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A Palaeolimnological Determination of a Regional Industrial Signal in the Sediments of Mpumalanga Highveld Pans

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Jesse Patrick Spratt

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Declaration

I hereby declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

05/12/2019

Jesse Patrick Spratt

Date

Abstract

Fresh water endorheic wetlands are a scarce resource in South Africa and are threatened by human activities such as mining, abstraction, farming and other industry. The Mpumalanga Lake District (MLD) is a unique region comprising of over 300 endorheic pans differing in type. This provided the ideal regional setting for a pilot palaeolimnological study. The overall aim was to identify a regional industrial signal for anthropogenic influence by understanding the uniqueness of these pans through a palaeolimnological approach using historical lake sediments. A historical sediment record was established in order to identify any temporal changes in physiochemical characteristics over the last approximately 130 years. Four sites were selected so as to analyse a spatial aspect of contamination and to compare physical characteristics of pans in the MLD. Sediment samples were collected in the form of four lake sediment cores which were sub-sampled at 0.5 cm in order to understand down core trends. A bathymetric approach was adopted in which GPS, depth and water quality data were obtained in order to understand the physiochemical characteristics and morphology of these pans. Analyses performed included radio-isotopic dating through ^{210}Pb, organic carbon content analysis through Loss on Ignition methods, sediment grain size analysis using laser diffraction and the analysis of the composition of major elements in these lake sediments using x-ray fluorescence (XRF) spectrometry. Bathymetry data was used to produce maps representing the physical morphological characteristics of these pans. Sediment data including major elements, organic carbon content and grain size data was analysed statistically and represented graphically in order to understand down core trends.

Identified was the uniqueness of these pans and the MLD region as a whole. The pans differed in size, depth and in terms of the sediment properties of organic carbon, carbonate and sediment grain size distribution. Results showed a distinct difference between sites TPE compared to the other three sites in terms of bathymetry and limnology. It was determined that there are multiple fluctuations throughout the sediment record which represents a seasonal variation in climatic conditions. An attempt to observe trends of environmental and climatic change was made with varied success. An identification of a possible regional industrial signal was made with respect to major element compositional changes however the distinction between natural and anthropogenic sources was difficult to determine.

Dedication

This dissertation is dedicated to my family and friends as without their constant support this study would not have been possible. They provided me with the motivation to cross the finish line and prove to myself that I can do it.

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1. Introduction

1.1 Background

The water quality issue is of growing concern in South Africa especially when considering a history of extensive primary human activities and extensive industry (Tiwary, 2001; Ochieng *et al*., 2010). Activities such as mining, energy production and other industrial activities threaten and impact the sustainability of fresh water sources and the associated ecological health (Tiwary, 2001). Industry contributes inadvertently and greatly towards local environmental pollution (Tiwary, 2001). Other major sources such as coal combustion through energy production and industrial activities are a principal threat to aquatic ecosystems with respect to acidification from acid deposition processes (Josipovic *et al*., 2010, 2011). The deterioration of ground and surface water due to pollution factors associated with coal mining, processing, combustion and other industrial activities require extensive research to determine the extent of pollution and apply management strategies (Ochieng *et al*., 2010). This forms the basis for this research project which examines the issues that come with extensive industrial and economic expansion in South Africa and specifically Mpumalanga.

Natural freshwater sources such as those found in the Mpumalanga Lake District (MLD) are of greatest concern and this is therefore the focus area of this research. These aquatic ecosystems are highly sensitive and are consistently threatened and possibly degraded in the pursuit of national industrial and economic expansion (De Klerk *et al*., 2012). Aquatic ecosystems such as the Mpumalanga Lake District are a vital source of fresh water which sustains a vast and varied biodiversity, which if degraded could lead to the demise of many endemic plant and animal species (De Klerk *et al*., 2012; Ferreira *et al*., 2012). The degradation of such aquatic ecosystems could also impact the local communities in terms of multiple socio-economic aspects (Tiwary, 2001). This ultimately strengthens the reasoning for this research as it attempts to define a point where socio-economic development and ecological sustainability can balance out. Further research into this field can ultimately ensure the sustainability of natural freshwater environments and advance the understanding of the industrial contamination extent over South Africa. The endorheic depressions or pans of the Mpumalanga Lake District (MLD) (*Figure 3.5*) form the point of interest for this research project (De Klerk *et al*., 2012; Wellington, 1943). This is due to their uniqueness, as these natural aquatic ecosystems are very sparse, as well as their proximity to rapid economic and industrial expansion (Bell *et al*., 2001; De Klerk *et al*., 2012). This includes proximity to coal production and combustion which dominates the Mpumalanga Highveld (Bell *et al*., 2001). This is a possible influencing factor as South Africa generates 32 % of the total energy in Africa, most of which is fossil fuel combustion which mainly consists of coal combustion (Pretorius *et* al., 2015). This vast energy production is largely situated around the coal fields of the Mpumalanga Highveld (Pretorius *et al*., 2015). Another important reason for the chosen study location is that there is a lack of studies conducted that have focused on this expansive grouping of endorheic pans. This provides the gap for new research on the area to emerge. Therefore the selected study area is ideal for such a research project as this could open a door to this field of study in the area which could lead to a more sustainable future.

Anthropogenic pollution in the form of industrial contamination is a major source for the degradation of any natural ecosystem and therefore this source and others like it need to be assessed and their impacts determined. This, therefore, needs to be done by determining historical contamination so that an understanding of trends and change can be made (Birks & Birks, 2006). This could then be used to predict future trends (Birks & Birks, 2006). Such findings can only benefit the scientific world as to better the understanding about the field of palaeolimnology and how it can link to understanding current conditions relating to climate, ecology and anthropogenic influence (Birks & Birks, 2006). Palaeolimnological studies are utilised in determining and reconstructing past environmental and ecological conditions of aquatic ecosystems (Birks & Birks, 2006). However, palaeolimnology is not currently and has not been extensively studied in South Africa in terms of the country’s fresh water; so this research project hopes to aid in bridging a gap in research in South Africa, from which further research can emerge, not only specific to this field.

1.2. Aims & Objectives

This research project is a pilot project in the field of palaeolimnology specifically focussed on the Mpumalanga Lake District. This is the first approach of its kind in this region and the aim of this is to open the region up to further studies through the use of lake sediments and a palaeolimnological approach. The aim of this research project is to make use of the geochemical analysis of lake sediment cores in order to possibly reconstruct the pollution history in the Mpumalanga Lake District (MLD) region, specifically the area of Chrissiesmeer, over the past 130 years. This is done using a palaeolimnological approach through sediment geochemistry and bathymetric analysis. From the evidence, an inference could possibly be made as to determining the extent of the net combined impact that anthropogenic activities have on what is understood to be a natural and pristine area. Through the analysis of major elements found in lake sediments an understanding can be made as to how extensively the pans in the MLD have been contaminated through time or how these pans have physio-chemically changed over time. Through sediment analysis (grain-size analysis, organic content and carbonate content), an understanding can be made as to the historical conditions that may have influenced the development and contamination of these pans.

An overarching aim for this research project is to gain an understanding of the uniqueness of the pans in the MLD and how the aquatic environments have been impacted or have changed over time by either natural environmental or anthropogenic factors. This is all done with the aim of creating awareness of the extent of anthropogenic pollution from coal mining, combustion and other related industrial activities, for the local and tourist population that makes use of the Mpumalanga Lake District. This is because there is an increase in prospecting for coal within the MLD which could result in the degradation of these natural pans. If these aims are achieved then this research project could contribute to the understanding of the uniqueness of endorheic pans and how they function in the regional extent.

The objectives concerning this research project are as follows:

- To understand the lake morphology of the endorheic pans of the Mpumalanga Lake District through bathymetry analysis.

- To determine the extent that anthropogenic influence has on the pans in the Mpumalanga Lake District.

- To determine if these pans vary spatially with regard to physiochemical characteristics.

- To examine recent (130 years) temporal variations in sedimentation history using a ^{210}Pb dated lake sediment core.

- To determine any environmental or climatic changes or events which could have influenced the development of the pans in question in terms of sediment deposition characteristics.
    - To identify any physical disturbances through time
    - To investigate how intact the sediment record is

1.3. Structure

This dissertation focuses on determining and therefore understanding the characteristics of the endorheic pans of the Mpumalanga Lake District and whether contamination from rapidly expanding industry could play a major role in shaping these characteristics. A review of literature follows in which key points about possible influencing factors are presented as well as a review of previous studies in the same field and/or study location. A presentation of influential aquatic ecosystems and a background to coal mining in South Africa are also included in this chapter. From this follows a detailed description of the study site for this research project in which regional setting, geology, climate and site background are all presented. Following on from this, the methods utilised for this research project are presented in detail. This includes methods ranging from field sampling to sample analysis and from statistical data analysis to graphical representation. After the methods chapter, the results of the various analyses conducted are presented through visual representation and descriptive analysis. This chapter includes bathymetry results, organic and carbonate content results, grain size analysis results and major element composition results achieved through sedimentological and statistical analysis. Following the presentation of these results, a discussion is formed in the next chapter. This discussion chapter creates links between what was analysed and what was already known meaning links are made from the results to the existing research presented in the literature review. These links also expose new gaps in research and what needs to be done in order to take this research field of palaeolimnology further in South Africa. After a discussion is presented, conclusions are drawn with respect to the achievement of the aforementioned research aims and objectives. In this chapter a brief presentation is made on the limitations of this research project and what can be done to further it in the scientific field.

2. Literature Review

2.1. Fresh Water in South Africa

South Africa has a variety of water quality issues which are compounded by the lack of multiple large fresh water sources (Tiwary, 2001). Primary human activities such as mining and agriculture place massive strain on the fresh water supply in South Africa, which promotes the need for research into the extent and mitigation of pollution impacts (Ochieng *et al*., 2010). Fresh water sources are of great importance as over 70 % of water in both rural and urban usage is extracted from these sources such as rivers and wetlands (Ochieng *et al*., 2010). Fresh water sources such as wetlands provide a vital function to local and broader ecosystems and society (De Klerk *et al*., 2016). These fresh water sources are being degraded and depleted due to extraction and most significantly, contamination (Ochieng *et al*., 2010). Aquatic ecosystems such as wetlands and pans are threatened by unsustainable human activities such as mining, agriculture, industries, water abstraction and waste water disposal (De Klerk *et al*., 2012). Wetland loss in South Africa ranges between 35 % and 50 % while at the global extent, wetland loss is estimated to be approximately 50 % which suggest a global epidemic in the context of fresh water loss (De Klerk *et al*., 2016). Therefore due to wetland and freshwater degradation through increased pollution and contamination, there is a need for the conservation of natural wetlands through effective research and monitoring studies (De Klerk *et al*., 2012). There is also a need for research into past environmental conditions in order to understand any ecological changes that have led to the current composition of certain wetlands and lakes in terms of their ecological health and lake morphology.

2.2. Palaeolimnological Studies

Palaeoenvironmental studies such as palaeolimnology are important in the field of environmental sciences. Palaeolimnology concerns the study of past environmental and ecological conditions of aquatic ecosystems often through a multi-proxy approach (Birks and Birks, 2006). This form of study also concerns reconstruction of past environments and determining climatic changes which impact on the local and global scale (Battarbee *et al*., 2002; Birks and Birks, 2006). A multi-proxy approach such as reviewed by Birks and Birks (2006) and described in Battarbee *et al*. (2002)

shows the use of this approach in order to determine past climatic conditions and events and how this shaped the current environmental conditions of several lakes in Europe. Physical proxies such as the use of lake sediments, are a simple yet effective proxy in understanding past climatic and environmental changes (Birks and Birks, 2006; Bennion *et al*., 2010). The use of organic carbon and carbonate as a proxy in palaeolimnology, determined through the Loss-on-Ignition (LOI) method, is a simple and cost effective way of understanding changes in climatic conditions and therefore environmental conditions (Birks and Birks, 2006). This is done by understanding the relationship between organic carbon, carbonate and mineral content from which a determination can be made as to the climatic changes in terms of temperature and precipitation (Birks and Birks, 2006).

A study described in Battarbee *et al.* (2002) makes use of LOI, and therefore organic carbon and carbonate content, in order to understand any changes in climatic conditions. This study focused on European fresh water lakes as much research has been conducted on these Northern hemisphere lakes (Dean, 1999; Battarbee *et al*., 2002; Curtis *et al*., 2010). It was determined that the observed sharp decreases in percentage LOI correlated to a cool and wet period which coincided with other palaeolimnological multi-proxy studies in Europe showing a similar cool and wet period (Battarbee *et al*., 2002; Birks and Birks, 2006). This shows that changes in percentage LOI can help determine past climatic conditions and possibly climatic events which can shape the formation or composition of aquatic ecosystems such as lakes and wetlands.

A study, as described in Curtis *et al*. (2010) shows how advantageous a palaeolimnological study can be in terms of determining human activity impacts on aquatic ecosystems. This study focuses on the Athabasca oil sands region and makes use of a multi-proxy approach concerning diatom analysis, spheroidal carbonaceous particle (SCP) analysis, sediment isotopic analysis and mercury analysis as well as the dating of sediment cores using ^{210}Pb dating (Curtis *et al*., 2010). From the evidence analysed, it was determined that there was a notable increase in proxies such as SCPs and mercury showing the result of industrial intensification in the region as both had dramatically increased in the past 100 years (Curtis *et al*., 2010). This therefore provides evidence of the success of palaeolimnological studies. The use of ^{210}Pb radiometric dating is fairly common in palaeolimnological studies due to it being a natural radioactive decay product which occurs in lake sediments from both atmospheric deposition and its occurrence in the substrates of a drainage basin (Oldfield, 1977). It is therefore commonly occurring in lake sediments and has a half-life of 22.26 yrs making it accurate for more recent dates (Oldfield, 1977).

One of the goals for palaeolimnological studies is to determine the impact that anthropogenic activity has had on aquatic ecosystems and related terrestrial environments such as catchments and possibly beyond that scope (Birks and Birks, 2006; Bennion *et al*., 2010). In order to achieve this goal, palaeolimnological studies need to determine the baseline or pristine condition of the past aquatic ecosystem in question (Bennion *et al*., 2010). This is, however, not a simple determination to make as past natural variations in climatic conditions can leave signals which seem similar to that of anthropogenic influence such as an increase in organic production which may have similar signals as eutrophic conditions (Bennion *et al*., 2010). Therefore, palaeolimnological studies need to distinguish between natural variability and anthropogenic influences, and this is where, once again, the use of proxies is beneficial (Birks and Birks, 2006; Bennion *et al*., 2010).

2.3. Endorheic Wetlands

Adding to the issues of water quality in South Africa, there is a lack of large natural freshwater sources and therefore this places great importance on the areas where natural pans and wetlands are located (Hart and Appleton, 1997). Research into natural wetlands in South Africa has been very sparse in terms of monitoring ecological health and water quality, despite the importance in the hydrological cycle, and as a freshwater source (Ferreira *et al*., 2012). The estimate of wetlands in South Africa that have been destroyed or degraded is approximately 35 % to 50 %, which adds to the issues surrounding water quality (De Klerk *et al*., 2012; De Klerk *et al*., 2016). Endorheic wetlands are more commonly referred to as pans and are defined as closed basins which accumulate water from sufficient precipitation with no surface inflow source or outflow (De Klerk *et al*., 2016; Ferreira *et al*., 2012). Subsurface water inflows can also be a source for endorheic pans which means that these pans are often located just above the groundwater table resulting in much seasonal variation due to the fluctuations of the groundwater table (De Klerk *et* al., 2016). Pans can dry up due to arid conditions with a severe lack of precipitation and fluctuations in the water table and this can be evident in the sediment accumulation. Pans are classified according to their formation and physical characteristics. These include open pans, salt pans, sedge pans, reed pans and grass pans (De Klerk *et al*., 2016). These different types of pans host varying and unique ecologies making them important in terms of research and monitoring.

Pans in general are associated with saline environments and tend to have elevated levels of Total Dissolved Solids (TDS) (Russell, 2008). This is due to a number of causal processes such as weathering and precipitation of surrounding sediments. A main causal process for increased levels of salinity is that of the concentration of evaporation over the introduction of precipitation (Russell, 2008). The process of evaporation concentration drives the development of pans and changes the physiochemical characteristics over time and at a seasonal scale (Russell, 2008). During processes of evaporation concentration, there are increases in sodium content and chloride in the sediments due to mineral precipitation (Russell, 2008). This gives an idea as to the changes in evaporation concentration.

