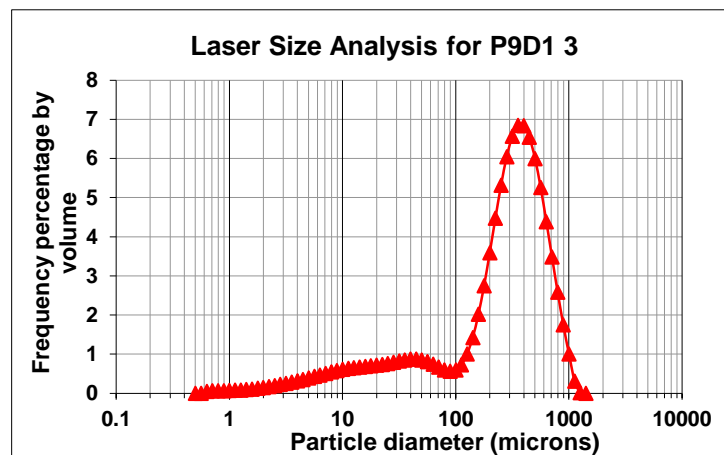
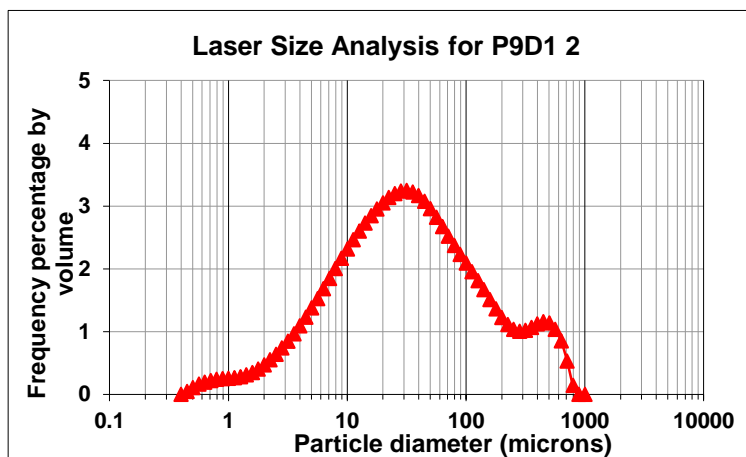
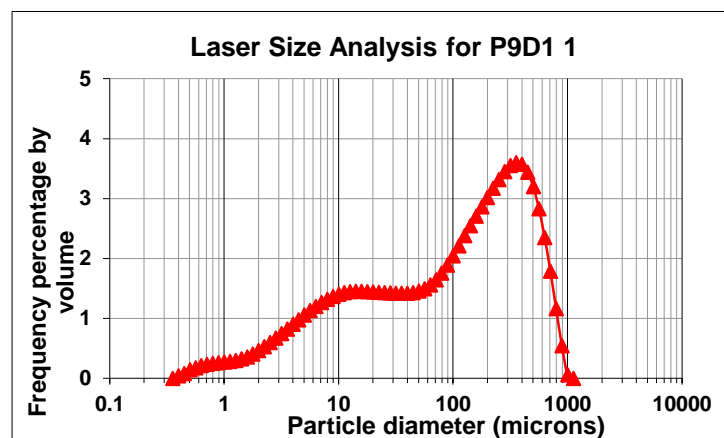
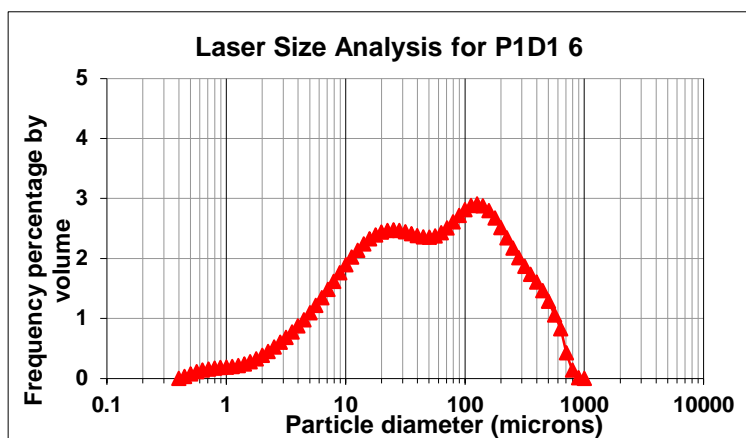
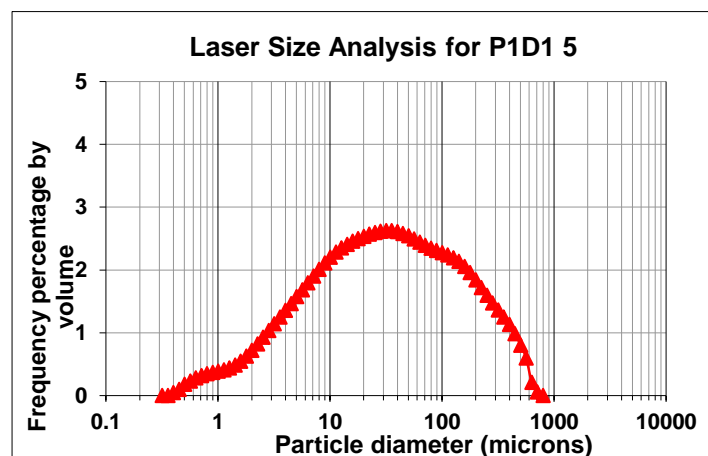
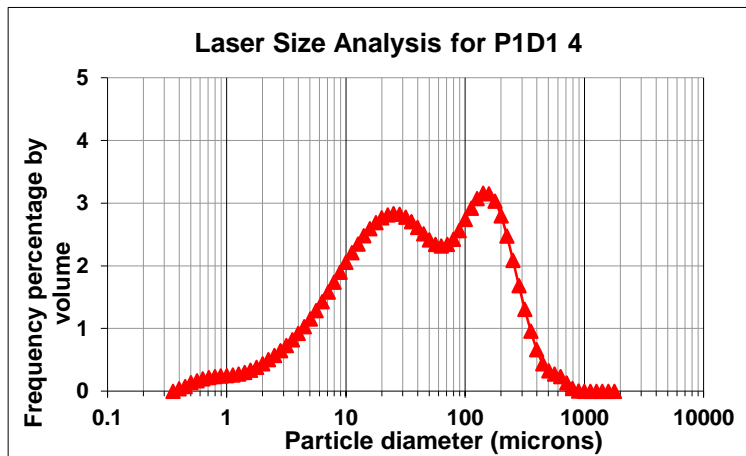


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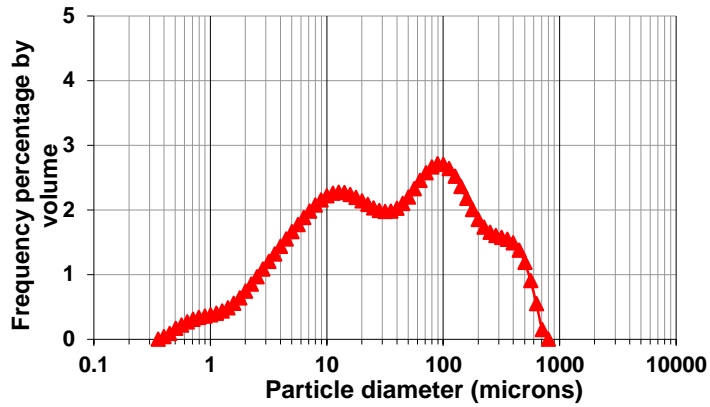


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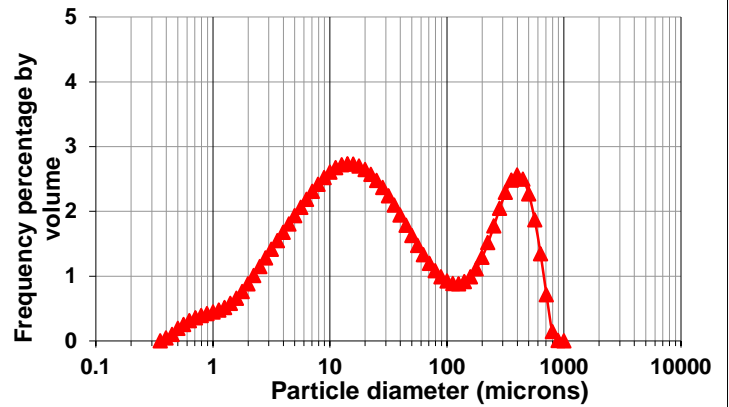




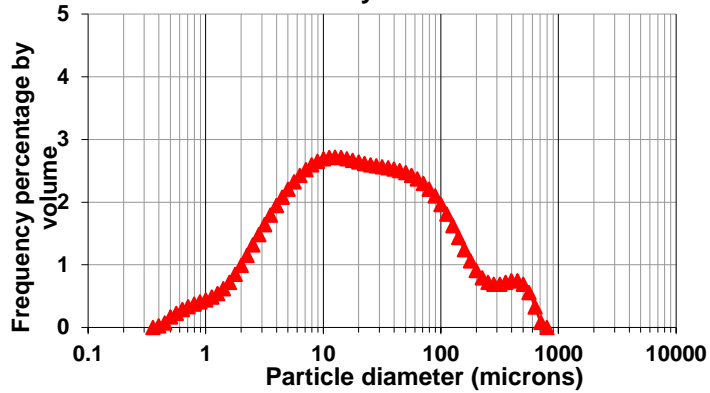
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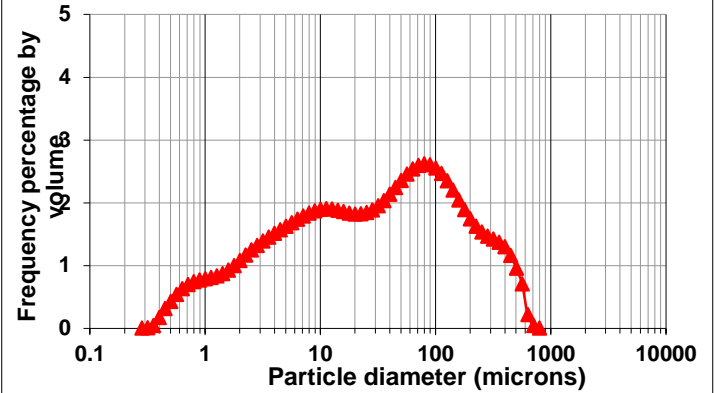
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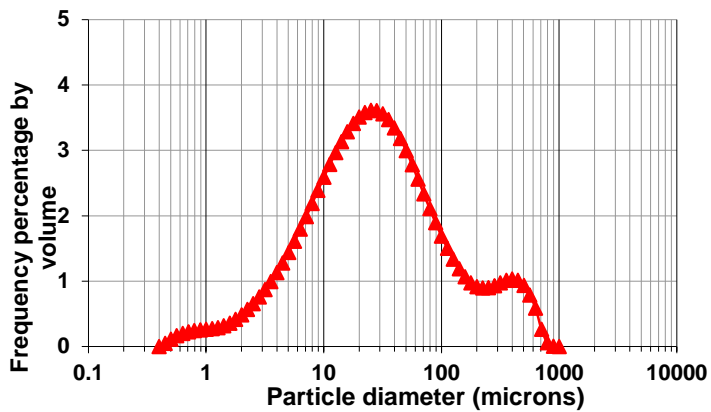
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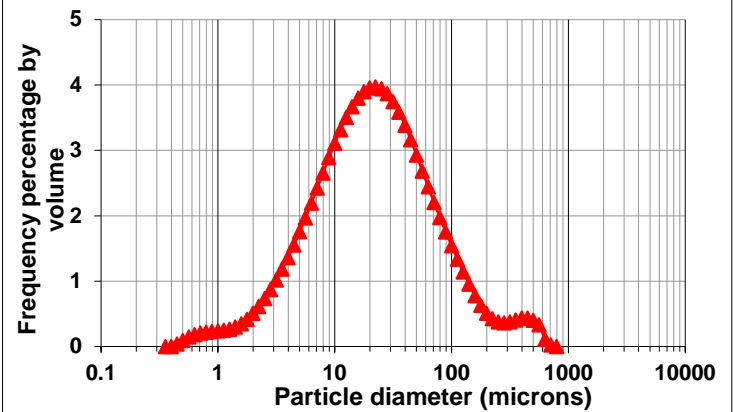
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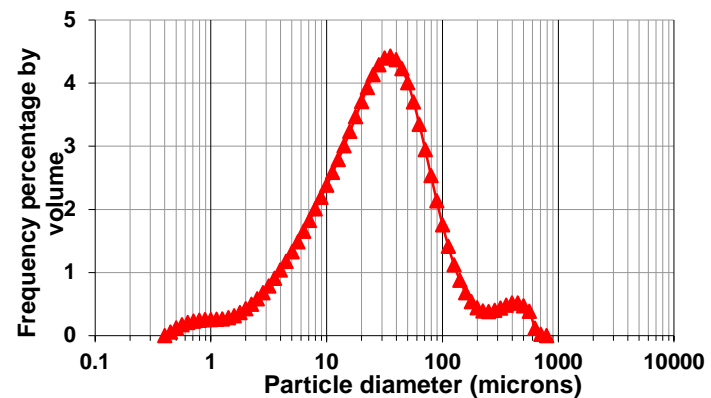
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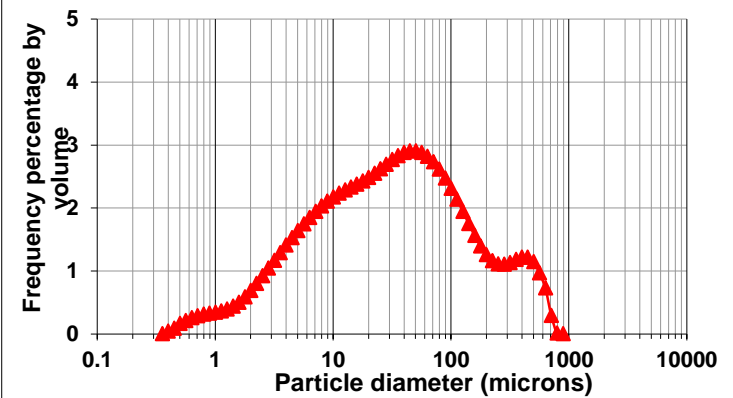
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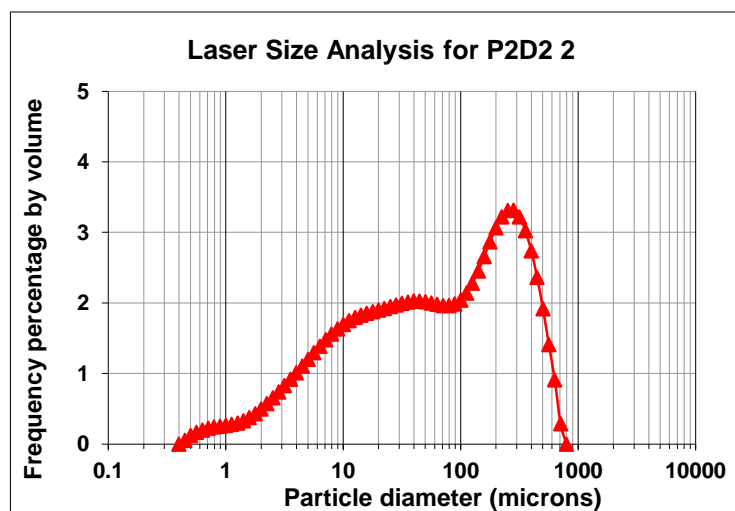
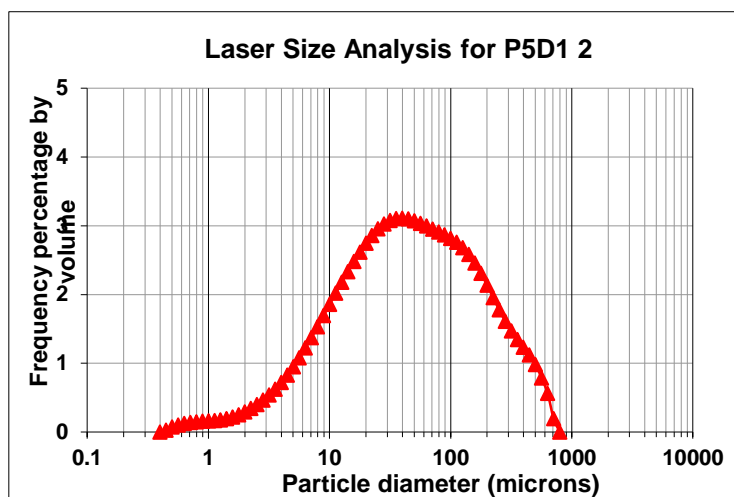
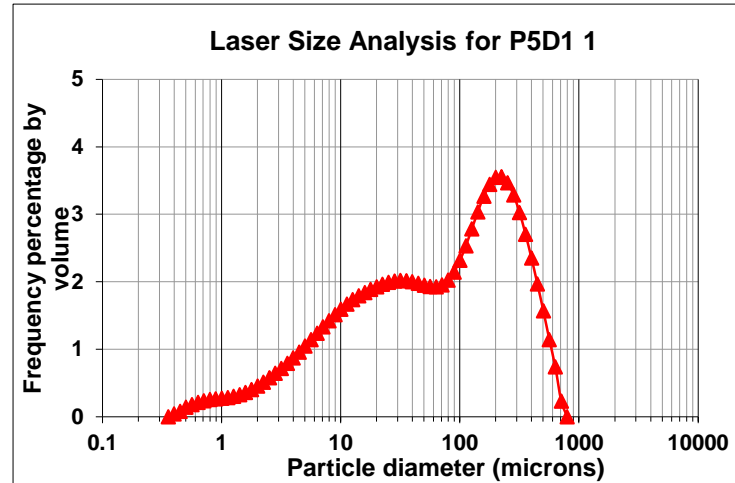
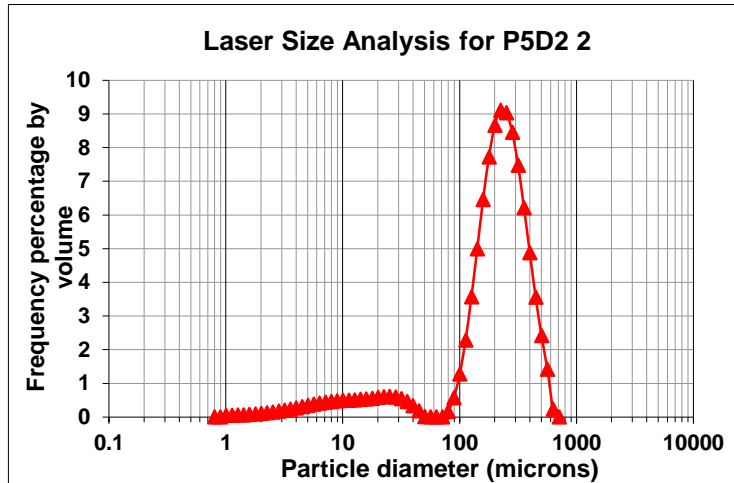
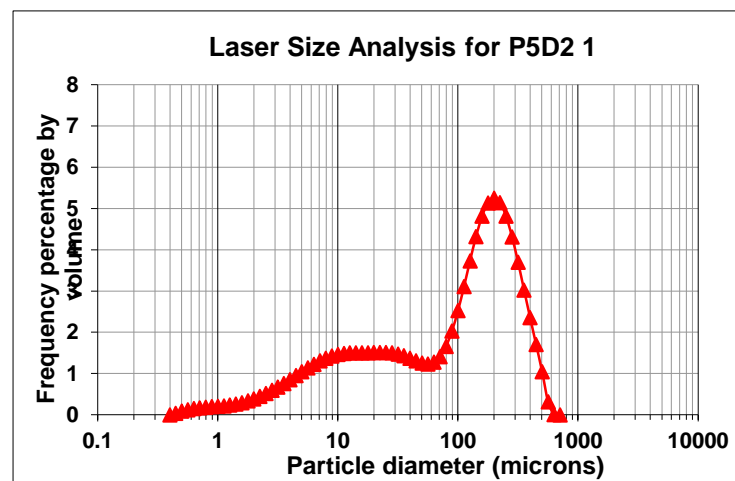
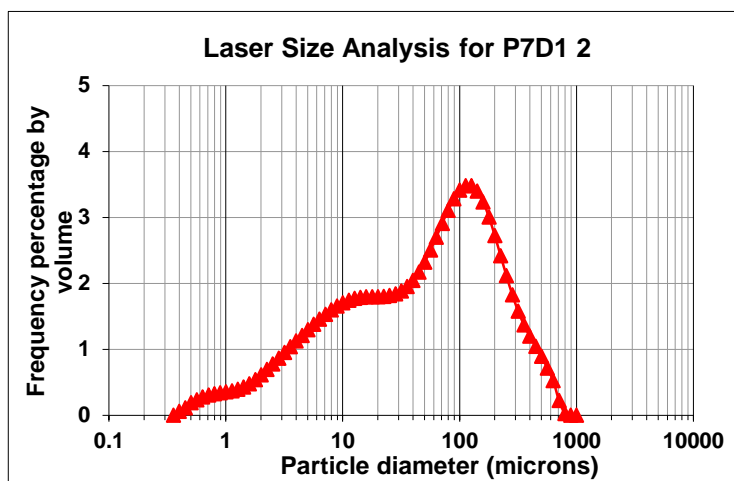
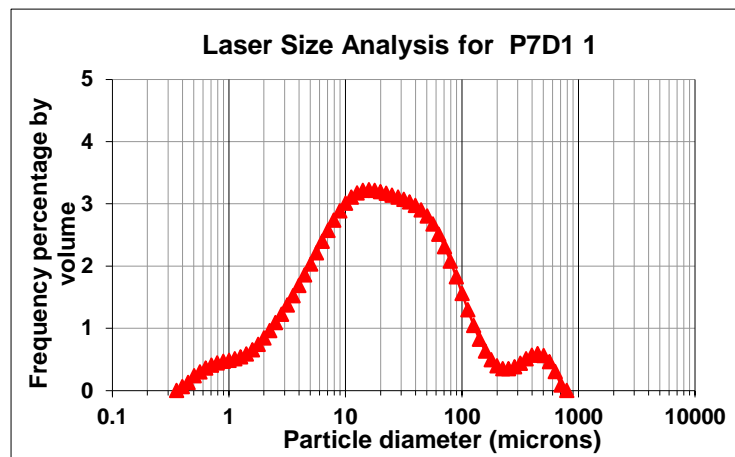
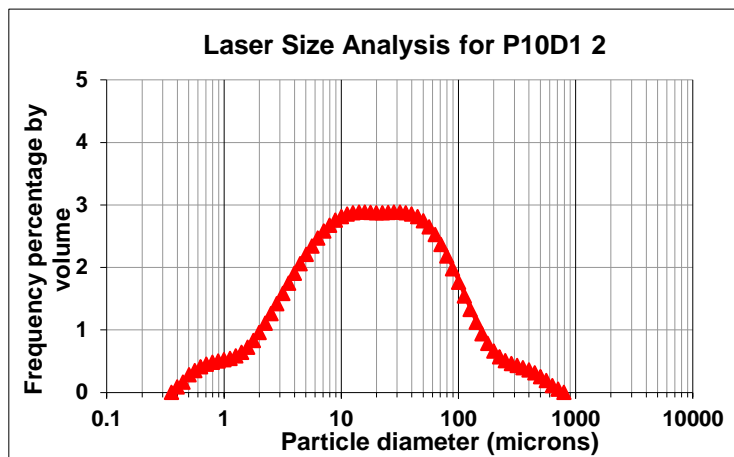