With respect to South Africa, most pans are found in the drier regions such as the Northern Cape however the unusually large number of pans found in the much wetter Mpumalanga Lake District, or MLD, makes it a unique area for hydrogeology and limnology research (De Klerk *et al*., 2016). The pans found in the MLD could provide evidence for regional and local pollution through their sediments (Sun *et al*., 2002; Peng *et al*., 2005). These sediments become a sink for toxic elements and contaminants which can be used as a proxy to understand the possible impact of primary human activities such as coal mining, processing and combustion and other industries (De Klerk *et al*., 2012). These sediments can also be used as a determination to variations in local climate, such as temperature and precipitation, as grain size distribution analysis provides evidence for dry and wet periods (Sun *et al*., 2002). Grain size distribution analysis provides important information concerning depositional conditions and sediment history which could provide clarity on past climatic and environmental conditions (Blott and Pye, 2001). Depositional processes in endorheic pans vary due to climatic conditions and this therefore provides a record of not only local climate changes and events, but also at a regional scale (Sun *et al*., 2002). According to a study by Peng *et al*. (2005), a higher median grain size of the lake sediments reflects an increase in precipitation and possibly slightly cooler climatic conditions (Peng *et al*., 2005). Therefore the greater distribution of large grains shows that during that specific period there was a climatic change or event resulting in increased precipitation. The converse is then evident that a distribution of more smaller grain sizes reflects a dry period (Peng *et al*., 2005). Therefore grain size distribution analysis of lake sediments is a vital part of a multi-proxy approach to this research project. Grain size distribution analysis provides evidence for various sediment characteristics such as source material, transportation dynamics and depositional conditions which can be used as proxies for understanding local and regional environmental conditions particularly in terms of climate (Blott and Pye, 2001; Peng *et al*., 2005)

The pans of the Mpumalanga Lake District vary greatly when compared to one another in terms of hydrochemical and physical morphological characteristics. There are apparent seasonal variations which are most notable in extended dry periods where evaporation dominates the processes associated with these pans (Russell, 2008). This is particularly interesting due to the close proximity of the pans as well as the possible surface flow linkages between the pans as proposed by Wellington (1943). Although there are some hydrochemical similarities between the pans of the MLD, the differences, physically and chemically, are highly notable which suggests that these linkages are not as simple to identify as was previously thought (Russell, 2008).

The pans of the MLD do undergo evaporation concentration processes however these pans are not as significantly influenced as those located in more arid regions (Russell, 2008). These pans can see increases in sodium and potassium through the weathering of parent material in the Vryheid Formation when influenced by evaporation concentration (Russell, 2008). There are also increases in magnesium and calcium carbonate evident under evaporation processes (Russell, 2008). These changes in major elements are however not consistent from pan to pan as evaporation processes influence each pan differently dependant on ground water supply, reservoir size and the physiochemical aspects defining each pan.

These environmental and climatic changes include changes in moisture availability such as precipitation and temperature (Heiri *et al*., 2001). An increase in percentage organic content is determined as periods of more moisture availability while a decrease in percentage organic content shows evidence of drier periods (Heiri *et al*., 2001). Evidence of changes in percentage organic content could also be used to determine changes in sedimentation regimes and sedimentation events such as floods (Curtis *et al*., 2010).

2.4. South African Coal

Coal mining in South Africa is one of the largest industries of the mining sector accounting for about 3.3 % of the annual global production total from coal reserves making up 3.5 % of the planet's coal (Chamber of Mines, 2017). In 2014, about 260 Mt of coal was extracted out of the ground in South Africa, most of this being extracted for thermal power generation through combustion (Chamber of Mines, 2017). This large primary industry has a great impact on the local and regional environment due to extensive mining methods, geological composition and mine mismanagement (Bell *et al*., 2001). Geologically the coal fields of South Africa form part of the Karoo Supergroup (Bell *et al*., 2001). The extent of the coalfields in South Africa is primarily located in the eastern Highveld between the towns of Witbank, Middelburg and Ermelo as well as around Standerton and Secunda (Jeffrey, 2005). The Witbank Coalfield is of notable importance as it is one of the most extensively mined coal fields which are generally used for thermal power generation and export (Bell *et al*., 2001; Chamber of Mines, 2017). The Witbank Coalfield is found within the Vryheid Formation which forms part of the Ecca Series group (Bell *et al*., 2001; Wellington, 1943). This geological formation consists of sandstone and shale with shallow coal deposits making it ideal for open cast and mechanised mining methods (Bell *et al*., 2001; Chamber of Mines, 2017).

The coal mined and subsequently combusted in South Africa has been characterised as a bituminous coal which is rich in minerals and highly variable in organic matter (Falcon & Ham, 1988). Throughout the coal production process from extraction all the way to combustion there are many sources of possible pollution which could impact greatly on regional and local natural environments and aquatic ecosystems

(Tiwary, 2001; De Klerk *et al*., 2012). Most of the coal extracted in South Africa is destined for thermal power generation plants or coal conversion into liquid fuels (Jeffrey, 2005). The energy sector in South Africa is responsible for the largest contribution of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) at 70 % and 55 % respectively, out of all major industries in the country resulting in significant impacts on environmental and human health (Pretorius *et al*., 2015). The combustion of coal for energy production and other industries generally produces large amounts of fly ash and bottom ash which is comprised of many trace and major elements that can have adverse effects on the surrounding environment (Rowe *et al*., 2002; Pretorius *et al*., 2015). The by-products of coal combustion tend to release varying amounts of Iron (Fe), Magnesium (Mg), Mercury (Hg), Zinc (Zn), Calcium (Ca), Potassium (K), Manganese (Mn), Chromium (Cr) and Nickel (Ni) which can all have varying impacts on aquatic ecosystems (Popovic *et al*., 2001; Rowe *et al*., 2002). This is concerning as accumulation of these elements in aquatic organisms can lead to adverse environmental health impacts such as species loss and general aquatic health degradation (Rowe *et al*., 2002). With respect to this research project, more focus is placed on major elements which are significant from the extraction of coal to its combustion such as Fe (Bell *et al*., 2001). An increase in Fe over time in aquatic ecosystems can be attributed to many contamination sources such as open cast mines and water run-off from these mines and mine dumps (Geldenhuis & Bell, 1998; Bell *et al*., 2001).

2.5. Contamination Sources

The main sources of water contamination associated with coal mining and other coal production activities include direct drainage in the form of Acid Mine Drainage (AMD) and mine water, sediment runoff from the mine site, various effluent spills and leachate from the overburden dumps as well as fly ash produced through fossil fuel combustion (Tiwary, 2001; Pretorius *et al*., 2015). AMD is possibly the pollution source that poses one of the biggest threats to fresh water sources the most (Tiwary, 2001; Akcil and Koldas, 2006). AMD is caused by the exposure of sulphide bearing minerals, such as pyrite, to oxygen and water which undergoes oxidation and in two stages produces firstly sulphuric acid and ferrous sulphate and secondly, ferric hydroxide and more sulphuric acid (Geldenhuis and Bell, 1998; Bell *et al.*, 2001;

Tiwary, 2001; Akcil and Koldas, 2006; McCarthy, 2011). AMD is detrimental for the surrounding environment, specifically aquatic environments, as it results in lower pH levels, high levels of sulphate and heavy metals (Tiwary, 2001; Akcil and Koldas, 2006). The water associated with coal mines contains higher levels of Total Suspended Solids (TSS), Total Dissolved Solids (TDS) and heavy metals (Tiwary, 2001; Akcil and Koldas, 2006). This contaminates both ground and surface water bodies and may have implications for the surrounding environment and ecology (Tiwary, 2001).

Coal mining, specifically open cast coal mining operations produce vast amounts of dust, gaseous pollutants and other suspended particulate matter which could contaminate nearby water bodies (Ghose and Majee, 2001). During open cast mining operations, overburden is removed in order to expose the coal deposit and this causes vast amounts of fine suspended particulate matter which can be mobilised by wind (Ghose and Majee, 2001). Windblown suspended particulate matter could fall over water bodies, altering the water chemistry characteristics (Denis *et al.*, 2007). Spontaneous combustion of coal during the coal production process, which has been evident across the Witbank Coalfields, adds to the suspended particulate matter which can be evident in the sediments of nearby water bodies (Denis *et al.*, 2007). Coal fires emit large amounts of nitrogen oxides (NO_x) and sulphur dioxide (SO_2) into the atmosphere which contribute extensively to regional atmospheric acid deposition (Bell *et al*., 2001).

Atmospheric acid deposition is an additional form of pollution associated with industry, agriculture, mining and energy production (Conradie *et al*., 2016). Atmospheric acid deposition takes both wet and dry forms which can impact heavily on aquatic environments causing acidification (Josipovic *et al*., 2011). Wet deposition often takes the form of acid rain whereas dry deposition takes various forms in order to reach the ground such as wind transportation (Conradie *et al*., 2016). It has also been linked to large scale forest dieback and acidification of lakes in North America and Europe (Josipovic *et al*., 2010). With regard to South Africa, atmospheric deposition is an issue specifically with respect to the Mpumalanga Highveld where most of the nation’s coal mining and energy production takes place (Held and Mphepya, 2000; Josipovic *et al*., 2011). This region of South Africa accounts for 90 % of the national scheduled emissions of industrial dust, sulphur dioxide (SO_2) and nitrogen oxides (NO_x) (Held and Mphepya, 2000; Josipovic *et al*., 2011). Other contaminants to consider in terms acid deposition are ammonia (NH_3), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca) and chloride (Cl) (Galloway, 1995; Conradie *et al*., 2016). It has been determined that most of the acid deposition, both wet and dry, in the Mpumalanga Highveld is a result of the emissions from the coal mines and importantly, the coal thermal power plants which produce vast amounts of SO_2 emissions into the regional atmosphere (Josipovic *et al*., 2010; Josipovic *et al*., 2011). The research conducted with respect to acid deposition in the Mpumalanga Highveld region shows that great strain is placed on aquatic environments within and beyond this region (Galloway, 1995; Josipovic *et al*., 2010; Josipovic *et al*., 2011).

2.6. Mpumalanga Lake District

Most of the literature based around previous studies of the Mpumalanga Lake District (MLD) focusses on the ecology of the different pans instead of evidence of pollution over time. An early study by Wellington (1943) determined the formation of the pans in the MLD, specifically focussing on Lake Chrissie. Although a very old study, this provided some detail of the study area and geology. Wellington (1943) also determined that the pans in the MLD (*Figure 3.1*) area were joined by overflow channels leading eastwards forming the headwaters of the Umpilusi River system. This is irregular for endorheic pans but understandable when considering possible heavy precipitation events during the wet summer season and the gently sloping topography in that direction (Wellington, 1943). Wellington (1943) also determines the causes for the shapes of these pans which are suggested to be, amongst geological reasons such as erosion characteristics, the strong and consistent North-Northwest winds. This gives many of these pans their iconic kidney shape leading eastwards. This is important in understanding the formation of these pans over time and how they are continually reforming.

The earliest known scientific study on the MLD area was conducted by Hutchinson *et al*., (1932) but this consisted mainly of understanding the ecology of the area by studying aquatic invertebrates. More studies such as Ferreira *et al*. (2012) and Foster *et al*., (2015) focus on the aquatic ecology of the various pans in the MLD by using aquatic invertebrates. The study conducted by Foster *et al*., (2015) focuses on the differences between the pans located in the MLD compared to the pans in the North West province. It was determined that these two wetland areas had similar physio-chemical properties yet had a wide diversity in aquatic invertebrates and this was attributed to the differences in underlying geology, the geographic location and regional climate which all have direct influence on water quality (Foster *et al*., 2015). One important aspect that was not accounted for was the indirect influences on water quality such as industrial combustion and primary human activities. This provides a gap in research which is vital in understanding how and to what extent these aquatic ecosystems are being impacted. The study by Foster *et al*., (2015) also links to this research project in terms of particular sites used such as MP J (Tweelingspan East or TPE) and MP F (Magdalenasmeer or MDM).

The sediment study conducted by De Klerk *et al*. (2012) is an important study in terms of the concerned research area and the analysis of pan sediments in order to determine heavy and trace metals from various human activity sources. This study determined that there were seasonal variations in maximum heavy metal concentrations which corresponded with seasonal trends of organic carbon content showing that during the rainy season of summer, there was a higher metal concentration possibly due to wet atmospheric deposition (De Klerk *et al*., 2012). This shows that there is evidence of anthropogenic contamination within the MLD region. The major difference between the De Klerk *et al*. (2012) study and this research project is that the aforementioned study was concerned only with reed pan sites where as my research will consist of the use of open endorheic pans. Another difference is that the aforementioned study assessed the seasonal variations of both water and sediment quality parameters rather than having a temporal and spatial approach (De Klerk *et al*., 2012).

The pans of the MLD are of close proximity to one another which would generally suggest that they share both multiple physio-chemical or geochemical characteristics. However this is not the case according to the study by Russell (2008) in which it was determined that these pans show varying chemistry characteristics. Inorganic chemistry of the studied pans of the MLD varied substantially due to changes in evaporation processes between pans (Russell, 2008). It is suggested that the processes of evaporation and precipitation are key to maintaining the quality of water in the pans (Russell, 2008).

3. Methods

3.1. Study Area

3.1.1. Regional Setting

The study area concerned in this research project is the Mpumalanga Lake District (MLD) located in the province of Mpumalanga, South Africa. Specifically the area around Lake Chrissie or Chrissiesmeer (26° 16’ 52” S; 30° 12’ 38” E). The MLD is comprised of over 300 endorheic pans of different types including open pans, salt pans, reed pans, grass pans and sedge pans making it an ideal study area for water quality and wetland ecology related studies (De Klerk *et al*., 2016). The MLD is one of two major endorheic wetland areas in South Africa, with the other being located in the North West province (Foster *et al*., 2015). The local climate consists of warm, wet summers and cold, dry winters with a mean annual rainfall of about 900 mm per year and a mean annual potential evaporation of about 1,700 mm per year (Schulze, 1997; Russell, 2008; De Klerk *et al*., 2012; De Klerk *et al*., 2016). Potential evaporation outweighs precipitation in the area which results in the evident seasonal variations. The area around Lake Chrissie forms the headwaters of several major river catchments, namely the Vaal, Olifants, Komati, Usutu and Mpuluzi catchments (Wellington, 1943; De Klerk *et al.*, 2012). Although the MLD area is home to multiple catchment headwaters, the general landscape topography is fairly flat with an average elevation of 1,700 m above sea level with the selected sites ranging from 1,667 m.asl to 1983 m.asl (Wellington, 1943). The aforementioned catchments are in close proximity to some of the pans in the MLD, however, the rivers themselves do not connect above ground with any of the pans. According to Wellington (1943), and as represented in *Figure 3.1*, the pans were once part of a larger river catchment and show evidence of connections between the pans. These connections may only become evident with heavy precipitation events.

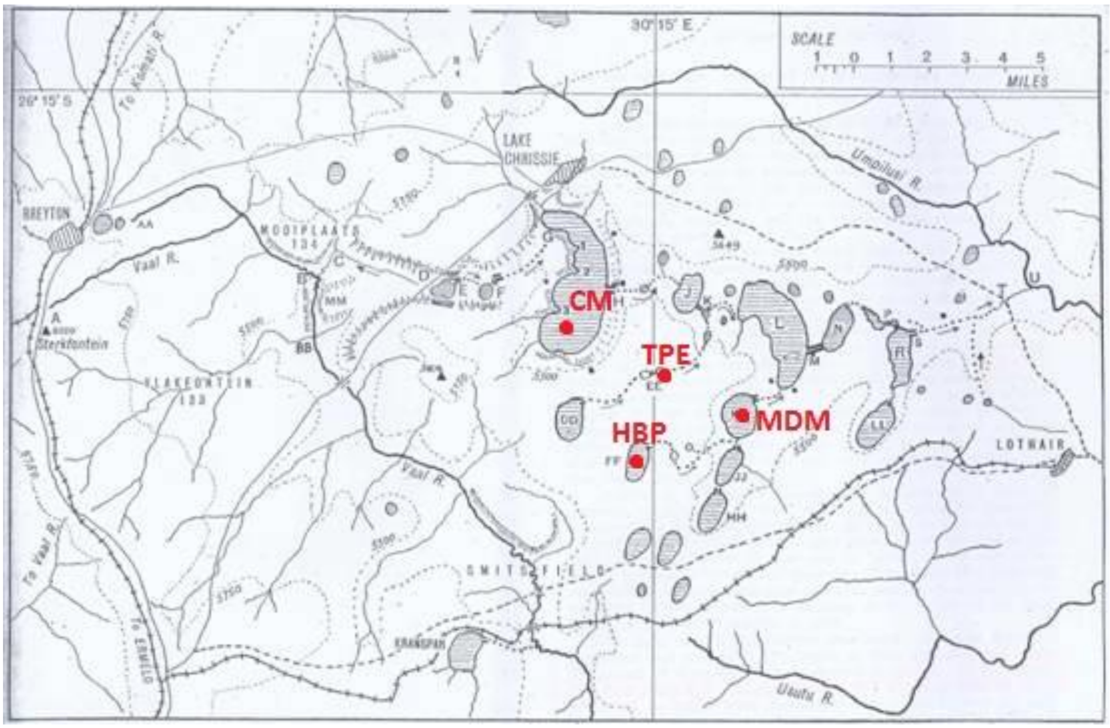


Figure 3.1: Possible connections between pans in the MLD, proposed by Wellington (1943) with added study sites (after Wellington, 1943); CM (Chrissiesmeer), TPE (Tweelingspan East), MDM (Magdalenasmeer) and, HBP (Hendrik Beukes Pan).

The pans of the MLD are distinctive and fairly unique due to their nature and formation. The varying types of pans, from open pans to grass pans, and the varying limnological characteristics of these pans, such as saline and brackish waters, in the same area show the uniqueness of the MLD region. Many of the pans tend to also have a distinctive elongated shape in a North to South direction which has been previously attributed to the prevailing wind direction (Wellington, 1943). There are however some pans that have a more circular to oval shape which could be attributed to a more regular geology on which the pan is located (*Figure 3.1*).

Of major concern are the human activities in the region which consist of mainly coal mining, thermal power generation and agriculture (Ferreira *et al*., 2012). The study area is in relatively close proximity to open cast coal mines, coal processing plants and coal fired thermal power plants. The multiple thermal power stations in regional proximity to the proposed study area are represented in *Figure 3.2*. The thermal power stations are located in this area due to the proximity to the vast coal reserves in the region allowing for easy and cost effective access to these reserves. These include the Camden power station approximately 30 km South, Arnot approximately

50 km North West, Hendrina approximately 66 km North West and Komati approximately 75 km North West. These thermal power stations could impact the study area through emissions related atmospheric pollution such as atmospheric acid deposition.

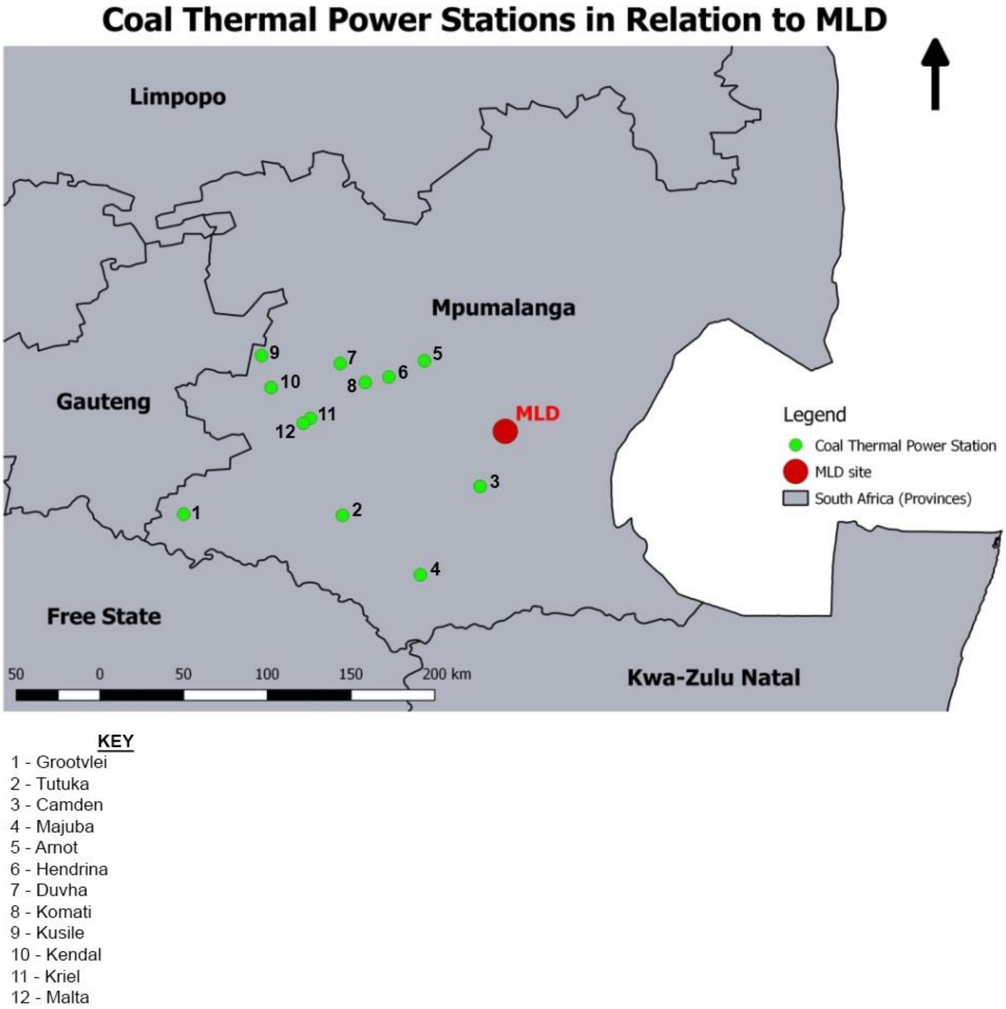


Figure 3.2: Map showing the relationship of coal thermal power stations in Mpumalanga to the MLD site (Data Source: Eskom).

3.1.2. Geological Setting

The regional geology consists of mainly Ecca Series sandstone in which much of South Africa's coal is found (Bell *et al*., 2001; Wellington, 1943). The Ecca Series group is part of the much larger Karoo Supergroup which has strata predominantly composed of sedimentary deposits (Bell *et al*., 2001; Russell, 2008). These coal fields are shallow in formation making the region ideal for open cast mining (Bell *et al*., 2001). The selected study site of the MLD is located on the Eastern edge of large coal fields (*Figure 3.3* and *Figure 3.4*) known as the Witbank Coalfield and the Ermelo Coalfield which are geologically within the Vryheid Formation as part of the Ecca Series group (Bell *et al*., 2001; Jeffery, 2005; Wellington, 1943). These geological groups are identified by the strata of feldspathic sandstone on which the pans of the MLD are located (Wellington, 1955). There is also evidence of dolerite formations around the MLD region (Wellington, 1955). Some sandstone and dolerite extrusions can be seen on the edges of these pans which have been exposed by erosion processes.

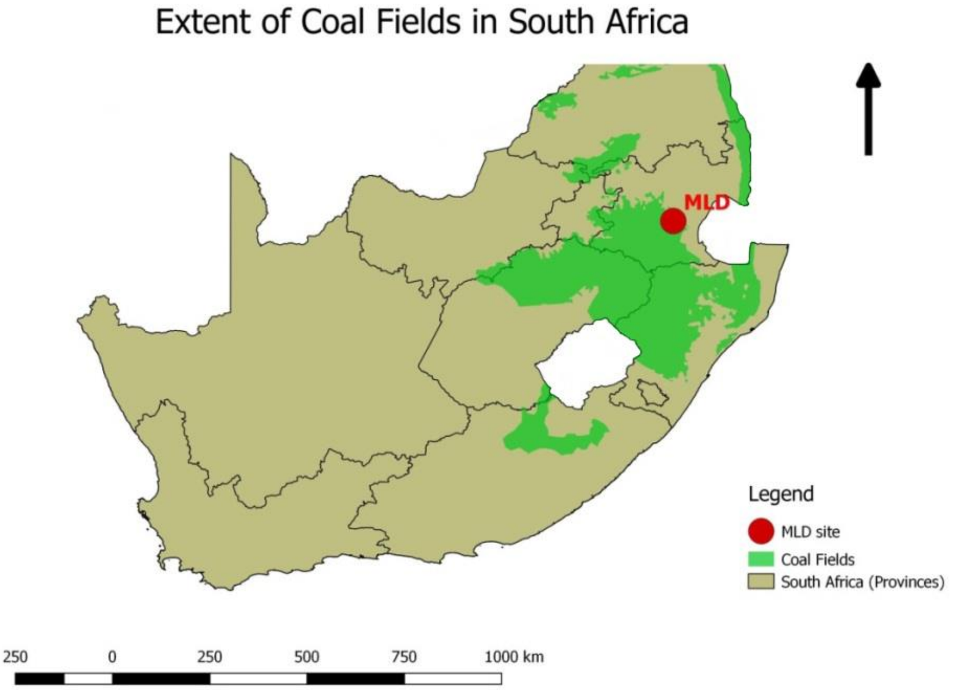


Figure 3.3: Map showing the extent of the coal fields with respect to the MLD site (Data Source: USGS, 2018).

The formation of these pans in this specific area are due to the varying underlying geology, flatter surfaces and underground water storage along with lateral seepage (Russell, 2008). The origin of these pans can not only be linked to geology alone as pans are found on the same strata as surrounding areas where there are no pans even at the same elevation and close proximity suggesting multiple aspects influencing the origin of these pans (Russell, 2008).

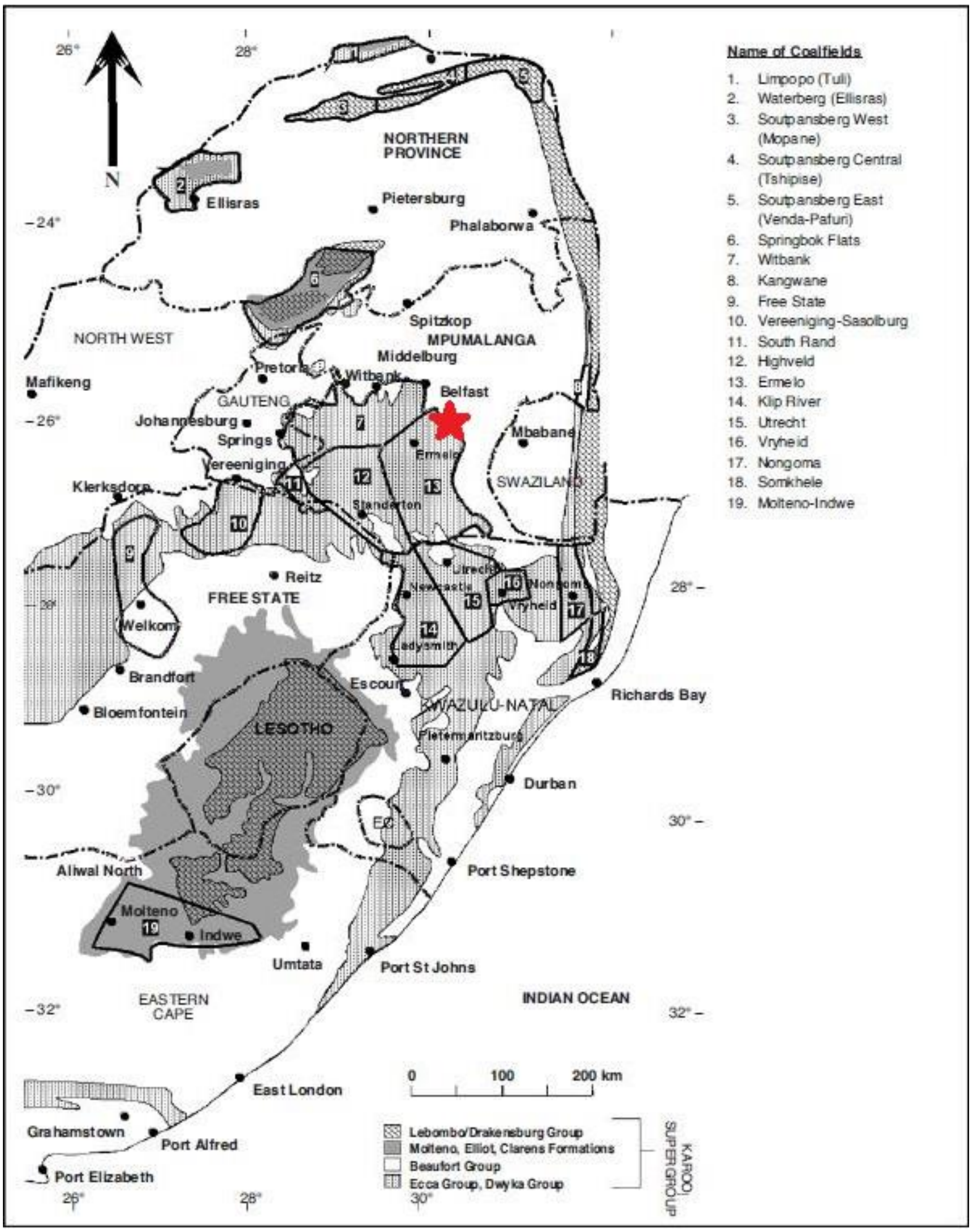


Figure 3.4: The MLD site marked in relation to the various South African coalfields (after Jeffrey, 2005, p. 96)

3.2. Sample Sites

The sample or study sites were selected based on a number of criteria. These criteria included: 1) access to the pan in terms of both permission and access by vehicle, 2) the pan had to be an open pan free of any grass, reeds or peat islands, 3) the pan had to be deep enough for the use of an inflatable boat, 4) the pan needed to be a relatively permanent pan with no seasonal drying up regime, and 5) the pans had to yield a sediment core with as little clay deposits in it as possible. From these criteria, four sites were selected in total as represented in *Figure 3.5*. These sites are far enough apart that they do not directly influence each other in terms of surface flow.

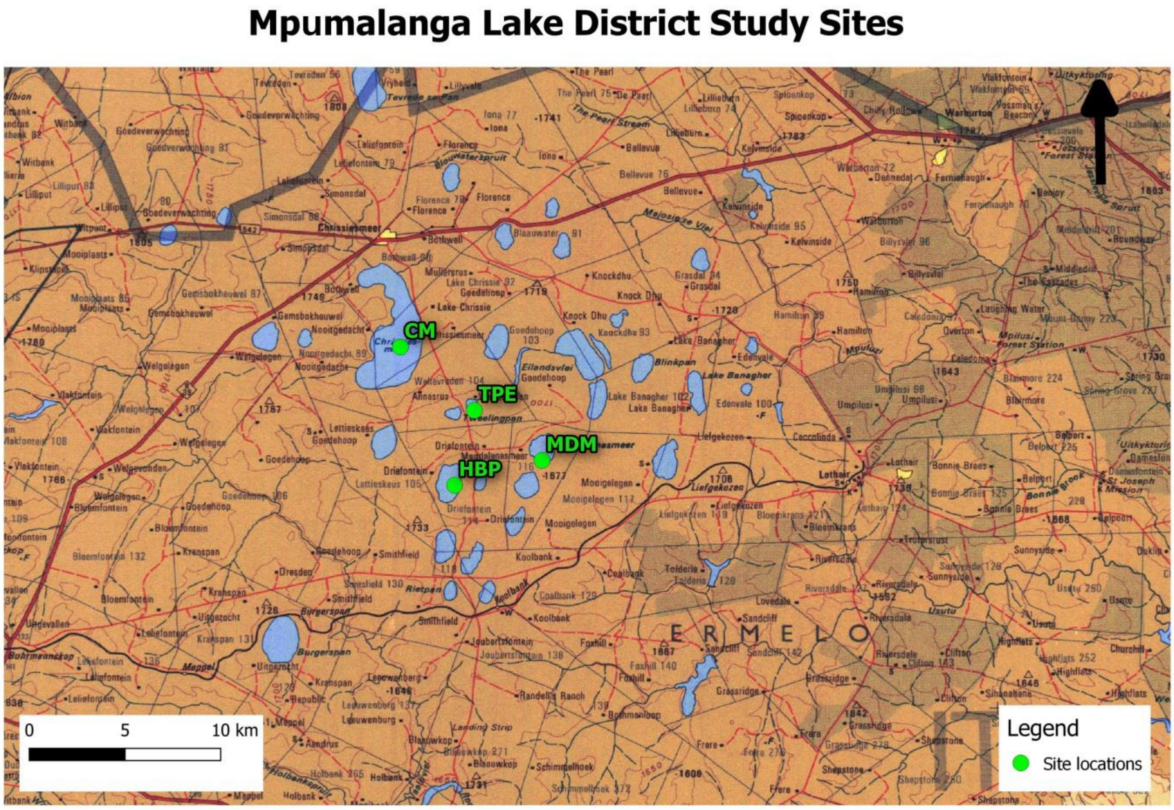


Figure 3.5: Four selected study sites within the Mpumalanga Lake District

3.2.1. Chrissiesmeer (CM)

The site of Chrissiesmeer (CM) is located on Lake Chrissie (26˚ 19' 49.12" S, 30˚ 13' 8.98" E; *Table 3.1*) which borders the town of Chrissiesmeer at its northern most point. The pan itself is the largest pan in the MLD at approximately 9.59 km^2. Although this pan is large compared to any other pan in the MLD, it is fairly shallow with its deepest point at only 1.3 m. The pan is an elongated kidney shape with possible inflow points at its most north-western point and its most south-western point. The area immediately surround the pan consists of a mosaic of grassland and sandstone outcrops. There is a holiday campsite on the western shore which uses the pan for water sports and fishing. There is also presence of a small scale sewage treatment plant on the northern most edge of the pan which functions for the town of Chrissiesmeer and possibly causes seepage into the pan. There is almost no evidence of water plants such as reeds and the water has a high turbidity resulting in visibility issues. Lake Chrissie is a brackish pan meaning that there is a fair amount of salinity present and this is mixed with fresh ground water or surface inputs.