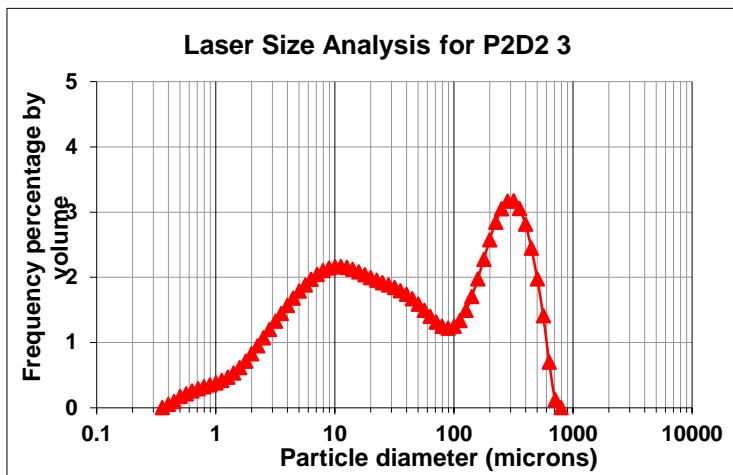
Laser Size Analysis for P2G1 3



Laser Size Analysis for P10D1 1







Appendix 4: Literature Review – Methods for testing acidity

Following is a discussion of the many ways in which acidity may be quantified as described in relevant literature.

Benthic sediments found in drain networks around the country are well-known to contain reactive sulphides at high levels. Burton et al. (2006) documented a study representing the first detailed quantification of elemental sulfur in sediment profiles from ASS landscapes along the coast. Sulfate concentration was also considered in the study performed by Lin et al. (1996). In their study, estimation of the reduced-S content in coastal sulfidic soils/sediments was made by measuring the net increases in titratable acidity and in sulfate concentration in soil extracts after treatment of a sample with 30% hydrogen peroxide. Further comparisons were made between reduced-S content estimated from the sulfate measurement and that measured by a Leco CNS analyser (Lin et al. 1996).

In terms of oxidation, and the role gases such as oxygen play in the process, Carlin et al. (2004) developed a model for steady state transport of oxygen into soils with an exponentially decreasing biological sink with depth and an exponentially increasing chemical (pyrite) sink with depth in south east Queensland. Gas samplers and gas chromatography were used to calculate the difference between the flux of oxygen and carbon dioxide, which was credited to the oxidation of pyrite (Carlin et al. 2004).

In Malaysia, Shamsuddin et al. (2004) analysed total carbon, texture and pyrite contents. Minerals were determined by using X-Ray diffraction (XRD) analysis after saturation with magnesium. Using XRD, as well as light microscopy and analytical scanning electron microscopy, Bush and Sullivan (1999) were also able to examine the specific distribution and morphology of pyrite found within three Holocene estuarine sediments. This information not only identifies pyrite contents but also contributes additional information about the rate of sulphide oxidation and acid production.

These aforementioned methods demonstrate the range of different ways in which acidity may be assessed. There have also been a number of laboratory and field method tests that have been developed to give qualitative and quantitative results related to sulfides and their oxidation.

Vegas-Vilarrubia et al. (2008) evaluated the usefulness of four common easy-to-apply field survey tests for potential acid sulfate diagnosis in some Histosols and Entisols, soils with high organic matter or lack of identifiable horizons, in wetlands. These include incomplete oxidation by fast air-drying, incubation, fast oxidation with hydrogen peroxide, and the indirect determination of sulphide with lead acetate. These tests were selected based on their ability to meet the needs of people in difficult-to-reach areas and lay-operators in terms of simplicity, ease of application and cost. The first incomplete oxidation test involves the measurement of pH prior to and following 1-week exposure to air to promote pyrite oxidation (Brinkman and Pons, 1972, as reported in Vegas-Vilarrubia et al, 2008). Quicker measurements are obtained with fast oxidation using hydrogen peroxide. This test is a useful field assay to predict the minimum pH an acid-sulfate soil would attain following complete oxidation (Van Beers, 1962, as reported in Vegas-Vilarrubia, 2008). The test involves adding hydrogen peroxide with heat and measurement of pH following the completion of effervescence; however it is more qualitative than quantitative and is not as effective with samples containing large amounts of organic matter. The third test described involves a lengthy process where slow oxidation is carried out in moist conditions with pH measured before and after. The final test is an indirect method that involves treating moist soil with zinc and hydrochloric acid in a test tube, covering with lead acetate impregnated filter paper and correlating the sulphide content with the resultant colouring of the paper (Vegas-Vilarrubia et al. 2008). In assessing the use of all these methods, which were compared with results from XRD, Vegas-Vilarrubia et al. (2008) concluded that all the described

field tests work well in mineral wetland soils, but are not always reliable with highly organic soils. Thus, these tests need to be approached with caution in relation to samples collected for the purposes of this study. For use in treating QLD soils, Ahern et al. (1998), described the field test using hydrogen peroxide as a simple method that involves adding a few ml of peroxide to a small amount of sample to start effervescence, followed by continued addition to ensure the reaction appears complete, before measuring pH (Ahern et al. 1998). This method has also been described as one that needs to be treated with caution when highly organic samples are being studied.