Table 3.1: List of sample sites with site details and coring locations

Site	Latitude (South)	Longitude (East)	Altitude (Meters above sea level)	Depth (m)	Approximate Area (km^2)	Core Length (cm)	Comments
CM	26˚ 19' 49.12"	30˚ 13' 8.98"	1673	1.3	9.59	30 (CM1) 29 (CM2)	High turbidity, Some shallow inflow points
TPE	26˚ 21' 35.96"	30˚ 15' 14.11"	1683	2.4	0.43	10 (TPE1) 11 (TPE2)	Low turbidity, little to no inflow
MDM	26˚ 23' 0.6"	30˚ 17' 8.41"	1667	1.4	1.76	11 (HBP1) 14 (HBP2)	Fairly high turburdity, little to no inflow
HBP	26˚ 23' 42.61"	30˚ 14' 40.6"	1671	0.4	1.66	22 (MDM1)	Very high turbidity, little to no inflow

3.2.2. Tweelingspan East (TPE)

The Tweelingspan East (TPE) site is located on the eastern pan of the Tweelingspan which are a set of pans divided by a natural levee which has a road running over it (26˚ 21' 35.96" S, 30˚ 15' 14.11" E; *Table 3.1*). This is a site of great interest as it is different to the rest of the selected sites in terms of its limnology, size and depth. The water in TPE has less turbidity than the other sites and is much deeper than the other sites with its deepest point at 2.4 m. The TPE site is smaller than the other sites with an approximate area of only 0.43 km^2. The immediate surroundings of the TPE site consist mainly of grassland with rocky outcrops on its northern boundary and a shallow natural levee to the west which, in the wet season, could connect TPE to the western pan of the Tweelingspan. Both pans are similar visually and thus it was determined that the limnology would be very similar. Between these two pans there is little to no evidence of surface flow inputs and therefore it was determined that TPE was replenished by groundwater springs.

3.2.3. Magdalenasmeer (MDM)

The Magdalenasmeer (MDM) site is located to the south-east of TPE and is a moderately sized pan for the area at approximately 1.76 km^2 (26˚ 23' 0.6" S, 30˚ 17' 8.41" E) (*Table 3.1*). The MDM site is visually similar to the CM site in terms of water quality and its surroundings. The water is fairly turbid representing brackish water. The immediate surroundings consist of grassland, livestock grazing fields and shallow sandstone outcrops. The pan is fairly shallow, similar to CM, at only 1.4 m at its deepest point. MDM had little to no evidence of surface water inputs and it was therefore determined that groundwater and the water table play a large role on its water level.

3.2.4. Hendrik Beukes Pan (HBP)

The Hendrik Beukes Pan (HBP) site is located to the south-west of MDM and is an interesting site in terms of its size and its depth (26˚ 23' 42.61" S, 30˚ 14' 40.6" E) (*Table 3.1*). The HBP site is by far the shallowest of the four sites with its deepest point at 0.4 m which is puzzling as with an approximate size of 1.66 km^2, it is similar in size to MDM. The depth could be due to sediment inflow or the gradual slopes which completely surround HBP. The other three sites are located on flat ground with little gradient change but HBP has a definite slope gradient influence. The immediate surroundings consist of grasslands and areas of exposed soil which are possibly used for fields of cultivated crops. This could influence the inflow of sediments into HBP during precipitation events. The water quality in HBP is extremely turbid resulting in poor visibility which could be influenced by the sediment inflow. Although HBP is surrounded by gradual slopes, there is no visual evidence of surface water inputs and therefore it was determined to rely on the ground water table.

3.3. Field Work

3.3.1. Bathymetry

The field sampling consisted of a palaeolimnological assessment of the four selected endorheic pans, these being the sites of Chrissiesmeer (CM), Tweelingspan East (TPE), Magdalenasmeer (MDM) and Hendrik Beukes’ Pan (HBP). This first involved a bathymetric analysis of each site measuring the depth of the pans in order to find the deepest point at which sediment samples and water quality data were to be obtained. In order to obtain the deepest point of each site, while determining the overall shape of the pans with regard to area and depth, a hand held depth echo sounder instrument was used which measured depth in meters (m) at intervals of 0.1 m starting at 0.3 m. For shallower waters a plank ruler was used and the depth was read off. This was seldom the case except for site HBP where the pan was generally shallow and the depth echo sounder would not produce a reading. The method utilised for obtaining a good spread of depth points was to travel along transects in a zig-zag pattern across the width of each pan taking a depth reading at approximately every 10-15 m. The zig-zag pattern was assumed to be the best method as this covered the most area in the time allowed and this would allow for a good spread of depth points. At first points were recorded in a written record but this was a risk as there is chance for recording incorrect points. The first two sites of CM and TPE were recorded by hand and the sites of MDM and HBP were recorded by logging all recorded points into the handheld GPS and writing down each depth point with a ranking number related to the GPS points. This was a quicker process and allowed for the GPS points to be imported directly into a spreadsheet in order to analyse. This depth data or bathymetry data was analysed and represented in the form of bathymetric maps of the pans which represented the change in depth with respect to their overall shape. These bathymetry maps were created using ArcGIS 10.5.1 geographical information systems (GIS) software. A Kriging interpolation tool was used to turn the depth point data into a smooth representation of depth with respect to space. The WGS 1984 UTM 36S geographic coordinate system was used in order to accurately represent the size of the pans with respect to their geographical position. This all provided maps with a clear representation and understanding of the bottom of these pans. From creating these maps, the deepest point of each site was determined which was then cored in order to obtain a sediment core with the greatest length of historical sediment accumulation. It was estimated that the deepest point would have the most continuous sediment record due to periods of drying up and that this sediment accumulation may provide sample cores which could present the longest time record from which changes can be identified.

3.3.2. Physiochemical Characteristics

The other limnological methods for field sampling included a vertical profile assessment of water quality conditions and the extraction of sediment core samples for various sediment related and element compositional analyses, the methods of which are described later on. The vertical profiling of water quality conditions was conducted using a YSI Professional multi-parameter probe at interval depths of 0.5 m. This would result in a clear vertical profile of how the water quality parameters of temperature (˚C), pH (pH units), electrical conductivity (μs/cm) and dissolved oxygen (mg/L and %), change with regard to depth (De Klerk *et al*., 2012). All of these variables were measured to add depth to data resource (Table 4.1). The reasoning behind vertical profiling of water quality conditions was that a basic understanding of the physiochemical characteristics and water stratification of the selected endorheic pans was required which would assist in describing the limnology and characteristics of these pans. This data was however not vital to the achievement of the research aims. This water quality data was only used to aid the understanding of the physical lake morphology of these pans through understanding the tendency for drying out and a possible relation to physiochemical properties such as salinity. In terms of sediment related data, lake sediment cores were obtained prior to any laboratory or data analysis methods.

3.3.3. Sediment Coring and Extrusion

The methods for extracting the sediment cores followed quite similarly to the USEPA (2001) methods. Two sediment cores were extracted from each of the four sites by the use of a gravity corer from an inflatable boat from the deepest point of each pan site, determined through bathymetric analysis previously. The reasoning behind the extraction of sediment cores rather than surface sediments was in order to determine the depth of contamination which relates to time, although the benthic layer or active layer is of most interest due to the ongoing or active contamination from settling sediments (USEPA, 2001). The length of the sediment core however depended on the availability of suitable sediments and the depth of those sediments. It depended on the depth at which clay and rocks were predominantly present. Therefore the sediment core lengths vary. The sediment cores were kept intact inside the coring tube until extrusion could take place. The extrusion process consisted of slicing the core at 0.5 cm intervals using a threaded bar to push the sediment core through the plastic tube. Each of the 0.5 cm extruded sediment segments from the core was then separated into zip lock plastic bags and labelled with the site and depth of each sample (Jones *et al*., 1997; Curtis *et al*., 2010). All stages of the extraction and extrusion process were strictly controlled in order to ensure that no contamination could take place. Transportation and storage of the sediment samples consisted of keeping the sediment samples cold, at around 4 ˚C, as to minimise any physiochemical or organic changes that could take place (Curtis *et al*., 2010).

Sample sediment cores that were obtained through field work are as follows. For CM, two cores were extracted namely CM1 (30 cm) and CM2 (29 cm). For TPE and HBP, two cores were extracted for each site namely TPE1 (10 cm), TPE2 (11 cm), HBP1 (11 cm) and HBP2 (14 cm). For MDM, two cores were extracted yet only one was extruded (MDM1 (22 cm)) as the other was lost due to contamination with sediments mixing. Stratigraphic observations were made on the cores in terms of changes in colour and changes in sediment type. All cores apart from the cores from TPE had definite colour changes around the similar margin of 8 cm and in the TPE cores, this change was not evident. There were also changes in sediment type in all the cores at around 15 cm where there was evidence of more clay sediments. Cores from TPE and HBP did not share this same characteristic due to the length of core obtained. Changes in sediment type were observed at around 9 cm for both these sites. The cores selected for sediment analysis were based on their length of sediment record, therefore the selected cores for sediment analysis were CM2, TPE2, HBP2 and MDM1 with CM1 being sent for radiometric dating analysis.

3.4. Sample Analysis

3.4.1. Age Determination

The sediment sample analysis included radiometric dating of sediments, organic carbon and carbonate analysis, grain size analysis and major element analysis. This is all in the aim of understanding a full historical record of the pan sediments for the past approximately 130 years.

The sediment samples collected from site CM underwent radiometric dating analysis in order to understand a historical record of sediment accumulation. Core CM1 was sent for radiometric dating analysis due to the visual evidence that the stratigraphy in the sediment core was intact and due to its length which would hopefully yield the most accurate and longest timeline of sediment accumulation. The dating concerned samples from 0 cm depth to 23.5 cm depth. The radiometric dating method in question is Lead-210 (^{210}Pb) dating and was conducted by the University College London (Oldfield, 1977; Jones *et al*., 1997; Appleby *et al*., 1998; Rose *et al*., 2004). The use of ^{210}Pb dating is one of the most common forms of dating with regard to short-term sediment deposition and accumulation rates studies and is used extensively in palaeolimnological studies (Oldfield, 1977; Jones *et al*., 1997; Humphries *et al*., 2010). This dating method involves the use of gamma spectrometry in order to determine ^{210}Pb via its gamma emissions (Appleby *et al*., 1998; Rose *et al*., 2004). This radiometric dating method therefore provided an accurate record of the sediment accumulation within Chrissiesmeer (site CM) over time giving an understanding of the age of the sediments with respect to depth. This was a crucial aspect in this research as any anomalies or events observed in the sediment analysis of the samples could be linked to an age and therefore a date in history in order to understand and reconstruct the environment of the endorheic pans in question.

3.4.2. Sediment Analysis

A vital environmental proxy to this research project required understanding the percentage of organic content and carbonate content of the sediment sample through the process of Loss on Ignition (LOI). The determined percentage organic content and carbonate content is an important but simple to use proxy which can be used to determine past environmental and climatic conditions and changes (Heiri *et al*., 2001. The use of percentage carbonate content was to understand moisture availability as well as possibly identifying any changes in acidity of the sediment (Dean, 1999; Heiri *et al*., 2001). Factors that could influence organic content and carbonate content include changes in water body organic productivity and allogenic organic and inorganic inputs (Shuman, 2003). There is an inverse relationship between organic content and carbonate content which can be used to indicate changes in the pH level due to the precipitated calcium carbonate ($CaCO_3$) (Dean, 1999). This is, however, not always the case due to changes in organic productivity within the water body in question (Dean, 1999). High levels of organic productivity can also lead to decreased oxygen which can result in a higher accumulation of metals such as iron and manganese (Dean, 1999). This just shows the importance of the LOI method in palaeolimnological studies such as this.

The LOI method in question follows the protocols set by the University College London (UCL) and their Environmental Change Research Centre as well as methods set out be Heiri *et al*. (2001). The first step in the LOI process was to obtain the percentage of organic content in the sediment samples. This included firstly the drying of the sediments in a drying oven in individual foil trays at a temperature of

105 ˚C for 12 hours, after which the dry weights for each sample were obtained using a 4 decimal scale (Heiri *et al*., 2001; Curtis *et al*., 2010). The samples were then individually placed into ceramic crucibles and placed in a furnace at 550 ˚C for 2 hours and were then re-weighed in order to obtain the sample dry weight after 550 ˚C (Heiri *et al*., 2001; Cutis *et al*., 2010). The dry weight after 550 ˚C (DW_{550}) was then subtracted from the initial dry weight after 105 ˚C (DW_{105}), this was then divided by DW_{105} and then multiplied by 100 in order to obtain what was assumed to be equivalent to the percentage loss on ignition at 550 ˚C in each sample as represented by the LOI_{550} equation below.

$$LOI_{550} = ((DW_{105} – DW_{550}) / DW_{105}) * 100$$

The LOI method was taken one step further to estimate the percentage carbonate content of each sample. This method required placing the DW_{550} samples obtained in the organic content LOI method back into the furnace at 950 ˚C for 4 hours in order to burn off any $CaCO_3$ (Heiri *et al*., 2001). The resultant dry weight at 950 ˚C (DW_{950}) was then re-weighed and this weight was subtracted from the DW_{550}, this was then divided by the initial DW_{105} and then multiplied by 100 in order to obtain a percentage of carbonate content as represented by the LOI_{950} equation below.

$$LOI_{950} = ((DW_{550} – DW_{950}) / DW_{105}) * 100$$

Careful consideration was taken at every step in order to avoid any form of contamination from pre-cleaning foil trays and crucibles as well as separating samples back into individual new plastic bags. This is all in the aim of obtaining accurate data from which changes can be seen throughout the sample set which could determine environmental and climatic changes.

The next step in sediment analysis and another vital proxy in this palaeolimnological study is sediment grain particle size analysis. This in achieved through measuring particle sizes by laser diffraction. The sediment sample, which already underwent the LOI process was then analysed using the Malvern Mastersizer 3000 in order to obtain the distribution of particle sizes (Fitchett *et al.*, 2016). This form of laser diffraction analysis uses a set of lasers to determine the refraction of light from the sediment particles passing through it which then provides a distribution of particle sizes (Ryzak & Bieganowski, 2011; Fitchett, 2015). A proven Standard Operating

Procedure (SOP) for silt and clay was used from an existing project by Fitchett (2015) in order to keep the methods constant across all sites and samples. This involved adding a wet sample to a solution which then underwent ultrasonic stirring which broke down agglomerated sediments in order for the laser diffraction to measure individual particles (Fitchett, 2015). The particles were measured in particular size categories and a Phi size (Φ) was obtained which was then converted into grain size classification under the Wentworth scale, shown in *Table 3.2* (Wentworth, 1922; Blott and Pye, 2001).

The resultant different grain or particle sizes could possibly provide an understanding of sediment accumulation rates and dynamics as well as any climatic events which can influence sediment accumulation (Peng *et al*., 2005; Sun *et al*., 2002). In total, four sets of data were obtained in order to determine changes in sediment grain size as a proxy for any environmental change. These were the sediment grain size distribution (according to *Table 3.2*), mean grain size, skewness and kurtosis (Blott and Pye, 2001; Fitchett *et al.*, 2016). Mean grain size is calculated arithmetically and represents the average grain size distribution for the sample as a higher mean results in smaller grain particle sizes (Briggs, 1977; Blott and Pye, 2001; Masselink *et al*., 2014). Skewness measures the symmetry of the distribution around the mean and therefore the more positively skewed the distributions are, the smaller the grain particle sizes (Briggs, 1977; Blott and Pye, 2001; Fitchett, 2015). Kurtosis relates to the height of the distribution with normally distributed data being mesokurtic while flatter and smaller distributions being playtykurtic (Fitchett, 2015).

Table 3.2: Size grades of sedimentary particles (after Briggs, 1977; Masselink et al., 2014).

Phi size (ϕ)	Micrometers (μm)	Wentworth Scale[1]	Wentworth Scale[2]
-6.0	64 000.00	Pebbles	Cobbles
-5.5	44 800.00		Coarse gravel
-5.0	32 000.00		
-4.5	22 400.00		
-4.0	16 000.00		Medium gravel
-3.5	11 200.00		
-3.0	8 000.00	Granules	
-2.5	5 600.00		Fine gravel
-2.0	4 000.00		
-1.5	2 800.00		
-1.0	2 000.00	Sand	
-0.5	1 400.00		Coarse sand
0.0	1 000.00		
0.5	710.00		
1.0	500.00		Medium sand
1.5	355.00		
2.0	250.00		
2.5	180.00		Fine sand
3.0	125.00		
3.5	90.00		
4.0	63.00	Silt	
4.5	45.00		Coarse silt
5.0	32.00		
5.5	23.00		
6.0	16.00		Medium silt
6.5	11.00		
7.0	8.00		
7.5	5.50		Fine silt
8.0	4.00	Clay	
8.5	2.75		
9.0	2.00		Clay
9.5	1.38		
10.0	1.00		

3.4.3. Major Elements

In order to understand and determine any environmental changes by use of sediment as a proxy, major elemental compositions were analysed for each site and how this composition changes in terms of depth. Due to cost constraints, the resolution of samples was reduced although the entire length of the sediment cores were analysed. Instead of analysing every sample at a resolution of 0.5 cm, for the CM core, CM2, only the sample depths that matched up to the radiometric dating depth results were selected. For the rest of the sites, samples were selected at 2 cm intervals beginning from 0 cm or the surface sediments. This resulted in saving costs while still covering the full extent of the sediment core.

With regard to the major element analysis, sample preparation methods were conducted during the LOI methods where the sediment samples were dried at 105 ˚C for 12 hours (Heiri *et al*., 2001; Curtis *et al*., 2010). Preparation also included grinding each sample to a fine powder in a pestle and mortar after LOI was conducted. These selected samples were then analysed through a process of X-Ray Florescence (XRF) spectrometry conducted by the School of Geoscience's Earth Lab at the University of the Witwatersrand. This laboratory based process analyses the major elemental composition of each selected sample at a high resolution as to determine changes in major elements over time (Boyle, 2000; Baranowski *et al*., 2001). The major elements of concern in this analysis are as follows; Silicon (Si), Aluminium (Al), Iron (Fe), Manganese (Mn), Magnesium (Mg), Calcium (Ca), Sodium (Na), Potassium (K), Titanium (Ti), Phosphorus (P), Chromium (Cr) and Nickel (Ni) (Boyle, 2000; Baranowski *et al*., 2001; Wagner & Hlatshwayo, 2005). These are common major elements found in sediments yet changes in the composition can show external influences such as contamination and/or environmental changes as well as climatic changes (Baranowski *et al*., 2001; Wagner & Hlatshwayo, 2005). Certain major element results were removed completely from the results and statistical analysis as they had an average composition value of 0.01 % and showed no changes throughout the record and would not add any value to the results for this research project. These major elements were Ni and Mn. Major elements were selected over trace elements for a number of reasons but the main factor was due to the financial costs involved in trace metal analysis. Another deciding factor was that major element analysis only required a small amount of sediment material, less than 5 grams, while trace metal analysis required large amounts of sediment material which would have required more bulking of samples which would impact the resolution of data obtained.

The result from the XRF method for major elements was a composition in percentage for each sample and when combined with the other samples from each site, showed a record of changes over depth and in the case of CM, time. These results then underwent statistical analysis in order to determine the relationships between similar sediment data distributions.

3.5. Statistical Analysis

3.5.1 Statistical Analysis of Sediment Data

The statistical analysis utilised for this research project was used in the aim of determining any changes in environmental conditions and/or climatic conditions over the last 100 years. The statistical analysis of sediment data consisted of determining clusters within data sets which demonstrate similarities within the sediment data and the major element data (Fitchett, 2015). The two statistical methods incorporated in this research project included CONISS (Constrained Incremental Sum of Squares) for the clustering analysis and the indirect ordination method of PCA (Principle Components Analysis) for understanding the influences and changes in major elements (Grimm, 1987; Fitchett, 2015). Both methods were carried out using R statistical coding program using the Vegan, Rioja and Cluster packages (Venables & Smith, 2015).

The clustering of data was done with the aim of determining similarities between major elements and sample depths in the form of clusters or zones, as well as between LOI data distributions and grain size distribution. Clustering is done by the CONISS method which produces cluster groups as a result and these groups can be used to understand similarities between the data sets with respect to depth and therefore time (Fitchett, 2015). The CONISS method was conducted on the major element data for each site. This resulted in cluster groups which were then compared to the LOI data and grain size distribution data.

The second method was to use the indirect ordination method of PCA which is a form of gradient analysis where major elements data were compared to one another within each site and how they influence each sample at certain depths (Legendre & Birks, 2012; Fitchett, 2015). This method was run on the percentage composition of major elements in each site. The result of this method is that bi-plots are produced which display the relationship between PCA1 and PCA2 in terms of the major elements data and the similarities between sample points (Fitchett, 2015). These results are then combined with the clustering results and points in the bi-plots are then coloured as per the cluster groups and this shows possible periods of change over depth and therefore time (Legendre & Birks, 2012). In terms of the PCA bi-plots, points separated by 180˚ are complete opposites and those separated by 90˚ have no similarity at all (Fitchett, 2015). Similarity between sample points is determined by the distance and angle separating them so that close points have a strong similarity while points far apart are more dissimilar (Legendre & Birks, 2012; Fitchett, 2015). This form of statistical analysis is important as it provides a determination of the similarities within and between major elements and samples which can represent changes over time.

3.5.2. Graphical Representation

The graphical representation of statistical data on major elements, LOI data distributions and grain size distribution data was carried out using stratigraphic plotting software C2 (Juggins, 2007). Most of the graphical representation took the form of stratigraphic plots while PCA analysis results were represented in bi-plots and CONISS results (Appendix 1) represented in dendrograms both created using R (Venables & Smith, 2015). Selected major elements which had the highest composition percentage were shown in box plots using measures of central tendency and each major element was compared to each other between all four sites in order to understand the differences between site compositions (Lane, 2014). With regard to the stratigraphic plots for major elements, the cluster zones determined from the CONISS method and the resultant dendrograms were added in order to show zones of similarities and changes with regard to depth and therefore age. The same cluster zones were applied to the stratigraphic plots for LOI distribution data and grain size distribution data in order to analyse any similarities or differences between proxies in terms of changes which could represent periods of environmental change (Fitchett, 2015).

The stratigraphic plots for CM were plotted against age while the stratigraphic plots for TPE, MDM and HBP were plotted against depth. This was due to CM being the only samples to have undergone radiometric dating. Initially the other sites were assumed to have similar sedimentation rates due to their proximity in location and therefore the age between CM sediments and TPE, HBP and MDM sediments would be similar with regard to depth. In order to determine if this was the case, a visual cross correlation was utilised. This simple method involved using the percentage organic carbon content from the stratigraphic plots for each site and manually matching up the peaks and depressions of the plots. Peaks and depressions were used as due to the sites proximity, it was assumed that events such as drying up periods would affect all the sites at the same time period but possibly not to the same extent. Once the peaks were matched up, a date could be correlated across all sites using the dates obtained for site CM. This provided clarification to the initial assumption that all four sites had similar sediment accumulation rates.

The multiple graphical representations are used in the results chapter to identify points of interest, changes over time as well as similarities and differences between sites with regard to a certain proxy. This would then lead on to helping in facilitating a discussion on evidence of environmental and/climatic changes over time and how anthropogenic activity has influenced these changes.

4. Results

4.1. Introduction

This chapter (*4. Results*) depicts and attempts to explain the results obtained in terms of lake morphology and bathymetry, the chronology of lake sediments and the major elemental compositions of the sediments in the studied sites.

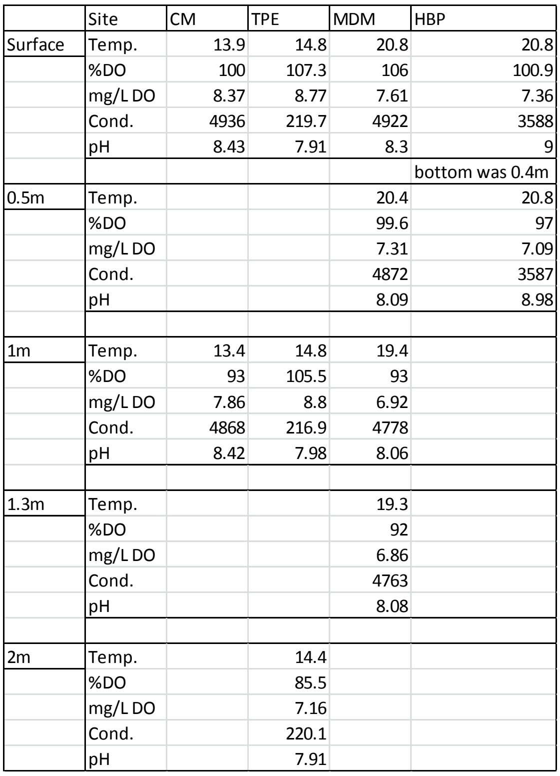
4.2. Lake Basin Morphology

The lake basin morphology of the selected study sites of CM, TPE, MDM and HBP, as represented in *Figure 4.1*, shows the bathymetric patterns of the study site pans in terms of their depth and shape characteristics. This is the pan floor shape and this provides an understanding of bathymetric patterns, the shape of the pans, possible sediment accumulation dynamics and the deepest points at which the sediment cores were taken. *Figure 4.1* depicts all the sites so as to compare them in terms of shape, size and average depth. With the addition of basic water quality data from a vertical profile analysis, a more comprehensive understanding may be obtained about the bathymetry and function of these pans.

The selection of coring points was of vital importance as depicted in *Figure 4.1* and mentioned in *Table 3.1*. These points depicted the deepest points of the pans in question which was vital due to the threat of possible drying out events which would have impacted the length and possibly resolution of the cores. The selection of cores from the deepest points resulted in the greatest likelihood of continuous water presences and hence continuous sedimentation.

Site CM is the largest site with its deepest point being between 1.2 m and 1.3 m. From the bathymetric maps (*Figure 4.1*) it can be noted that there are several deep points at which sediment may collect. There is a deep point towards the southern boundary as well as one in the centre of the pan. The shallow points at its northern boundary show evidence of possible surface flow input such as a stream. It was also noted that CM has an elongated kidney shape which is referred to by Wellington (1943). In terms of a vertical profile of water quality (*Table 4.1*), site CM showed little change in terms of temperature (˚C), percentage dissolved oxygen (%DO), conductivity (μS/cm) and pH value over the depth of 1.3 m. Most notable though is the value of conductivity which at the surface was 4936 μS/cm and at 1 m depth decreased to 4868 μS/cm. The water was highly turbid with high levels of TSS, while high TDS is indicated by the high electrical conductivity values. Site CM had a pH value of 8.43 across the vertical water profile which was higher than the other three sites apart from HBP which had a high pH value. The water temperature was between 13.9 ˚C at the surface and 13.4 ˚C at 1m depth which compared to the other three sites is much colder. Compared to the other sites of TPE, MDM and HBP, CM seems to have a more variable bathymetric shape although this could be due to its size of approximately 9.59 km^2.

Table 4.1: Water quality data of vertical profile for all sites.



	Site	CM	TPE	MDM	HBP
Surface	Temp.	13.9	14.8	20.8	20.8
	%DO	100	107.3	106	100.9
	mg/L DO	8.37	8.77	7.61	7.36
	Cond.	4936	219.7	4922	3588
	pH	8.43	7.91	8.3	9
					bottom was 0.4m
0.5m	Temp.			20.4	20.8
	%DO			99.6	97
	mg/L DO			7.31	7.09
	Cond.			4872	3587
	pH			8.09	8.98
1m	Temp.	13.4	14.8	19.4	
	%DO	93	105.5	93	
	mg/L DO	7.86	8.8	6.92	
	Cond.	4868	216.9	4778	
	pH	8.42	7.98	8.06	
1.3m	Temp.			19.3	
	%DO			92	
	mg/L DO			6.86	
	Cond.			4763	
	pH			8.08	
2m	Temp.		14.4		
	%DO		85.5		
	mg/L DO		7.16		
	Cond.		220.1		
	pH		7.91		

The sites of TPE, MDM and HBP have more conventional circular shapes with site MDM (Magdalenaspan or Magdalenasmeer) showing some evidence of elongation but due to its size of only approximately 1.76 km^2, it may not be influenced the same way as CM in terms of wind and sediment dynamics (Wellington, 1943). The deepest point of site MDM was between 1.3 m and 1.4 m and was located just south of the centre of the pan (*Figure 4.1*). Note that MDM site reaches a deep area, demarcated by the light blue colour, within a short distance from the shoreline (*Figure 4.1*). The vertical water profile data for site MDM was similar to site CM except for temperature and pH. The water temperature of MDM ranged from 20.8 ˚C at the surface to 19.4 ˚C at 1 m depth. This represents and almost 7 ˚C difference between MDM and CM.

The pH value for MDM changed slightly with regard to depth as it ranged from 8.3 at the surface to 8.06 at 1 m depth. This shows that site MDM and CM are not as similar as initially assumed (*3.2 Sample Sites*).

HBP was noted to be an interesting site as the pan was a similar size to MDM, at approximately 1.76 km^2, yet it was a very shallow pan with its deepest point at around 0.4 m (*Figure 4.1*). The differences between these two sites are a point of interest which could be explained by topography or sediment dynamics. The use of vertical water profile data for site HBP was difficult due to its shallow depth. Therefore there was very little change over the 0.4 m of depth. Most notable are the temperature, conductivity and pH values with the surface water temperature being 20.8 ˚C which was the same as site MDM. The pH value was higher than the other sites at 9 but the conductivity was of most interest as it was approximately 3588 μS/cm which was less than both CM and MDM even though it was initially assumed that site HBP had the highest conductivity value and possibly the highest TDS concentration of all four sites which could relate to higher levels of turbidity (*3.2 Sample Sites*).

The site of TPE also held much interest as this site was the smallest site in terms of area at 0.43 km^2, yet is much deeper than the other three sites at between 2.3 m and 2.4 m at its deepest point (*Figure 4.1*). This site had a circular shape with its deepest point being located in the centre of the pan (*Figure 4.1*). The gradient from the shoreline was not as sharp as MDM but travelled to a greater depth overall. Sediment accumulation was therefore determined to collect from all sides equally at its deepest point. The interest in site TPE is encouraged with the assistance of the vertical water profile data as this site varies from the other three sites. The water temperature ranged from 14.8 ˚C at the surface to 14.4 ˚C at 2 m depth which is more similar to the water temperature of site CM. Site TPE had a lower average pH value than the other sites of 7.93. The conductivity of site TPE ranges from 219.7 μS/cm at the surface to 220.1 μS/cm at 2 m depth. This conductivity is much less than the other three sites and relates to what was initially assumed as this site had the best water clarity with little to no visible turbidity which possibly relates to a lower level of TDS. Once more this highlights the difference between TPE and the other three sites.

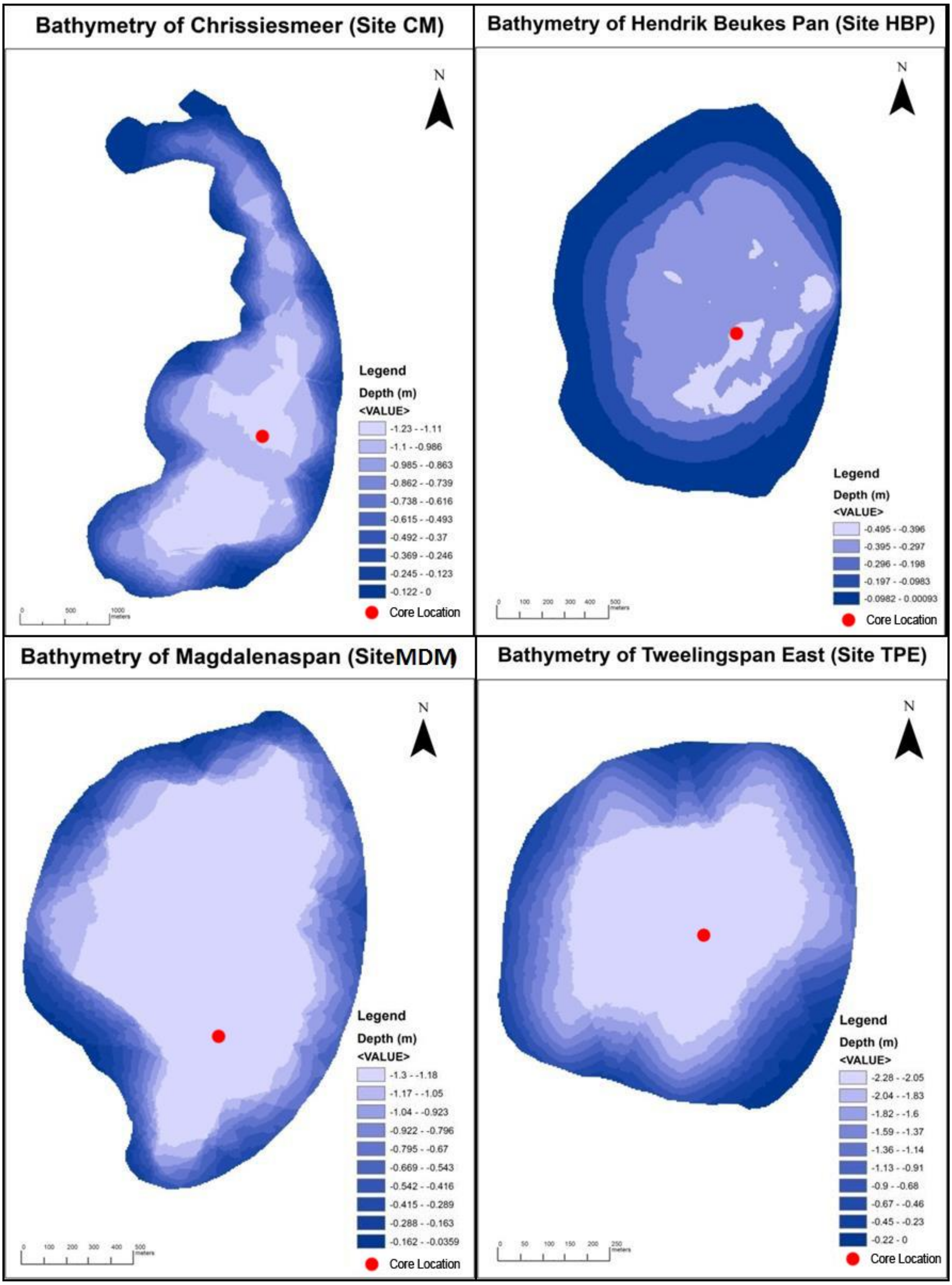


Figure 4.1: Bathymetry maps for sites CM, TPE, MDM and HBP with depths shown.