Following the use of basic field tests, there are also a number of methods that have been developed for use in the laboratory. Within the ASS manual, there are a set of guidelines for Acid Sulfate Soils Laboratory Methods (Ahern et al. 1998b) which provide a standardised approach to routine laboratory determination of actual and potential acid production from oxidation of iron sulphides, primarily pyrite, found mainly in estuarine and coastal sediments. These guidelines describe the need for actual acidity (indicated by pH <5.5 or measured TAA) to be taken into account in liming or other calculations. As part of the broader manual, Ahern et al. (1998b) have acknowledged the peroxide oxidation combined acidity and sulfate method as the standard method for determining potential risk for environmental impact and total oxidisable sulfur as a low cost method for calculating potential acidity from oxidation of pyrite. The lab method for determining acidity proposed by Ahern et al. (1998b) has previously been used for sediments taken from the Shoalhaven catchment and is described in the thesis produced by Blunden (2000). The method for total actual acidity involves the suspension of material with KCl, titration against NaOH until pH 5.5, addition of hydrogen peroxide and further addition of NaOH until a pH 5.5 is retained. The total volume of sodium hydroxide used in this method is used to calculate total actual acidity. For estimating potential acidity, additions of 30% hydrogen peroxide were applied to KCl sample suspensions, samples were heated over a water bath and additions were continued until the end of effervescence. Aliquots were then titrated again to pH 5.5 with NaOH for determination of the total potential acidity (Blunden 2000).

Following publication of the ASS manual, Lin et al. (2000) claimed to have proposed an improved analytical procedure for the determination of total actual acidity (TAA) in acid sulfate soils. The method they developed involves the use of a superior extracting solution, 0.5 M BaCl₂, as opposed to the 1 M NaCl employed by Konsten et al. (1988). This method was identified as an improved experimental design to obtain correction factors for calculating total actual acidity and increased accuracy levels (Lin et al. 2000).

Further, a numerical scheme for the simulation of pyrite oxidation, and the generation of acidic oxidation products, in acidic material with a macropore dominated structure has been derived and described by Indraratna and Blunden (2000). Working with soils from the south coast of NSW and in conjunction with a commercially available water flow model to simulate regimes, a three dimensional pyrite oxidation numerical model was recognised as suitable for the assessment of generated acidity and acid sulfate soil management strategies at the paddock scale (Indraratna and Blunden 2000).

Appendix 5: Trace Element Analysis Results (XRF data)

	Element	S	Cl	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr
Sample Number	Dimension	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
P6D4 1	HONS756	25490	12080	136	99	23	25	42	123	16	2	4	1	49	92	193
P6D4 2	HONS757	28640	33540	111	142	24	27	28	106	15	2	8	1	58	101	145
P6D4 3	HONS758	25290	17850	102	133	23	27	25	97	13	2	7	1	43	96	161
P6D4 4	HONS759	20180	35190	118	143	15	25	32	81	16	1	7	1	48	108	151
P6D3 1	HONS760	24270	4187	112	181	13	23	29	79	13	< 1	5	1	25	95	169
P6D3 2	HONS761	19140	6213	117	143	15	27	28	92	15	2	9	1	22	108	144
P6D3 3	HONS762	21230	6772	121	114	16	27	30	88	16	2	10	< 1	23	110	152
P6D3 4	HONS763	19180	18360	125	145	19	28	34	96	17	2	8	1	39	108	139
P6D3 5	HONS764	17040	13980	118	130	19	28	27	92	16	3	10	1	34	115	133
P6D3 6	HONS765	10450	726	142	65	< 3.0	10	31	59	9	< 1	1	< 1	38	58	78
P6D3 7	HONS791	14260	17150	134	90	19	28	29	97	17	2	12	1	36	121	222
P4D1 1	HONS766	31090	9166	89	268	75	95	22	189	13	2	10	1	33	103	94
P4D1 2	HONS767	36110	3382	89	246	48	64	30	186	9	3	8	1	29	72	116
P1D1 1	HONS768	355	1335	128	139	16	35	32	102	19	2	20	1	6	152	72
P1D1 2	HONS769	3930	389	91	276	12	21	20	70	12	2	6	< 1	5	99	85
P1D1 3	HONS770	14060	2926	70	349	22	36	20	131	12	2	6	< 1	9	85	90
P1D1 4	HONS771	10200	441	69	485	14	30	23	111	8	2	9	< 1	7	66	67
P1D1 5	HONS772	2123	859	103	259	7	18	25	47	16	2	9	1	6	123	81
P1D1 6	HONS773	9710	644	68	365	13	21	15	61	8	2	8	< 1	12	74	86
P9D2 1	HONS774	9637	7264	131	170	15	23	30	68	19	2	10	1	55	135	119
P9D2 2	HONS775	12210	15440	63	400	10	21	17	70	8	2	5	1	37	65	223
P9D1 1	HONS776	12790	3365	48	427	3	17	18	31	5	< 1	5	< 1	13	51	65
P9D1 2	HONS777	26890	4406	66	498	15	25	17	70	7	2	9	1	59	59	73
P9D1 3	HONS778	1329	18	41	317	< 3.3	9	9	26	3	2	2	< 1	8	26	20
P9D1 4	HONS779	7243	203	29	630	5	18	11	19	2	1	3	< 1	11	28	23
P3D1 1	HONS780	18800	1438	80	287	26	39	18	115	11	2	11	< 1	14	84	65
P3D1 2	HONS781	8038	5392	61	244	10	22	12	59	10	2	5	< 1	9	84	58

	Element	S	Cl	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr
P3D1 3	HONS782	3760	1330	84	341	15	22	22	50	10	2	6	1	8	81	62
P3D1 4	HONS783	5904	1048	118	129	15	29	38	164	17	2	10	1	30	108	94
P3D1 5	HONS784	11720	1921	84	198	12	31	15	48	12	2	9	1	12	97	52
P3D6 1	HONS785	28720	7089	103	115	16	23	26	81	14	2	6	< 1	36	98	139
P3D6 2	HONS786	21960	10340	102	104	11	28	20	97	14	3	8	< 1	28	107	109
P3D6 3	HONS787	29160	7337	96	143	27	38	26	193	14	1	6	1	45	99	119
P3D6 4	HONS788	24820	3860	96	142	26	37	21	60	14	2	7	< 1	28	104	106
P3D6 5	HONS789	21900	8054	94	139	14	32	22	100	14	2	9	< 1	23	108	97
P3D6 6	HONS790	26650	10890	84	176	12	25	20	76	12	2	7	< 1	52	97	109
P6D7 1	HONS792	17690	3677	131	169	14	22	36	73	14	2	7	1	22	85	155
P6D8 2	HONS793	18340	4300	103	171	12	19	33	60	13	2	6	1	20	84	159
P6D8 3	HONS794	16050	4756	173	115	16	24	53	81	18	< 1	5	1	31	89	152
P6D8 4	HONS795	20740	1235	145	99	19	24	44	87	17	2	9	1	17	101	192
P6D8 5	HONS796	26310	6778	109	200	32	30	50	119	10	2	4	1	40	52	106
P6D8 6	HONS797	23830	2688	135	112	17	23	41	83	16	2	8	1	19	95	193
P6D8 7	HONS798	19660	3784	140	147	18	22	43	75	15	2	6	1	23	85	163
P6D8 8	HONS799	23340	1760	118	181	17	22	34	80	13	2	6	1	16	81	164
P6D8a 1	HONS800	17570	2742	108	102	34	31	49	137	11	2	6	1	41	57	113
P6D8a 2	HONS801	14590	3536	142	103	18	25	43	86	17	2	11	1	20	93	147
P6D8a 3	HONS802	7218	254	94	368	27	25	19	42	6	2	15	< 1	7	40	80
P6D8a 5	HONS803	12680	437	132	103	6	19	32	55	14	< 1	12	1	11	77	107

	Element	Y	Zr	Nb	Mo	Cd	Sn	Sb	Cs	Ba	La	Ce	Hf	Ta	W	Hg	Pb	Bi	Th	U
Sample Number	Dimension	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
P6D4 1	HONS756	30	245	10	< 1	< 2	3	< 3	< 4	381	18	52	6	3	< 1	< 1	20	< 1	9	5.2
P6D4 2	HONS757	32	267	11	< 1	< 2	6	< 3	< 4	340	26	<10	7	2	< 1	< 1	17	< 1	11.4	5.5
P6D4 3	HONS758	30	231	10	< 1	< 2	5	< 3	< 4	322	38	66	6	2	< 1	< 1	16	< 1	10.5	4
P6D4 4	HONS759	31	258	11	< 1	< 2	5	< 3	< 4	373	19	41	6	2	< 1	< 1	18	< 1	11.7	5.1
P6D3 1	HONS760	25	303	10	< 1	< 2	2	< 3	< 4	381	32	38	7	2	< 1	< 1	14	< 1	9.8	4.2
P6D3 2	HONS761	31	273	11	< 1	< 2	3	< 3	< 4	361	23	50	7	2	< 1	< 1	17	< 1	10.9	4.8
P6D3 3	HONS762	32	266	11	< 1	< 2	5	< 3	< 4	357	39	68	6	2	< 1	< 1	18	< 1	11.6	5.1
P6D3 4	HONS763	32	225	11	< 1	< 2	5	< 3	< 4	345	50	103	7	2	< 1	< 1	19	< 1	11.5	4.9
P6D3 5	HONS764	32	246	12	< 1	< 2	6	< 3	< 4	353	33	74	7	2	< 1	< 1	19	< 1	12.7	3.9
P6D3 6	HONS765	15	103	5	< 1	< 2	< 1	< 3	< 4	201	<10	<10	2	2	< 1	< 1	14	< 1	4.9	< 1.0
P6D3 7	HONS791	33	224	12	< 1	< 2	4	< 3	< 4	342	31	80	7	2	< 1	< 1	21	< 1	13.2	4.8
P4D1 1	HONS766	43	296	12	< 1	< 2	7	< 3	< 4	304	40	70	8	1	< 1	< 1	17	< 1	11.3	4.9
P4D1 2	HONS767	68	308	10	< 1	< 2	3	< 3	< 4	243	38	112	9	2	< 1	< 1	15	< 1	10.3	4.6
P1D1 1	HONS768	43	258	15	< 1	< 2	6	< 3	< 4	455	52	98	8	2	< 1	< 1	31	< 1	16.7	3.5
P1D1 2	HONS769	25	279	10	< 1	< 2	11	< 3	< 4	326	26	46	5	4	< 1	< 1	22	< 1	9	2.8
P1D1 3	HONS770	27	275	10	< 1	< 2	7	< 3	< 4	265	43	61	5	1	< 1	< 1	26	< 1	7.9	2.3
P1D1 4	HONS771	22	190	7	< 1	< 2	10	< 3	< 4	227	28	54	5	2	< 1	< 1	15	< 1	5.9	0.8
P1D1 5	HONS772	29	324	13	< 1	< 2	8	< 3	< 4	381	29	61	7	7	< 1	< 1	18	< 1	12.9	4.9
P1D1 6	HONS773	22	227	8	< 1	< 2	6	< 3	< 4	248	36	<10	5	3	< 1	< 1	15	< 1	7.3	1.7
P9D2 1	HONS774	27	238	13	< 1	< 2	9	< 3	< 4	369	<10	82	5	2	< 1	< 1	24	< 1	14.4	6.4
P9D2 2	HONS775	20	266	8	< 1	< 2	10	< 3	< 4	261	32	38	5	5	< 1	< 1	13	< 1	7.4	2.8
P9D1 1	HONS776	15	212	6	< 1	< 2	8	< 3	< 4	218	31	<10	4	2	< 1	< 1	8	< 1	4.2	1.8
P9D1 2	HONS777	19	193	7	< 1	< 2	6	< 3	< 4	257	24	40	4	1	< 1	< 1	14	< 1	5.5	4.3
P9D1 3	HONS778	11	227	4	< 1	< 2	12	< 3	< 4	121	21	<10	3	2	< 1	< 1	4	< 1	1.4	3.8
P9D1 4	HONS779	8	132	4	< 1	< 2	7	< 3	< 4	125	24	27	3	5	< 1	< 1	5	< 1	1	1
P3D1 1	HONS780	31	274	10	< 1	< 2	6	< 3	< 4	334	33	72	6	1	< 1	< 1	14	< 1	9.5	2.3
P3D1 2	HONS781	19	208	8	< 1	< 2	7	< 3	< 4	325	30	69	5	2	< 1	< 1	14	< 1	7.1	2.3