The above *Figure 4.1* has highlighted the variations in structure and depth between the four pans of sites CM, TPE, MDM and HBP which reiterate the differences between the pans of the MLD region. This is an interesting aspect as all four pans are separated by little distance and very little altitude. These bathymetry maps (*Figure 4.1*) help to understand sediment accumulation dynamics and possible influencing characteristics. Sediment characteristics and dynamics could play a major role in differentiating these pans.

4.2. Radiometric Dates

4.2.1. Radiometric Dates for CM

The site of CM was of primary concern as it produced the longest sediment cores from which core CM1 was used to obtain dates which would be correlated to the other sites in terms of depth as it was initially assumed that sediment accumulation rates were very similar across all four sites. The radiometric dating results obtained from UCL are shown below in *Figure 4.2* which represents a historical sediment accumulation over the last approximately 130 years. In terms of this research project, these dates were calculated to range from 1888 until 2017 (the end of 2017 was when the samples were collected therefore 2018 was included in the range so as to include the whole of 2017). It can be noted that the dating results stopped at a depth of 23.5 cm as this was the limit of the ^{210}Pb dating technique and no clear results could be obtained further. There is a distinct change (*Figure 4.2*) in the dates at about 16 cm in depth where the dates are much closer together per sample compared to below 16 cm where the age covers about 15 years per sample point or about 40 years per 5 cm in depth. This sudden change at about 16 cm relates to the sediment accumulation rate as shown in *Figure 4.3*.

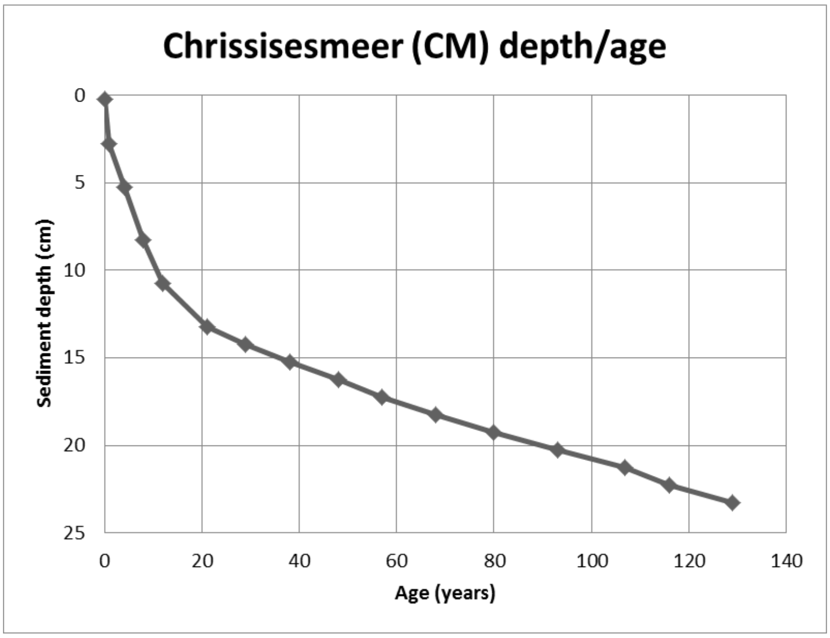


Figure 4.2: Dates for CM1 core

4.2.2. Sediment Accumulation for CM

The sediment accumulation rate for CM as represented in *Figure 4.3* is a result of the radiometric dating analysis as the sediment accumulation relates to depth and age. There is an inverse relationship between *Figure 4.2* and *Figure 4.3* as when there is an increase in the accumulation rate in *Figure 4.3*, there is a decrease in the age of the sediment. An important point to note is the sudden change in *Figure 4.3* at about 16 cm where there is an increase in the sediment accumulation rate. This relates to the change of the number of years per cm from *Figure 4.2* which also changes at about 16 cm. The change in sediment accumulation is vast as it changes from about 0.15 cm/yr^{-1} at 16 cm in depth, to about 1.5 cm/yr^{-1} at about 8 cm in depth where there is a point where the sediment accumulation rates is constant from 8 cm to 5 cm. This point at which the rate does not change is not represented in the dating results in *Figure 4.2* but does represent a point of change in sediment accumulation dynamics. After this static point there is a sharp increase in sediment accumulation rates as from 5 cm to 0 cm (surface) the accumulation rate increases from 1.5 cm/yr^{-1} to 2 cm/yr^{-1}. This change in sediment accumulation rate represents a change in sediment dynamics over time.

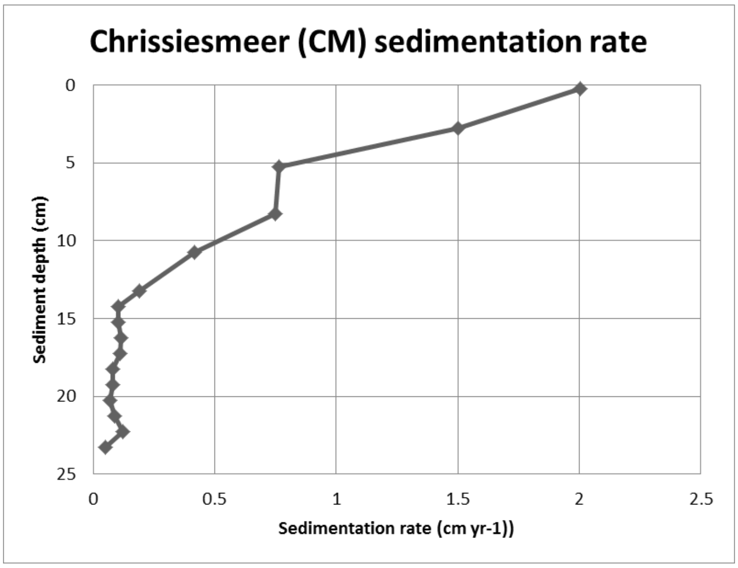


Figure 4.3: Sedimentation rates for site CM

The analysis of radiometric dates and sediment accumulation rates is for the site CM and the sediment accumulation rates across all four sites of CM, TPE, MDM and HBP are not assumed to be highly similar. The sediment accumulation is dependent on multiple factors and even though all four sites are in close proximity to one another, their sizes and characteristics vary, as described in *4.2 Bathymetry*. Although radiometric dating was not carried out on the sites of TPE, MDM and HBP, the dates observed for site CM could be correlated across to the other sites.

4.2.3. Radiometric Dates Correlation to other Sites

The only site with evident dates associated to depth is CM and in order to identify dates for the sites TPE, MDM and HBP, a manual visual correlation was carried out. This manual visual correlation made use of LOI data to look for abrupt changes as stratigraphic markers, to see whether there are similar markers apparent in the other cores. This also provided clarification on sediment accumulation rates which were initially assumed to be similar due to the proximity of all four sites. The result of this correlation, evident in *Figure 4.4*, showed that the initial assumption that all four sites had similar sediment accumulation rates was not entirely true.

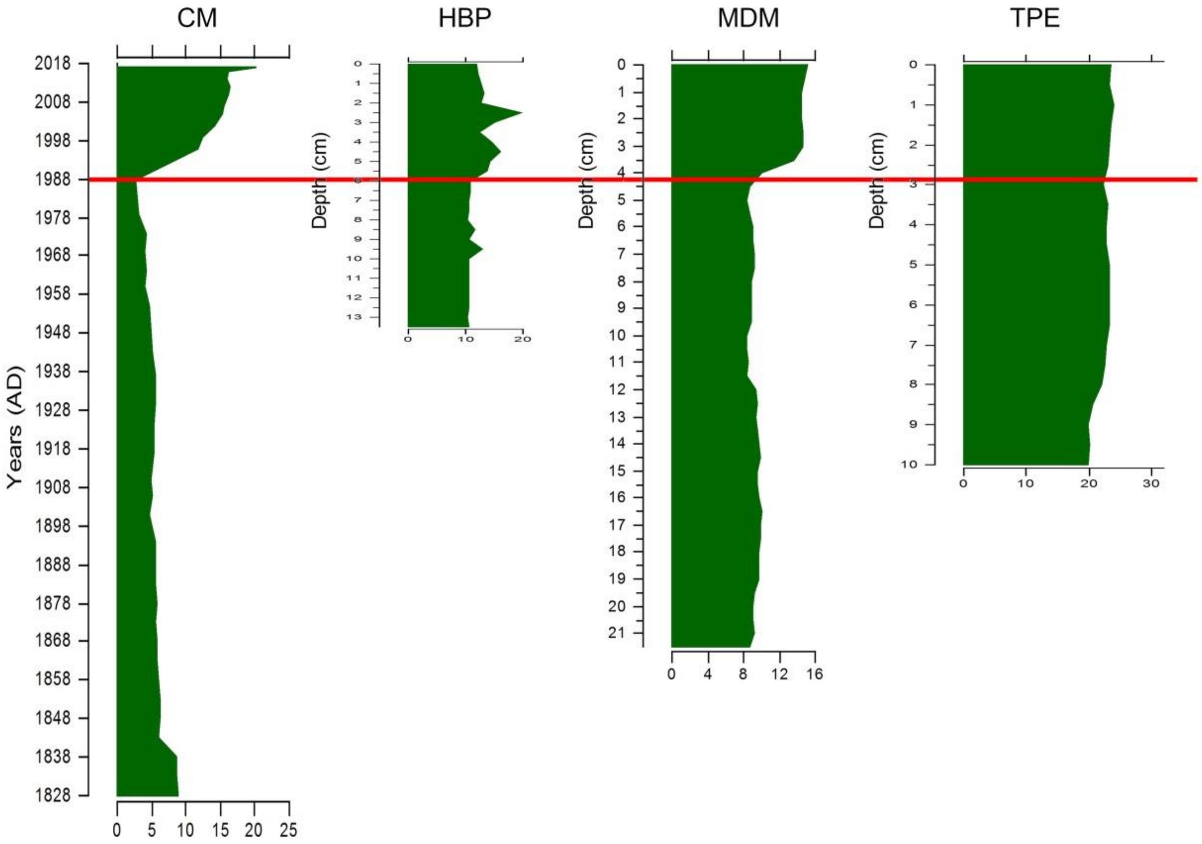


Figure 4.4: Visual correlation of dates between sites using percentage organic carbon content.

Site CM was used as the reference for the correlation of dates for the other three sites. Over the span of a 129 year sediment record for site CM, it was calculated that the sediment accumulation was at a rate of 0.18 cm/year. This however did not accurately represent the sediment accumulation dynamics as over the 30 year period from 1988 to 2018, an accumulation rate of 0.58 cm/year was calculated. These accumulation rates for CM are an average calculation and therefore do not give an absolutely accurate representation of the sediment accumulation dynamics at play but rather provide some clarity in understanding in how site CM relates to the other sites.

In terms of the visual correlation for dates between sites, the year 1988 was used as a reference date as this is a major point of interest for CM with regards to changes in organic carbon content. This point of interest at 1988 is a depression or dip after a major peak which in CM spans from 2018 back to 1988 (*Figure 4.4*). This same peak and then dip was evident across the other three sites of HBP, MDM and TPE.

Therefore it was assumed that these peaks and dips in question from 2018 back to 1988 were the same event across all four sites and therefore these events would be at the same time period. By a process of matching up the peaks and dips across all four sites, it was possible to approximate the dates for points of interest across the other three sites of HBP, MDM and TPE. From this it was also possible to approximate the sediment accumulation rates for these sites using the 30 year period from 1988 to 2018. For site HBP (*Figure 4.4*), the sediment accumulation rate was approximated to be 0.2 cm/year or an accumulation of 1 cm every 5 years. For site MDM (*Figure 4.4*), the sediment accumulation rate was approximated to be more similar to CM at 0.14 cm/year or an accumulation of approximately 1cm every 6.9 years. The site of TPE was a site of great interest due to the difference in bathymetry. There is once again interest as the approximated sediment accumulation rate is far less than the other sites at 0.09 cm/year or an accumulation of approximately 1 cm every 10 years.

By using the approximated sediment accumulation rate for the sites of HBP, MDM and TPE, it is possible to identify a date which corresponds to a certain depth when identifying a particular peak, point of interest or change in data. These are approximated sediment accumulation rates and therefore the dates are also approximated. It is important to understand that many other factors such as sediment supply, geology and geomorphology could play a role in influencing these approximated dates. This is generally to provide some clarity on how the sites differ in terms of age with respect to depth.

4.3. Site CM

4.3.1. Sediment Properties

The sediment analysed from site CM underwent an LOI process as well as grain size distribution analysis which all together provides information as a proxy of possible environmental and climatic change. These changes are evident from the points of interest or events identified in the stratigraphic plot of *Figure 4.5*. These points of interest or events fall within zones which will be identified and compared to each other in order to depict any changes over time. The zones for *Figure 4.5* were obtained from the cluster results from the CONISS analysis run on the major elements data shown in *Figure 4.6* showing clustered groups of significance.

Zone CM0 (so named as it was beyond the limits of the ^{210}Pb dating technique and therefore any date after 1888 was extrapolated using the sediment accumulation rate) shows very little change over the span of 1828 to 1888 (*Figure 4.5*). There is however a slight decrease in percentage organic carbon (%Organic) from 1828 to approximately 1843 with a decrease of approximately 4 % after which the %Organic is constant at 5 %. Percentage carbonate (%Carbonate) is fairly constant at 3 % (*Figure 4.5*). Grain size varies over this time period with two points of interest at 1835 and 1848 where there is a decrease in %Sand grains with an increase in both %Silt and %Clay. This is also reflected in the mean size of the grains at the same dates.

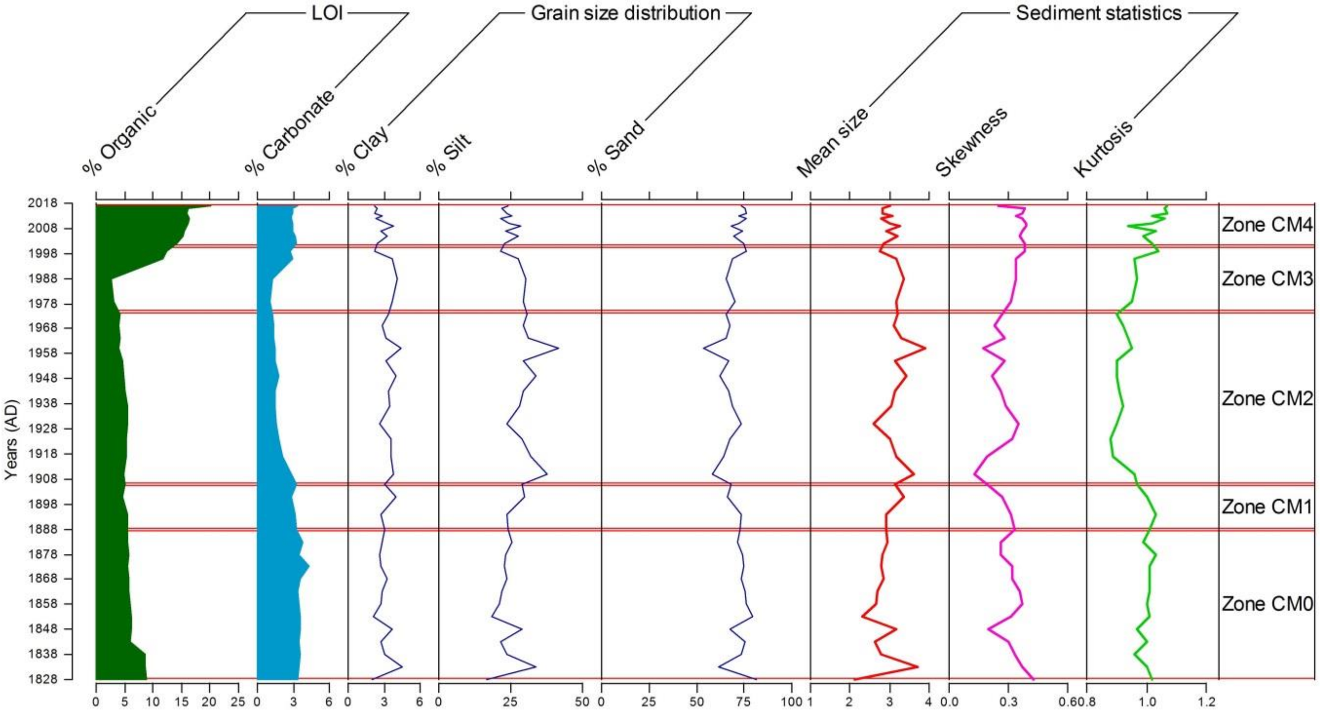


Figure 4.5: CM stratigraphic plot for LOI and grain size distribution

The Zone CM1 (*Figure 4.5)* spans from 1888 to 1906 showing a slight decrease in %Organic and %Carbonate while showing a slight decrease in %Sand resulting in more silt and clay grains. Zone CM2 spans from 1906 to 1975 representing a large portion of the sediment core in which little changes in terms of %Organic and %Carbonate with only a slight gentle decrease from 3 % to approximately 1.5 %. There are larger fluctuations with regard to the grain size distribution with a prolonged event from 1906 to around 1928 and a sharp peak at 1960 in %Silt. This is reflected in the mean size and skewness. Zone CM3, which spans from 1975 to 2001, depicts the most dynamic change with regards to organic carbon and carbonate. At the point 1988 (*Figure 4.5*) there is a sharp and substantial increase in %Organic, from approximately 3 % to 15 % over the span of 13 years, and %Carbonate, from approximately 1.5 % to 3.5 % over the same time span. Towards 2001 there is a slight increase in %Sand with fewer fluctuations throughout the zone. Zone CM4 spans a short time period from 2001 to 2018. There is a continued increase in organic carbon with the %Organic increasing from 15 % to 18 % and then a sharp increase at approximately 2017 to 22 %. Carbonate remains constant with small fluctuations in the grain size distribution none of which are considered significant in terms of change.

4.3.2. Major Elemental Composition

In terms of the composition of major elements in the sediments of site CM, a stratigraphic plot (*Figure 4.6*) was produced depicting the composition of selected major elements with more than 0.1 % composition. These major element stratigraphic plots were produced with the aim of identifying changes in composition percentage within the same zones as *Figure 4.5*. Comparisons could then be made as to similar changes with respect to a temporal scale. The zones depicted in *Figure 4.6* are the same zones as *Figure 4.5* as derived from the CONISS cluster method. A notable observation from *Figure 4.6* is that SiO_2 contributes the greatest composition across all sites. Of greater interest are the major element compositions of Al_2O_3, Fe_2O_3, MgO and TiO_2.

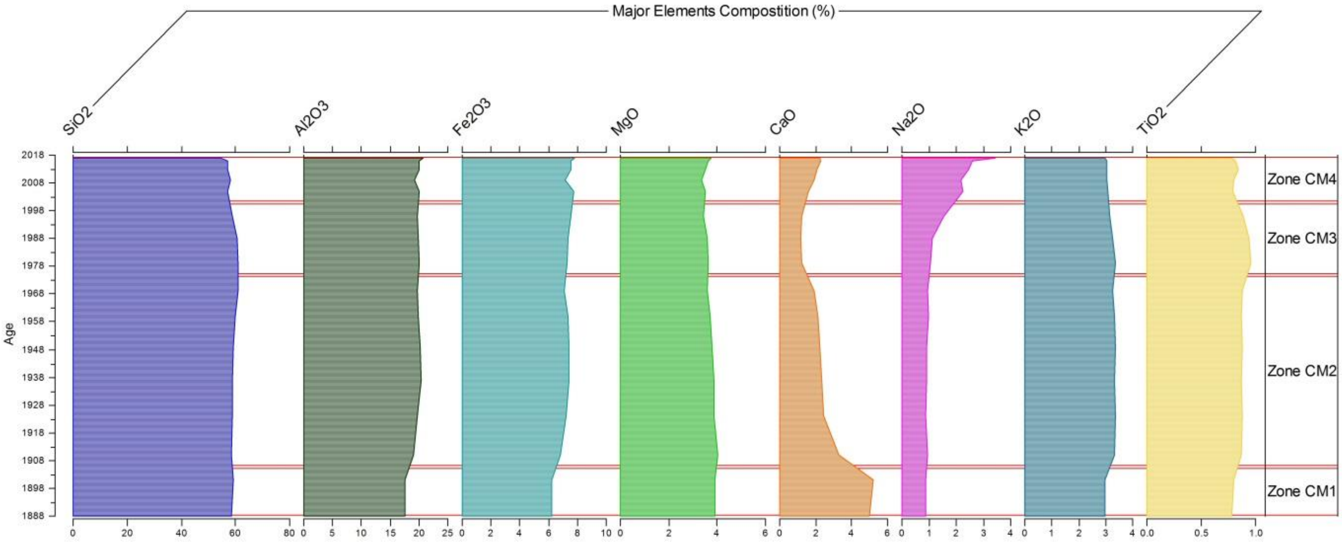


Figure 4.6: CM stratigraphic plot for major elements

Only samples from 1888 to 2018 were analysed as these related to the radioisotope dates obtained so as to maintain consistency. Therefore the zones begin from Zone CM1 where little change in composition is noted apart from CaO where there is a slight increase evident up to 1902 and then a sudden decrease going beyond Zone CM1 into Zone CM2. There are also slight increases evident in Al_2O_3 and Fe_2O_3 with Al_2O_3 increasing from 17 % to 19.5 %. Within Zone CM2 there is prolonged gentle change for most major elements with SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 all increasing slightly towards 1975. Once again, CaO shows a significant and prolonged decrease from 4 % to <2 %. Zone CM3 shows some significant change with regard to SiO_2, CaO, Na_2O and TiO_2. There is a decrease in SiO_2 composition from 60 % to 57 % over the period of 1975 to 2001. Na_2O shows a strong increase towards 2001 with an increase from 1 % to 2 %. Of greater interest in Zone CM3 are the changes between CaO and TiO^2 which observes an increase in TiO_2 initially with an inverse decrease in CaO and then a decrease in TiO_2 towards 2001 with an increase in CaO towards 2001. This fluctuation pattern between TiO_2 and CaO relates in terms of dates and represents a possible inverse relationship between these two major elements. This fluctuation between TiO_2 and CaO occurs around 1988 which is a point of interest in terms of organic carbon and carbonate (*Figure 4.5*). Zone CM1 which spans from 2001 to 2018 shows interesting fluctuations between all major elements at approximately 2008 where there is a noticeable dip in all major element compositions. Towards 2018 there is also a sharp increase in Na_2O to 3.5 %. The notable fluctuations or events within Zone CM3 and Zone CM4 are of interest and the aim is to identify and compare similar fluctuations and events across all four sites from which change can be inferenced.

4.3.3. PCA for Major Elements

The use of a principle components bi-plot for site CM assists in identifying the affinity major elements have with regard to samples and therefore zones as depicted in *Figure 4.4* and *Figure 4.5*. These aforementioned zones created through CONISS clustering are consistent with the clusters or zones apparent in the principle components bi-plot for CM major elements (*Figure 4.7*). Samples and major elements distribution are plotted against principle components 1 and 2 (*Figure 4.7*).

Zone CM1 consists of samples CM22 and CM23 located in quadrant 1 of *Figure 4.7*. Quadrants are numbered from top right and clockwise. There is a strong affiliation to CaO in this zone. Quadrant 3 therefore has very low or weak affiliation to CaO. Zone CM1 consists of samples with a strong positive principle components score of around 0.7 in PC1. Zone CM2 consists of samples in quadrant 2 which have a positive principle components score of between 0.1 and 0.4 in PC1 but negative in PC2. Zone CM2 has a strong affiliation to SiO_2 as all these samples are grouped together around SiO_2 in *Figure 4.7* except for sample CM21 which is more affiliated to MgO. Zone CM3 consists of samples located within quadrant 3 which have a negative principle components score of around -0.3 in PC1. This zone is affiliated to a variety of major elements but none that are strongly related to the samples within this zone. Al_2O_3 and TiO_2 dominate quadrant 3 and therefore hold some influence on Zone CM3. Zone CM4 dominates quadrant 4, with a negative PC1 score and a positive PC2 score. Quadrant 4 is dominated by Na_2O which therefore has a strong affiliation to Zone CM4. This strong affiliation of Na_2O to Zone CM4 relates to *Figure 4.6* showing a sudden increase in composition towards the surface sample CM0.

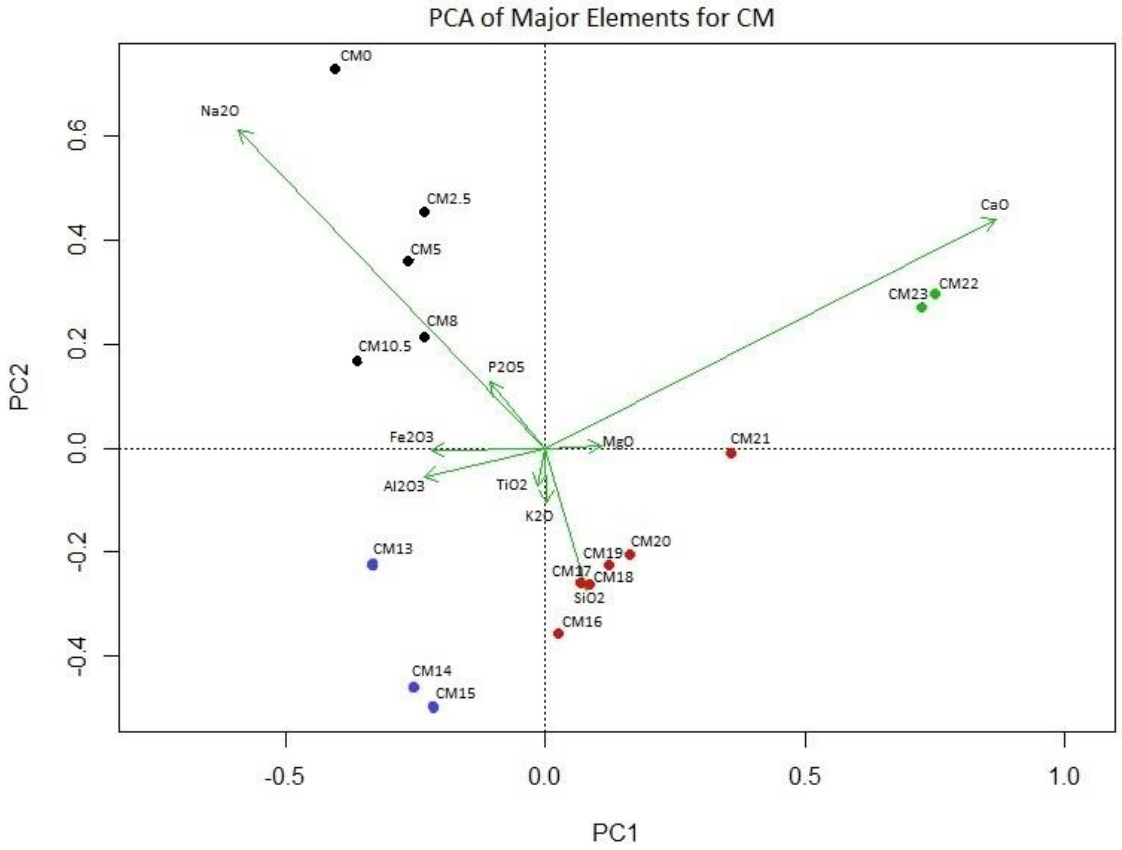


Figure 4.7: PCA of CM major elements

The observed affiliations between particular major elements and zones derived by clusters of samples show some relation to compositional changes in zones from *Figure 4.6*. These relationships will be compared to the other three sites of TPE, MDM and HBP.

4.4. Site TPE

4.4.1. Sediment Properties

The sediment properties for site TPE were identified with respect to depth (cm) unlike site CM where they were identified with respect to age. Therefore a visual correlation for obtaining dates was conducted in *4.2.3. Radiometric Dates Correlation to other Sites*. The sediment accumulation rate of approximately 1cm every 10 years was used to obtain the approximate date relating to points of interest within zones. Therefore the 10 cm record represented in *Figure 4.8* spans back from 2018 for approximately 100 years. The zones in *Figure 4.8* comprise of the following dates. Zone TPE1 spans from 1918 to 1923, Zone TPE2 spans from 1923 to 1978 and Zone TPE3 spans from 1978 to 2018. The point of interest from site CM in *4.3.1. Sediment Properties* of 1988 was calculated to be at 3 cm for site TPE in *Figure 4.8*.

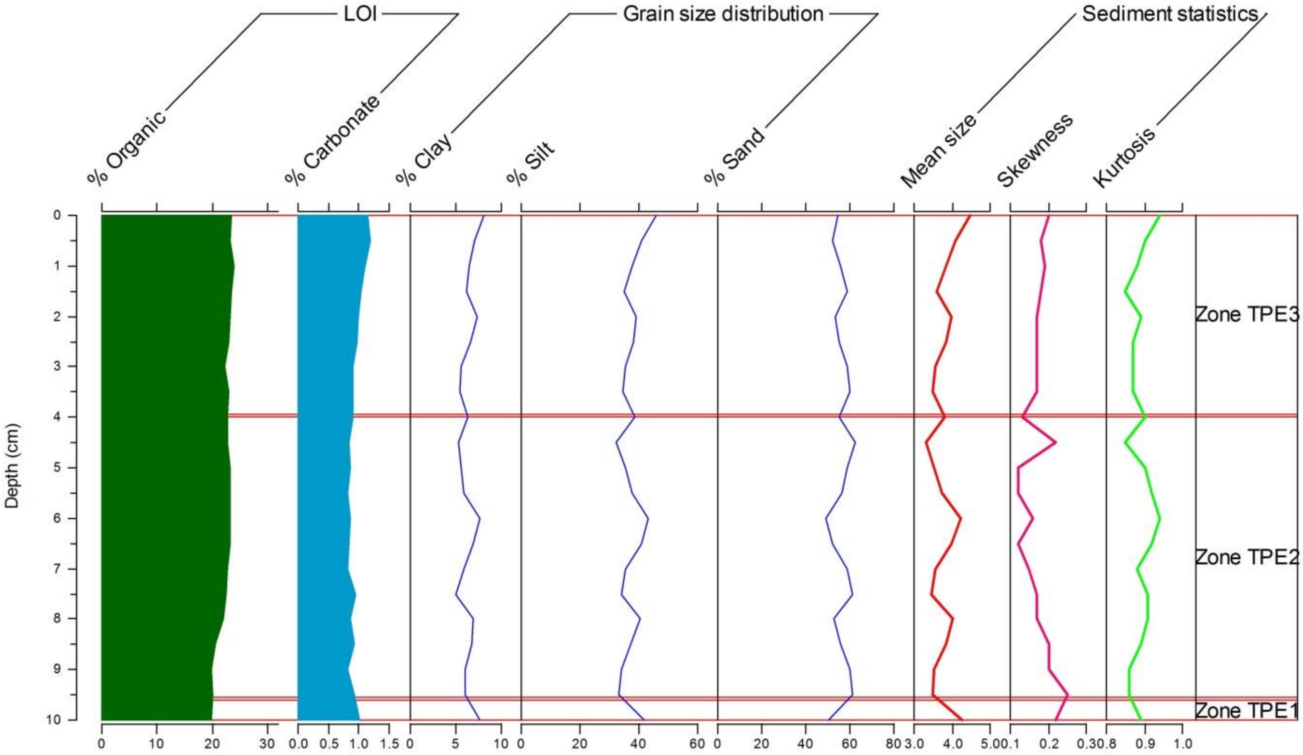


Figure 4.8: TPE stratigraphic plot for LOI and grain size distribution

Zone TPE1 (*Figure 4.8*) spans a short time period of approximately 5 years. There is very little change within this zone with the major interest being the slight decrease in carbonate and the increase in the composition of bigger sand grains to approximately 60 %. Zone TPE2 (*Figure 4.8*) spans a longer time period of approximately 54 years. There is once again little change in %Organic and %Carbonate with organic carbon content ranging between 20 % and 22 % with a slight increase at around 1938. There are multiple peaks in increased grain size composition with points of interest and possible events at approximately 1923, 1943 and 1973 where there is an increase in %Sand. These events are corroborated in mean size, skewness and kurtosis. Zone TPE3 (*Figure 4.8*) spans a period of approximately 40 years. Once again there is little fluctuation evident during this period with %Carbonate showing a slight increase towards 2018. Changes in both %Organic and %Carbonate show small percentages of change over a longer period of time but there are no events evident. It must be noted that %Organic in TPE

(*Figure 4.8*) is much higher than that in CM (*Figure 4.5*) with %Carbonate in TPE being less than that in CM. There are no significant events or points of interest in Zone TPE3 with regard to grain size distribution, only small fluctuations are evident.

4.4.2. Major Elemental Composition

The stratigraphic plots for the composition of major elements in the sediments of site TPE are shown in *Figure 4.9* and represent the changes in composition over time. The time scale for *Figure 4.9* correlates to the depth (cm) on the y-axis having been calculated in *4.2.3. Radiometric Dates Correlation to other Sites*. The zones in *Figure 4.9* represent the same zones as presented in *4.4.1. Sediment Properties*. As can be seen in *Figure 4.9*, there is little fluctuation in most of the major elements presented. However there are gradual changes which occur over the approximated 100 year time span.