	Element	S	Cl	V	Cr	MnO	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr
Sample Number	Dimension	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
P2G1 1	HONS804	53910	17020	100.2	222.2	0.03774	134.7	26.9	814.3	14.3	1.7	11.3	0.5	66.7	96.7	84.3
P2G1 2	HONS805	64710	3105	89.7	141.5	0.05774	122.9	22.6	476.2	11.7	2.3	9.8	0.7	65.2	96.1	105.6
P2G1 3	HONS806	113900	16660	78.7	132.3	0.03394	216.5	21	1016	9.6	0.9	10.2	0.4	140.1	69.6	99.3
P5D1 1	HONS807	10750	6403	49.2	305.1	0.01284	16.6	13.7	158.4	6.8	1.2	9.7	0.4	33.7	66.1	85.6
P5D1 2	HONS808	21190	8300	50.5	387.2	0.01688	32.4	21.8	168.6	6.5	2	4.1	0.2	84.4	63.6	136.6
P5D2 1	HONS809	8249	2272	20.5	352.2	0.00857	16.3	8.5	42.1	3.5	0.5	2.9	0.3	11.4	49.3	51.6
P5D2 2	HONS810	7063	1099	15.3	298.1	0.00885	12.1	8.2	26.4	2.6	1.7	2.6	0.1	6.4	40	42.1
P10D1 1	HONS811	8431	7470	105.4	208.6	0.00679	27.9	18.6	156.8	11.5	1.3	10.7	0.6	35	87.6	146.9
P10D1 2	HONS812	19280	9434	104.6	155.9	0.01391	45	15.6	156.9	12.2	2.1	20.3	0.6	67.4	97.8	101.6
P7D1 1	HONS813	12830	25040	89.1	136.1	0.0102	21.4	20.2	68.8	15.3	2.2	9.5	0.6	55.6	126.8	93.7
P7D1 2	HONS814	19720	8514	72.8	322.2	0.01767	25.9	17.8	67.7	9.6	1.7	7.9	0.3	26	80.5	79.8
P2D2 2	HONS815	13260	13920	81.9	355.3	0.01403	34.6	15	156.7	9.9	< 0.5	7.2	0.5	36.5	85.6	88.6
P2D2 3	HONS816	13810	7217	79.9	276.4	0.01	18	17	39.2	10.4	1.6	8.3	0.5	25.4	94.8	102

	Element	Y	Zr	Nb	Mo	Sn	Sb	Te	I	Cs	Ba	La	Ce	Hf	Ta	W	Pb	Bi	Th	U
Sample Number	Dimension	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
P2G1 1	HONS804	36.6	151.6	9.1	< 1.0	5.2	< 3.0	< 3.0	< 3.0	< 4.0	279.3	27.1	64.9	3.9	1.4	< 1.0	19.1	< 1.0	10.4	7.3
P2G1 2	HONS805	42.2	143.2	8.5	< 1.0	3.4	< 3.0	< 3.0	13.4	< 4.0	251.8	29	94.3	6.7	1.3	< 1.0	16.1	< 1.0	9.2	4.1
P2G1 3	HONS806	34.9	84.7	6.5	< 1.0	< 3.0	< 3.0	< 3.0	26.3	< 4.0	170.2	< 2.0	59.6	5.6	< 1.5	< 1.0	14.6	< 1.0	7.2	6.3
P5D1 1	HONS807	15.9	209.5	7	< 1.0	9.2	< 3.0	< 3.0	< 3.0	< 4.0	234.6	29.9	55	3.8	4.2	< 1.0	11.7	< 1.0	5	2.7
P5D1 2	HONS808	17.6	149.8	6.1	< 1.0	8.5	< 3.0	< 3.0	15.4	< 4.0	218.4	< 2.0	41.2	3.8	1.4	< 1.0	12	< 1.0	5	4
P5D2 1	HONS809	9.9	135.7	4.6	18.3	10.1	< 3.0	< 3.0	1.3	< 4.0	190.2	37.6	< 0.8	1.8	3.2	2.5	6.7	< 1.0	1.9	< 0.4
P5D2 2	HONS810	7.8	106	3.6	18.5	5.1	< 3.0	< 3.0	< 3.0	< 4.0	157.6	< 2.0	10.1	1.1	3.2	2.5	5.1	< 1.0	0.8	< 0.3
P10D1 1	HONS811	27.6	229.3	9.9	< 1.0	7.3	2.6	< 3.0	5.3	< 4.0	287	32.1	55.9	5.4	1.2	< 1.0	16.1	< 0.1	9.1	6.3
P10D1 2	HONS812	34.4	280.1	12.1	< 1.0	7.5	< 3.0	< 3.0	17.1	< 4.0	268.4	42.2	79.4	6.6	1.1	< 1.0	20.5	< 1.0	12	5.2
P7D1 1	HONS813	32	317.3	14.3	< 1.0	9.4	< 3.0	< 3.0	< 3.0	< 4.0	375.9	52	85.7	7.4	2.2	3.5	19.5	< 1.0	13.6	2.6
P7D1 2	HONS814	24.6	274.1	9.2	< 1.0	6.7	2.5	< 3.0	< 3.0	< 4.0	237.7	27.6	47.8	5.3	1.2	2.8	13.3	< 0.1	8.3	3.2
P2D2 2	HONS815	21.9	215.4	8.5	< 1.0	7.8	< 3.0	< 3.0	< 3.0	< 4.0	285.1	28.9	54.2	4.7	5.4	< 1.0	13.8	< 1.0	7.2	4.4
P2D2 3	HONS816	17	190.1	9	< 1.0	8.7	< 3.0	< 3.0	< 3.0	< 4.0	299.5	17.9	39.9	3.8	2.8	4	14.7	< 1.0	7.8	2.8

Appendix 6: Mineral Phase Distribution Results (XRD data)

Phase	Sample number Weight (%)															
	P1D1 1	P1D1 2	P1D1 3	P1D1 4	P1D1 5	P1D1 6	P2D2 2	P2D2 3	P2G1 1	P2G1 2	P2G1 3	P3D1 1	P3D1 2	P3D1 3	P3D1 4	P3D1 5
Quartz	49	62.9	66.8	75.2	62	75.6	51.5	47.3	40.6	19.1	18.4	76.4	74.1	75	49.9	80.8
Albite(low)	3.5	3.8	5.7	4.5	4.6	7	1.2		0.6	11.6	0.6	3.6	2.1	5	5.4	1.8
Labradorite	0.7	2.5	3.3	2.1	1.2	0.4	4.6	5.9	2.7	15.1	2	2.1	1.9	0.8	1.7	0.2
Calcite 1									0.2		0.2		0.2			
Kaolin, BISH12	6.9	3.2	2.7	3.6	3.8	2.8	0.5	2.3	3.4	2	4.5	3.2	2.7	2.7	4.9	3.6
Muscovite	16.6	7.5	5	5.8	12	6.8	8		21.5	19.5	12.9	5.1	10.4	6.5	15.5	5.8
Biotite	6.4	6.2	4.6	2	5.5	1.2	7.8	6.9	8.2		6.6	0.4	3.1	2.5	5.5	0.1
Illite 1	0.4	1.4	1.3	4.5	2.4	2.2					4.4	4.2	4.2	5.3	4.6	4.7
Mixed layer illite	5.9	5.9	5.2	0.4	6	0.3	6.5	11.2	4.4	15	1.9	0.3	0.3	0.3	0.4	0.3
Chlorite	4.4	2.9	2.4	1.2	0.6	2.3	6.6		0.6			1.9		1.2	1.2	0.6
Halloysite	5.7	3.6	1.3	0.2	1.7	0.1	11.3	6.8	7.1	12	3.8	0.1	0.1	0.2	10	0.5
Sodium Chloride		0.1			0.1	0.2	0.6		1.4		2.4	0.1	0.2	0.1		0.2
Pyrite	0.5		1.7	0.5		1.1	1.4	1.8	9.2	5.7	42.3	2.6	0.7	0.3	1	1.6
Chi - squared value	3.36	3.46	3.69	3.18	3.26	3.5	5.05	4.27	4.45	5.43	3.27	3.2	3.37	3.35	3.79	3.54

Phase	Sample number Weight (%)																
	P3D6 1	P3D6 2	P3D6 3	P3D6 4	P3D6 5	P3D6 6	P4D1 1	P4D1 2	P5D1 1	P5D1 2	P5D2 1	P5D2 2	P6D8a 1	P6D8a 2	P6D8a 3	P6D8a 5	P6D7 1
Quartz	48.6	47	51	51.6	53.8	58.6	59.9	50.6	67.7	58.5	71.5	69.6	37.7	37.1	72.6	49.9	44.1
Albite(low)	12.5	7.4	9.4	6.7	5.2	5.4	5.2	3.7					15.2	16.2	8.7	11.5	16
Labradorite		2.2	0.6	2.9			1.3	0.9	4.4	6.7	4.6	2.9	4.1	2.2	2.5	4.6	7.4
Calcite 1										0.2							
Kaolin, BISH12	4.2	3.6	3.6	3.6	4.1	3.4	3.7	2.1	1.8	1.7	2.1		2.6	4.2	4	3	2.5
Muscovite	11	11.6	7.2	10.3	11.1	9.4	7.7	5.7	17.1	16.5	15.8	7.6	6	5.1	3.7	3.4	4.6
Biotite	1.5	4.9	3.8	6	3.4	3.3	4.8	3.3	7.1	6.7	5.2	6.5		0.4	1	1.4	1.6
Illite 1			4.1	1.6		0.4	1.7	5.6					7.9	6.8	3.7	6.3	5.6
Mixed layer illite	4.6	5.9	4.6	4.9	5.4	5	4.6	5.4	0.3	2.4	0.2	3.5	6	5.6	0.4	0.4	3.1
Chlorite	2.2	6.2	2.7	3.3	4.6	4.1	2.3	1.2					0.4	0.2	0.3	0.9	1
Halloysite	8.3	6.9	7.4	4.5	6.1	4	2.6	8.2	1.3	5	0.1	9.3	11.6	17.8	0.4	14.5	10.3
Sodium Chloride	0.8	0.3	0.4		1.1	0.8	0.5	0.1		0.5			0.2	0.2	1.2	0.3	
Pyrite	6.3	3.9	5.2	4.6	5.2	5.6	5.7	13.1	0.5	1.8	0.6	0.6	8.5	4.1	1.5	3.8	4
Chi - squared value	3.37	3.82	2.96	3.57	3.36	2.88	3.5	3.04	5.49	4.69	5.86	5.7	3.32	3.29	3.22	3.22	3.35

Phase	Sample number Weight (%)																	
	P6D3 1	P6 D3 2	P6D3 3	P6D3 4	P6D3 5	P6D3 6	P6D3 7	P6D4 1	P6D4 2	P6D4 3	P6D4 4	P6D8 2	P6D8 3	P6D8 4	P6D8 5	P6D8 6	P6D8 7	P6D8 8
Quartz	49.9	45.8	39.6	37.4	42.3	26.9	33.4	34.3	47.2	40	45.4	45.6	32	38.5	53.6	38.4	41.6	55.3
Albite(low)	28.3	13.6	14.2	11	10.8	11.8	10.4	26.7	15.1	12.1	14.7	24.9	18.1	23.3	10.5	18.6	22.2	15.3
Labradorite	0.4	2.5	2.1	3	1.9	5.1	0.8	2.8	0.6	1.3	0.1	6.1	6.2	2.3	4.7	8.3	8.9	3.9
Calcite 1				0.2	0.2	0.6		0.2		0.1								
Kaolin, BISH12	4.1	3.6	4.6	4.1	4.5	3.6	6	3.4	4.5	3.2	3.9	1.8	2.5	3.2	2.4	2.6	2.8	3.1
Muscovite	5.9	8.3	11.5	10.7	12.3	7.6	14.7	7.1	9.7	12.1	11	1	9.1	4.6	0.1	4.7	4.5	1.1
Biotite		3.5	4	1.7	4	1.2	5.4		2.1	5	1.5				1.4			0.6
Illite 1	3.3	3.4		3	3.4	7.2	1.1	2.8	1.6	3.7	0.9	4.5	4.6	5.5	9	5.1	1.8	5
Mixed layer illite	0.4	3.8	6	4.5	4	7.4	5.4	3.5	3.7	5.1	4.6	3.9	3.9	1.8	0.6	4.2	3.7	0.4
Chlorite	1.2	1.8	4.7	2.5	3.3	2.7	5.4	1.2	0.7	3.4	2.5		0.2		0.6	1.1		
Halloysite	0.3	7.9	7.5	13.5	7.7	21.8	12.3	8.6	5.5	6.6	9.1	8.5	17.2	14.8	11.5	10.1	9.1	9.3
Sodium Chloride	0.1	0.3		0.6	0.6	0.5	0.6	0.9	1.1	1.1	0.6	0.2	0.5		0.4			0.4
Pyrite	6.3	5.4	5.8	7.8	4.9	3.7	4.4	8.4	8.3	6.4	5.5	3.5	5.6	6.1	5.3	7	5.4	5.7
Chi - squared value	3.72	3.53	3.72	3.46	3.66	2.63	4.69	3.4	3.08	3.12	3.47	3.69	2.98	3.37	2.9	3.46	3.52	3.43

Phase	Sample number Weight (%)									
	P7D1 1	P7D1 2	P9D1 1	P9D1 2	P9D1 3	P9D1 4	P9D2 1	P9D2 2	P10D1 1	P10D1 2
Quartz	36.2	57.2	86.2	73	95.2	91.8	47.6	78.4	44.3	43.9
Albite(low)	1.4		2.9	5.3	1.2	1.1	4.5	4.5	3.7	2.5
Labradorite	3.7	4	2.7	2.4		1	3.3	2.1	5.2	3.8
Calcite 1										
Kaolin, BISH12	1.1	2.5	1.5	2.5	0.6	0.6	4	2	1.2	3
Muscovite	19.7	17.8		1.7			18.4	4.4	21.2	21.5
Biotite	9.9	7.6		1			5.1	1.8	9.6	6.7
Illite 1			4.2	5.7	2.4	2.9	1	3.7		
Mixed layer illite	12.4	2.4	0.3	0.4	0.2	0.3	6.9	0.3	6.9	5.4
Chlorite	3	0.5	0.3	2.1		1.3	0.6	0.8	0.6	2.3
Halloysite	11.2	5.5	0.1	0.4	0.2	0.2	6.9	0.1	6.3	7
Sodium Chloride		0.2	0.2	0.3	0.1	0.1	0.4	0.4	0.1	0.4
Pyrite	1.6	2.2	1.7	5.2		0.8	1.3	1.5	0.9	3.6
Chi - squared value	5.02	5.07	3.57	3.27	3.38	3.62	3.53	3.27	5.33	4.26

Appendix 7: List of field oxidation pH values

Sample number	Batch number	pH	H ⁺ conc. (M)
P1D1 1	1	3.16	0.042425741
P1D1 2	1	3.04	0.047834889
P1D1 3	1	2.09	0.123687136
P1D1 4	1	2.44	0.087160851
P1D1 5	1	2.18	0.113041531
P1D1 6	1	2.23	0.10752843
P2D2 2	3	1.86	0.15567263
P2D2 3	3	2.24	0.106458504
P2G1 1	3	1.62	0.197898699
P2G1 2	3	1.96	0.140858421
P2G1 3	3	1.98	0.138069237
P3D1 1	2	2.26	0.104350485
P3D1 2	2	2.2	0.110803158
P3D1 3	2	2.81	0.060204992
P3D1 4	2	3.05	0.047358924
P3D1 5	2	1.81	0.163654137
P3D6 1	1	2.32	0.098273586
P3D6 2	1	2.06	0.12745397
P3D6 3	1	1.58	0.205975098
P3D6 4	1	1.7	0.182683524
P3D6 5	1	2.43	0.088036833
P3D6 6	1	2.18	0.113041531
P4D1 1	3	2.04	0.130028711
P4D1 2	3	2.45	0.086293586
P5D1 1	3	2.68	0.068563154
P5D1 2	3	3.14	0.043282798
P5D2 1	3	2.33	0.097295747
P5D1 2	3	2.3	0.100258844
P6D4 1	1	1.9	0.149568619
P6D4 2	1	1.74	0.175520401
P6D4 3	1	2.01	0.133988675
P6D4 4	1	1.95	0.142274072
P6D3 1	2	1.92	0.146606962
P6D3 2	2	2.05	0.128734904
P6D3 3	2	1.81	0.163654137
P6D3 4	2	1.98	0.138069237
P6D3 5	2	2.08	0.124930212

P6D3 6	2	2.79	0.061421214
P6D3 7	2	2.63	0.072078462
P6D7 1	2	2.09	0.123687136
P6D8 2	2	1.77	0.170332989
P6D8 3	2	3.11	0.044600955
P6D8 4	2	1.85	0.157237166
P6D8 5	2	3.19	0.041171871
P6D8 6	2	1.83	0.160413568
P6D8 7	2	1.95	0.142274072
P6D8 8	2	1.83	0.160413568
P6D8a 1	1	2.57	0.076535545
P6D8a 2	1	2.61	0.073534544
P6D8a 3	1	2.45	0.086293586
P6D8a 5	1	2.29	0.101266462
P7D1 1	2	2.24	0.106458504
P7D1 2	2	1.96	0.140858421
P9D2 1	3	1.95	0.142274072
P9D2 2	3	1.89	0.151071809
P9D1 1	3	1.51	0.220909978
P9D1 2	3	1.9	0.149568619
P9D1 3	3	3.52	0.029599435
P9D1 4	3	1.71	0.180865793
P10D1 1	3	2.37	0.093480726
P10D1 2	3	1.88	0.152590106
B1	1	7.22	0.000731802
B2	1	7.16	0.000777055
B3	2	5.7	0.003345965
B4	2	5.64	0.003552868
B5	3	5.72	0.003279711
B6	3	5.7	0.003345965

Appendix 8: Notes taken to describe soil characteristics (taken during time of pH testing)

Sample	Consistency / water	Colour of soil	Organics	Orange material on bag	Shell material
P1D1 1	Hard / clayey	Dark Brown			
P1D1 2	Watery	Almost black	small amount	yes	
P1D1 3	Watery	very dark brown	small amount	yes	
P1D1 4	a lot of water, minimal sediment	Black	a lot	yes	
P1D1 5	like concrete, moist but no actual water	grey / black / brown	minimal	yes	
P1D1 6	very watery	black	yes	yes	
P2D2 2	very soft / runny, some excess water	very dark grey / brown - black	some		
P2D2 3	soft	black	yes - a lot	yes	
P2G1 1	Very soft	dark brown - almost black	some		
P2G1 2	relatively firm, no excess water	black	small amount		
P2G1 3	very soft / moist	black	yes - a lot	very small amount of dull orange	
P3D6 1	minimal amount of sample, ver firm, relatively dry sample	very dark grey			
P3D6 2	a lot of sample, clayey	very dark grey	small amount		
P3D6 3	very wet,	very dark brown / black	very small amount	very small amount	
P3D6 4		dark grey / black	some	small amount	
P3D6 5	firm	very dark grey / brown	A little		
P3D6 6	grainy - a lot of organics	close to black	yes		yes
P3D1 1	Soft, excess water	dark grey / brown	yes - very small amount	yes	
P3D1 2	relatively firm, no excess water, sandy	grey / brown		yes - a lot	
P3D1 3	sandy	light brown / grey	some		

P3D1 4	relatively firm, no excess water	black / brown	yes - a lot	very small amount in corner of bag	
P3D1 5	quite soft, excess water	grey / brown	some	a lot of orange / dark red	
P4D1 1	slightly soft, small amount of excess water	dark grey / brown	very small amount	yes	
P4D1 2	very soft / wet	dark grey / brown	some		pieces of rocky material
P5D1 1	very soft, excess water, little bit sandy	black / brown	very small amount		
P5D1 2	very soft / smooth, excess water	black / dark brown	very small amount		
P5D2 1	slightly firm but very wet, sandy, excess water	dark grey / black			
P5D2 2	quite firm, small amount of excess water	dark grey / black			
P6D4 1	clay consistency, no excess water	dark grey / black			
P6D4 2	clayey, no excess water	dark grey / black	some		
P6D4 3	small amount of excess water, wet clayey	black	a lot		
P6D4 4	firm, no excess water	very dark brown / black			
P6D8a 1	very wet	dark brown	yes		yes
P6D8a 2	wet clayey	dark brown / grey / black	yes - a lot		
P6D8a 3	very wet, mostly water, some pebbly material	dark grey / black / brown	yes	yes - a lot	
P6D8a 5	firm - like concrete	dark grey	yes - a lot		
P6D8 2	wet mud, no excess water	very dark grey		very small amount in corner of bag	

P6D8 3	quite wet, excess water	very black, brown outside	minimal organics		
P6D8 4	firm, intact core	very dark grey			
P6D8 5	very wet	brown and black	some	little bit of dull orange	
P6D8 6	form intact core	dark grey	some		yes
P6D8 7	mud, minimal excess water	dark grey / brown			
P6D8 8	firm core, sandy	dark grey / black			
P6D3 1	reasonably firm, no excess water	dark grey / brown			
P6D3 2	reasonably firm, no excess water	dark grey / black	small amount	small amount	
P6D3 3	firm, no excess water	dark grey / black	some		yes
P6D3 4	firm - no excess water	dark grey	yes - a lot		
P6D3 5	firm, no excess water	dark grey	some		yes
P6D3 6	soft. No excess water	brown / black	yes - a lot	a lot of dark orange	
P6D3 7	relatively firm, no excess water	dark grey, black, brown	yes		large shell pieces
P6D7 1	relatively soft	very dark grey	small amount		
P7D1 1	soft, relatively firm	Dark grey / brown	little bit		
P7D1 2	a lot of water, very soft	very dark grey / black	yes - a lot		
P9D1 1	sandy, soft - slightly firm	dark grey			
P9D1 2	very soft	black	yes - a lot		
P9D1 3	muddy sand	dark brown	small amount		
P9D1 4	wet - sandy, excess water	dark grey / brown	yes - a lot		
P9D2 1	firm / some soft bits, no excess water	dark grey	some		
P9D2 2	relatively soft / wet	dark grey / brown	some		
P10D1 1	moist dirt, no excess water	dark brown	yes - a lot		
P10D1 2	quite dry / firm	dark grey / brown			

Appendix 9: Liming rate results calculated using sulfur concentrations from XRF analysis

Sample Number	S (ppm or mg/kg)	% S	S (kg per tonne)	weight of pyrite (kg) in one tonne	weight of pyrite (kg) in one wet tonne	Weight lime required (kg/tonne)	Weight (kg) of lime required per tonne of wet material (safety factor of 2)	Weight of lime required per m ³ of wet material (safety factor of 2)
P1D1 1	355.3	0.04	0.36	0.66	0.33	1.11	1.11	1.33
P1D1 2	3930	0.39	3.93	7.35	3.68	12.27	12.27	14.72
P1D1 3	14060	1.41	14.06	26.30	13.15	43.89	43.89	52.66
P1D1 4	10200	1.02	10.20	19.08	9.54	31.84	31.84	38.21
P1D1 5	2123	0.21	2.12	3.97	1.99	6.63	6.63	7.95
P1D1 6	9710	0.97	9.71	18.17	9.08	30.31	30.31	36.37
P2D2 2	13260	1.33	13.26	24.81	12.40	41.39	41.39	49.67
P2D2 3	13810	1.38	13.81	25.84	12.92	43.11	43.11	51.73
P2G1 1	53910	5.39	53.91	100.86	50.43	168.27	168.27	201.93
P2G1 2	64710	6.47	64.71	121.07	60.53	201.98	201.98	242.38
P2G1 3	113900	11.39	113.90	213.09	106.55	355.53	355.53	426.63
P3D1 1	18800	1.88	18.80	35.17	17.59	58.68	58.68	70.42
P3D1 2	8038	0.80	8.04	15.04	7.52	25.09	25.09	30.11
P3D1 3	3760	0.38	3.76	7.03	3.52	11.74	11.74	14.08
P3D1 4	5904	0.59	5.90	11.05	5.52	18.43	18.43	22.11
P3D1 5	11720	1.17	11.72	21.93	10.96	36.58	36.58	43.90
P3D6 1	28720	2.87	28.72	53.73	26.87	89.65	89.65	107.58
P3D6 2	21960	2.20	21.96	41.08	20.54	68.55	68.55	82.25
P3D6 3	29160	2.92	29.16	54.56	27.28	91.02	91.02	109.22
P3D6 4	24820	2.48	24.82	46.44	23.22	77.47	77.47	92.97
P3D6 5	21900	2.19	21.90	40.97	20.49	68.36	68.36	82.03
P3D6 6	26650	2.67	26.65	49.86	24.93	83.18	83.18	99.82
P4D1 1	31090	3.11	31.09	58.17	29.08	97.04	97.04	116.45
P4D1 2	36110	3.61	36.11	67.56	33.78	112.71	112.71	135.26
P5D1 1	10750	1.08	10.75	20.11	10.06	33.55	33.55	40.27
P5D1 2	21190	2.12	21.19	39.64	19.82	66.14	66.14	79.37
P5D2 1	8249	0.82	8.25	15.43	7.72	25.75	25.75	30.90
P5D1 2	7063	0.71	7.06	13.21	6.61	22.05	22.05	26.46
P6D4 1	25490	2.55	25.49	47.69	23.84	79.56	79.56	95.48
P6D4 2	28640	2.86	28.64	53.58	26.79	89.40	89.40	107.28
P6D4 3	25290	2.53	25.29	47.31	23.66	78.94	78.94	94.73
P6D4 4	20180	2.02	20.18	37.75	18.88	62.99	62.99	75.59
P6D3 1	24270	2.43	24.27	45.41	22.70	75.76	75.76	90.91
P6D3 2	19140	1.91	19.14	35.81	17.90	59.74	59.74	71.69

P6D3 3	21230	2.12	21.23	39.72	19.86	66.27	66.27	79.52
P6D3 4	19180	1.92	19.18	35.88	17.94	59.87	59.87	71.84
P6D3 5	17040	1.70	17.04	31.88	15.94	53.19	53.19	63.83
P6D3 6	10450	1.05	10.45	19.55	9.78	32.62	32.62	39.14
P6D3 7	14260	1.43	14.26	26.68	13.34	44.51	44.51	53.41
P6D7 1	17690	1.77	17.69	33.10	16.55	55.22	55.22	66.26
P6D8 2	18340	1.83	18.34	34.31	17.16	57.25	57.25	68.70
P6D8 3	16050	1.61	16.05	30.03	15.01	50.10	50.10	60.12
P6D8 4	20740	2.07	20.74	38.80	19.40	64.74	64.74	77.68
P6D8 5	26310	2.63	26.31	49.22	24.61	82.12	82.12	98.55
P6D8 6	23830	2.38	23.83	44.58	22.29	74.38	74.38	89.26
P6D8 7	19660	1.97	19.66	36.78	18.39	61.37	61.37	73.64
P6D8 8	23340	2.33	23.34	43.67	21.83	72.85	72.85	87.42
P6D8a 1	17570	1.76	17.57	32.87	16.44	54.84	54.84	65.81
P6D8a 2	14590	1.46	14.59	27.30	13.65	45.54	45.54	54.65
P6D8a 3	7218	0.72	7.22	13.50	6.75	22.53	22.53	27.04
P6D8a 5	12680	1.27	12.68	23.72	11.86	39.58	39.58	47.49
P7D1 1	12830	1.28	12.83	24.00	12.00	40.05	40.05	48.06
P7D1 2	19720	1.97	19.72	36.89	18.45	61.55	61.55	73.86
P9D2 1	9637	0.96	9.64	18.03	9.01	30.08	30.08	36.10
P9D2 2	12210	1.22	12.21	22.84	11.42	38.11	38.11	45.73
P9D1 1	12790	1.28	12.79	23.93	11.96	39.92	39.92	47.91
P9D1 2	26890	2.69	26.89	50.31	25.15	83.93	83.93	100.72
P9D1 3	1329	0.13	1.33	2.49	1.24	4.15	4.15	4.98
P9D1 4	7243	0.72	7.24	13.55	6.78	22.61	22.61	27.13
P10D1 1	8431	0.84	8.43	15.77	7.89	26.32	26.32	31.58
P10D1 2	19280	1.93	19.28	36.07	18.04	60.18	60.18	72.22

Appendix 10: Liming rate results calculated using pyrite concentrations from XRD analysis

Sample Number	Amount of pyrite (% weight)	weight of pyrite in one ton (kg)	weight of lime required (kg) per dry tonne	weight of lime required (kg) with safety factor of 2	weight of lime required (kg) per wet tonne (safety factor of 2)	Weight of lime required (kg) per wet m ³ (safety factor of 2)
P1D1 1	0.5	5	8.34	16.68	8.34	10.01
P1D1 2	0	0	0.00	0.00	0.00	0.00
P1D1 3	1.7	17	28.36	56.73	28.36	34.04
P1D1 4	0.5	5	8.34	16.68	8.34	10.01
P1D1 5	0	0	0.00	0.00	0.00	0.00
P1D1 6	3.5	35	58.39	116.79	58.39	70.07
P2D2 2	1.4	14	23.36	46.72	23.36	28.03
P2D2 3	1.8	18	30.03	60.06	30.03	36.04
P2G1 1	9.2	92	153.49	306.98	153.49	184.19
P2G1 2	5.7	57	95.10	190.20	95.10	114.12
P2G1 3	42.3	423	705.73	1411.46	705.73	846.88
P3D1 1	2.6	26	43.38	86.76	43.38	52.05
P3D1 2	0.7	7	11.68	23.36	11.68	14.01
P3D1 3	0.3	3	5.01	10.01	5.01	6.01
P3D1 4	1	10	16.68	33.37	16.68	20.02
P3D1 5	1.6	16	26.69	53.39	26.69	32.03
P3D6 1	6.3	63	105.11	210.22	105.11	126.13
P3D6 2	3.9	39	65.07	130.13	65.07	78.08
P3D6 3	5.2	52	86.76	173.51	86.76	104.11
P3D6 4	4.6	46	76.75	153.49	76.75	92.10
P3D6 5	5.2	52	86.76	173.51	86.76	104.11
P3D6 6	5.6	56	93.43	186.86	93.43	112.12
P4D1 1	5.7	57	95.10	190.20	95.10	114.12
P4D1 2	13.1	131	218.56	437.12	218.56	262.27
P5D1 1	0.5	5	8.34	16.68	8.34	10.01
P5D1 2	1.8	18	30.03	60.06	30.03	36.04
P5D2 1	0.6	6	10.01	20.02	10.01	12.01
P5D2 2	0.6	6	10.01	20.02	10.01	12.01
P6D8a 1	8.5	85	141.81	283.63	141.81	170.18
P6D8a 2	4.1	41	68.40	136.81	68.40	82.09
P6D8a 3	1.5	15	25.03	50.05	25.03	30.03
P6D8a 5	3.8	38	63.40	126.80	63.40	76.08
P6D7 1	4	40	66.74	133.47	66.74	80.08
P6D3 1	6.3	63	105.11	210.22	105.11	126.13
P6D3 2	5.4	54	90.09	180.19	90.09	108.11

P6D3 3	5.8	58	96.77	193.53	96.77	116.12
P6D3 4	7.8	78	130.13	260.27	130.13	156.16
P6D3 5	4.9	49	81.75	163.50	81.75	98.10
P6D3 6	3.7	37	61.73	123.46	61.73	74.08
P6D3 7	4.4	44	73.41	146.82	73.41	88.09
P6D4 1	8.4	84	140.15	280.29	140.15	168.17
P6D4 2	8.3	83	138.48	276.95	138.48	166.17
P6D4 3	6.4	64	106.78	213.55	106.78	128.13
P6D4 4	5.5	55	91.76	183.52	91.76	110.11
P6D8 2	3.5	35	58.39	116.79	58.39	70.07
P6D8 3	5.6	56	93.43	186.86	93.43	112.12
P6D8 4	6.1	61	101.77	203.54	101.77	122.13
P6D8 5	5.3	53	88.42	176.85	88.42	106.11
P6D8 6	7	70	116.79	233.58	116.79	140.15
P6D8 7	5.4	54	90.09	180.19	90.09	108.11
P6D8 8	5.7	57	95.10	190.20	95.10	114.12
P7D1 1	1.6	16	26.69	53.39	26.69	32.03
P7D1 2	2.2	22	36.70	73.41	36.70	44.05
P9D1 1	1.7	17	28.36	56.73	28.36	34.04
P9D1 2	5.2	52	86.76	173.51	86.76	104.11
P9D1 3	0	0	0.00	0.00	0.00	0.00
P9D1 4	0.8	8	13.35	26.69	13.35	16.02
P9D2 1	1.3	13	21.69	43.38	21.69	26.03
P9D2 2	1.5	15	25.03	50.05	25.03	30.03
P10D1 1	0.9	9	15.02	30.03	15.02	18.02
P10D1 2	3.6	36	60.06	120.12	60.06	72.07

Appendix 11: Liming rate results calculated using pH values and 'Look – up table' in S.C Council maintenance REF document (2011)

Sample	kg/m ³ using equation (safety factor of 2)	kg/m ³ using value for closest pH in table (safety factor of 2)	kg/tonne using equation value (safety factor of 2)	kg/tonne using value for closest pH in table (safety factor of 2)
P1D1 1	12.07	11	10.06	9.17
P1D1 2	13.53	11	11.27	9.17
P1D1 3	33.42	29	27.85	24.17
P1D1 4	23.95	19	19.96	15.83
P1D1 5	30.68	29	25.56	24.17
P1D1 6	29.25	24	24.38	20.00
P2D2 2	41.60	39	34.67	32.50
P2D2 3	28.97	24	24.15	20.00
P2G1 1	52.28	52	43.57	43.33
P2G1 2	37.82	39	31.52	32.50
P2G1 3	37.11	39	30.93	32.50
P3D1 1	28.43	24	23.69	20.00
P3D1 2	30.10	24	25.08	20.00
P3D1 3	16.84	13	14.03	10.83
P3D1 4	13.40	11	11.17	9.17
P3D1 5	43.63	39	36.36	32.50
P3D6 1	26.85	24	22.37	20.00
P3D6 2	34.39	29	28.66	24.17
P3D6 3	54.31	72	45.26	60.00
P3D6 4	48.45	52	40.37	43.33
P3D6 5	24.18	19	20.15	15.83
P3D6 6	30.68	29	25.56	24.17
P4D1 1	35.05	29	29.21	24.17
P4D1 2	23.72	19	19.77	15.83
P5D1 1	5.04	4	4.20	3.33
P5D1 2	3.12	3	2.60	2.50
P5D2 1	7.27	7	6.05	5.83
P5D1 2	7.50	7	6.25	5.83
P6D4 1	40.05	39	33.37	32.50
P6D4 2	46.64	52	38.86	43.33
P6D4 3	36.07	29	30.06	24.17
P6D4 4	38.19	39	31.82	32.50
P6D3 1	39.29	39	32.74	32.50

P6D3 2	34.72	29	28.93	24.17
P6D3 3	43.63	39	36.36	32.50
P6D3 4	37.11	39	30.93	32.50
P6D3 5	33.74	29	28.12	24.17
P6D3 6	17.16	16	14.30	13.33
P6D3 7	19.99	16	16.66	13.33
P6D7 1	33.42	29	27.85	24.17
P6D8 2	45.32	52	37.77	43.33
P6D8 3	12.66	11	10.55	9.17
P6D8 4	42.00	39	35.00	32.50
P6D8 5	11.73	11	9.77	9.17
P6D8 6	42.81	39	35.67	32.50
P6D8 7	38.19	39	31.82	32.50
P6D8 8	42.81	39	35.67	32.50
P6D8a 1	21.16	19	17.64	15.83
P6D8a 2	20.37	16	16.98	13.33
P6D8a 3	23.72	19	19.77	15.83
P6D8a 5	27.63	24	23.02	20.00
P7D1 1	28.97	24	24.15	20.00
P7D1 2	37.82	39	31.52	32.50
P9D2 1	10.81	12	9.01	10.00
P9D2 2	11.51	12	9.59	10.00
P9D1 1	17.12	23	14.26	19.17
P9D1 2	11.39	12	9.49	10.00
P9D1 3	2.10	1	1.75	0.83
P9D1 4	13.89	16	11.57	13.33
P10D1 1	25.60	24	21.33	20.00
P10D1 2	40.82	39	34.02	32.50