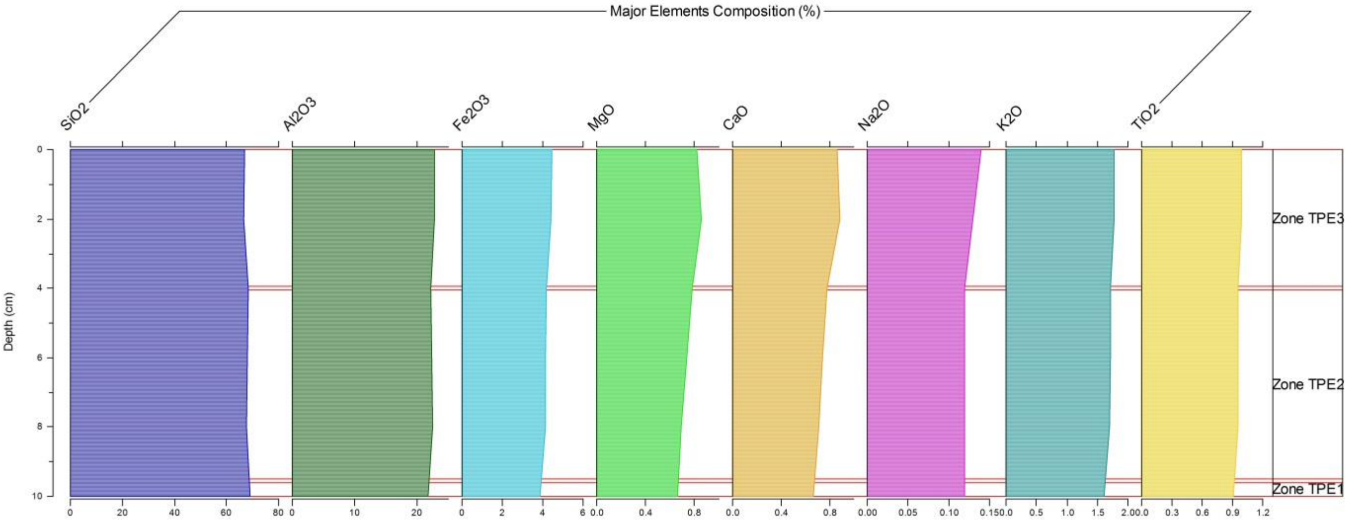


Figure 4.9: TPE stratigraphic plot for major elements

Zone TPE1 is once again a small zone only spanning 5 years and shows very little change over time with regard to major elemental compositions. Zone TPE2 shows prolonged change over time with Al_2O_3, Fe_2O_3, MgO, CaO and K_2O showing increases while SiO_2 represents a slight decline. MgO and CaO only represent changes of between 0.1 % and 0.2 % which shows a substantial increase when considering that their average composition is <0.5 % and <0.8 % respectively. Zone TPE3 represents more dynamic changes in compositions with increases in all major elements apart from SiO_2 which represents a slight decline. Once again MgO and CaO show increases of between 0.1 % and 0.2 % and have a peak at approximately

1998. There are apparent differences in percentage composition of major elements between sites TPE and CM. The compositions of major elements in TPE are generally less than CM apart from SiO_2 and Al_2O_3 which show greater percentage composition than in CM.

4.4.3. PCA for Major Elements

The clustering of samples into like groups through CONISS as represented by the zones in *Figure 4.8* and *Figure 4.9* is consistent with the clustering in the principle components bi-plot depicted in *Figure 4.10*. Through the low number of samples of 6, which is small compared to the other three sites, the clusters are not as well defined as the other sites. This is evident with respect to Zone TPE2 (samples TPE4, TPE6 and TPE8) which spans across PC2 ranging in scores from 0.4 to -0.2. This zone is therefore not well clustered as the samples are barely affiliated to various major elements such as Chromium in quadrant 4 which was excluded due to its composition being less than 0.01 %.

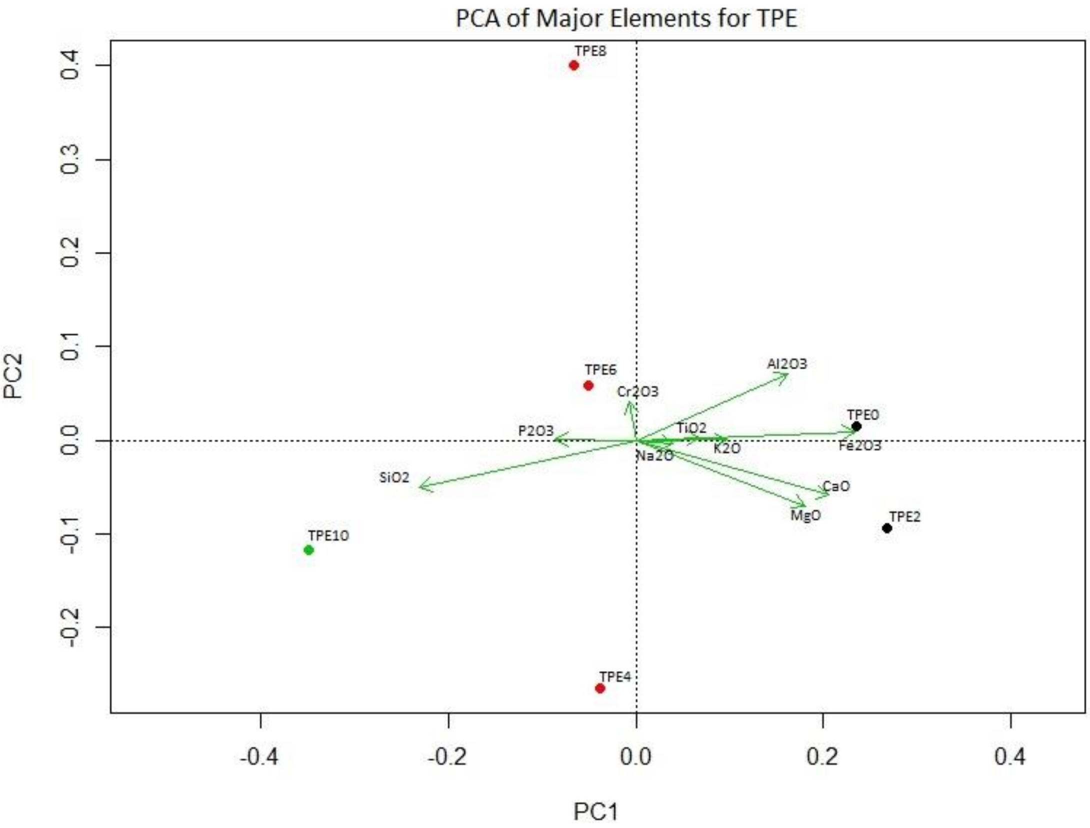


Figure 4.10: PCA of TPE major elements

The zones of Zone TPE1 and Zone TPE3 represent stronger clustering within each zone and their samples show a stronger affiliation to particular major elements. Zone TPE1 as represented by sample TPE10 has a strong affinity to SiO_2 in quadrant 3 with negative PC1 and PC2 scores. It also has a very weak affinity to Al_2O_3 in quadrant 1. Zone TPE3 is spread across quadrant 1 and 2 with sample TPE0 having a very strong affinity to Fe_2O_3 with positive PC1 and PC2 scores while sample TPE2 has an equal affinity to MgO and CaO with a positive PC1 score and negative PC2 score. The strong but equal affinity of sample TPE2 to MgO and CaO relates to the point of interest at 1988 (*Figure 4.9*) at which both major elements peaked.

4.5. Site MDM

4.5.1. Sediment Properties

Like site TPE, site MDM had no ^{210}Pb dates available and therefore a visual correlation of depth to CM dates was used in order to obtain approximate dates. The sediment accumulation rate for MDM was calculated to be an accumulation of 1 cm approximately every 7 years. Therefore the 21 cm record represents 147 years of a sediment record. The zones presented in *Figure 4.11* span the following dates. Zone MDM0 spans from 1871 to 1878, Zone MDM1 spans from 1878 to 1976 and Zone MDM2 spans from 1976 to 2018. The point of interest across all sites of 1988 is represented at approximately 4.3 cm in depth in *Figure 4.11*.

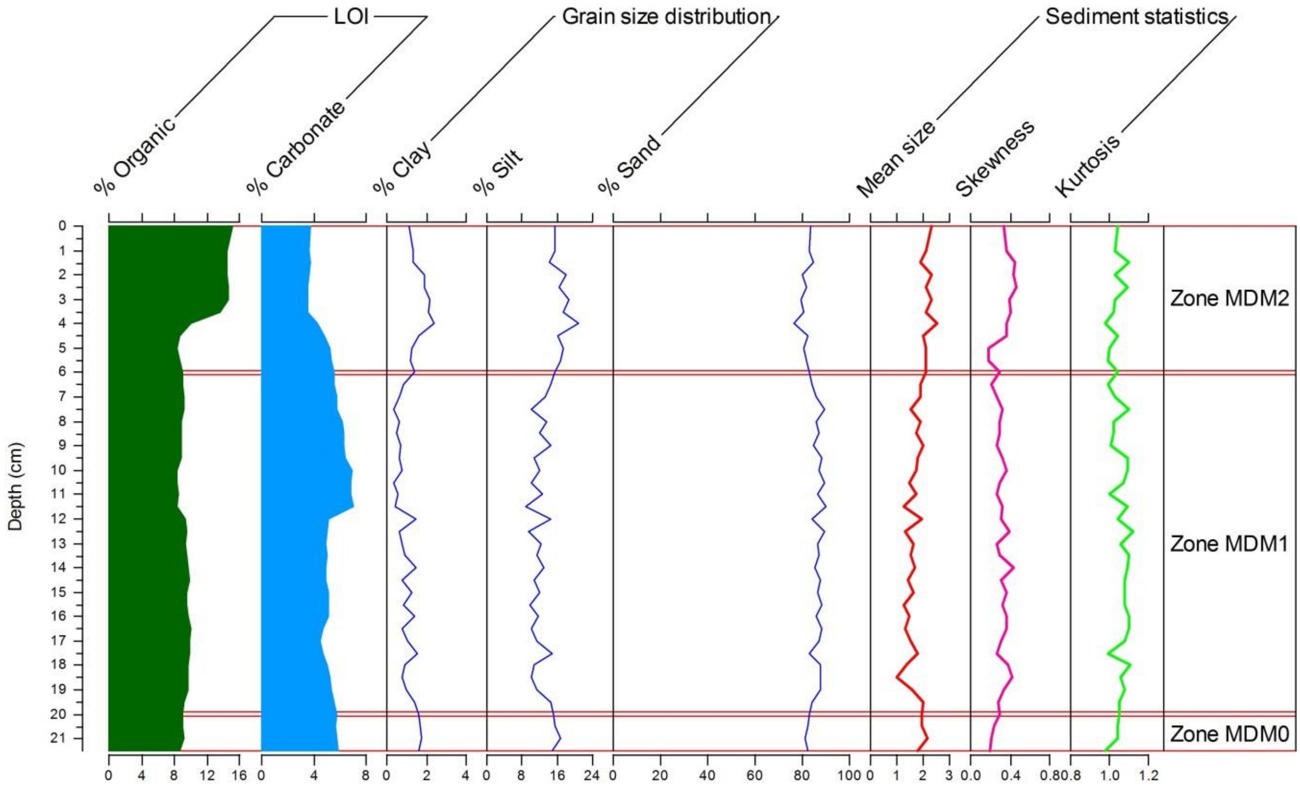


Figure 4.11: MDM stratigraphic plot for LOI and grain size distribution

Zone MDM0 is a small zone spanning approximately 7 years in which there is little change with only a slight decrease in %Carbonate by approximately 0.5 %. Zone MDM1 represents a zone spanning approximately 98 years and shows multiple fluctuations in both LOI data and grain size distributions. There is little change in %Organics while %Carbonate decreases slightly from 1878 and then increases gently until approximately 1934 where there is a sharp substantial increase by 2 %. There is then a gentle decrease after approximately 1948 from 8 % to 5 % at 1976. Grain size distribution fluctuates throughout Zone MDM1 with notable points of interest at 18 cm (1892) and 12 cm (1934) where %Clay and %Silt increases sharply. The point of interest at 12 cm (1934) relates to the sharp increase in carbonate content. Zone MDM2 represents the 1988 point of interest across all four sites despite the multiple fluctuations throughout this zone. At 1988, or approximately 4.3 cm in depth, there is a sharp increase in %Organic. At the point 4.3 cm, there is also a gradual decline in %Carbonate with substantial peaks in %Clay and %Silt while representing a dip in %Sand. After this point at 1988, there is a stabilisation in these sediment properties through to 2018 or 0 cm.

4.5.2. *Major Elemental Composition*

The major elemental composition for MDM was calculated to have only two zones as obtained from cluster analysis using CONISS. The Zone MDM0 (*Figure 4.11*) was beyond the scope of major element samples as data was only obtained up to 20 cm in depth. Therefore only Zone MDM1 and Zone MDM2 were presented in *Figure 4.12*. The dates attributed to Zone MDM1 and Zone MDM2 (*Figure 4.12*) are the same as the zones Zone MDM1 and Zone MDM2 in *Figure 4.11*. The composition of major elements for site MDM was more closely related to site CM (*Figure 4.6*). There are more abrupt fluctuations apparent than those of site TPE (*Figure 4.9*).

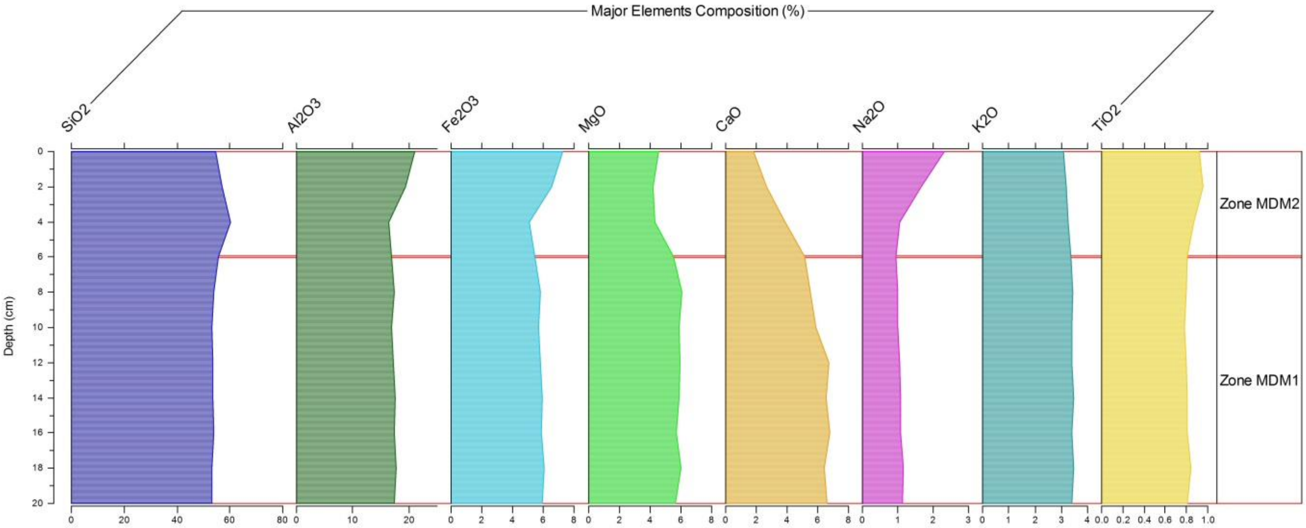


Figure 4.12: MDM stratigraphic plot for major elements

Zone MDM1 spans the period 1878 to 1976 and represents little change over a long time period of approximately 98 years. There is however evident change in CaO which increases slightly towards 12 cm (1934) and thereafter decreases substantially by 2 % from 7 % to 5 %. Zone MDM2 shows a more dynamic pattern of change with, most notably, a point of interest at around 4 cm which correlates to approximately 1988. At this point, there is a peak in SiO_2 of 60 %, a dip in Al_2O_3, Fe_2O_3 and MgO, and there is a point of change where both Na_2O and TiO_2 begin to notably increase. CaO has a sharp decrease throughout Zone MDM2 from 1976. After 1988 there are increases in Al_2O_3, Fe_2O_3 and MgO with a decrease in SiO_2. Zone MDM2 is the best example of how major elements may relate to the 1988 point of interest.

4.5.3. *PCA for Major Elements*

The zones represented in *Figure 4.11* and *Figure 4.12* created through the use of CONISS are consistent with the clustering of samples in the principle components bi-plot presented in *Figure 4.13*. A total of two cluster groups were calculated. Zone MDM1 (represented by the samples in red in *Figure 4.13*) represented a good clustering of samples while Zone MDM2 (Samples MDM0, MDM2 and MDM4) represents a wide spread across PC1 and PC2. The samples MDM4 and MDM2 are wide spread with little affiliation to any major element while MDM0 has a stronger affinity towards Al_2O_3, Na_2O and Fe_2O_3 which relates to the observations made in Zone MDM2 (*Figure 4.12*). Zone MDM1 is clustered mainly in quadrant 3 showing samples such as MDM12, MDM16, MDM14 and MDM20 have a very strong affinity to MgO. Sample MDM10 has an affinity to CaO and this relates to observations made in Zone MDM1 about CaO and its gradual decrease after 12 cm in depth.

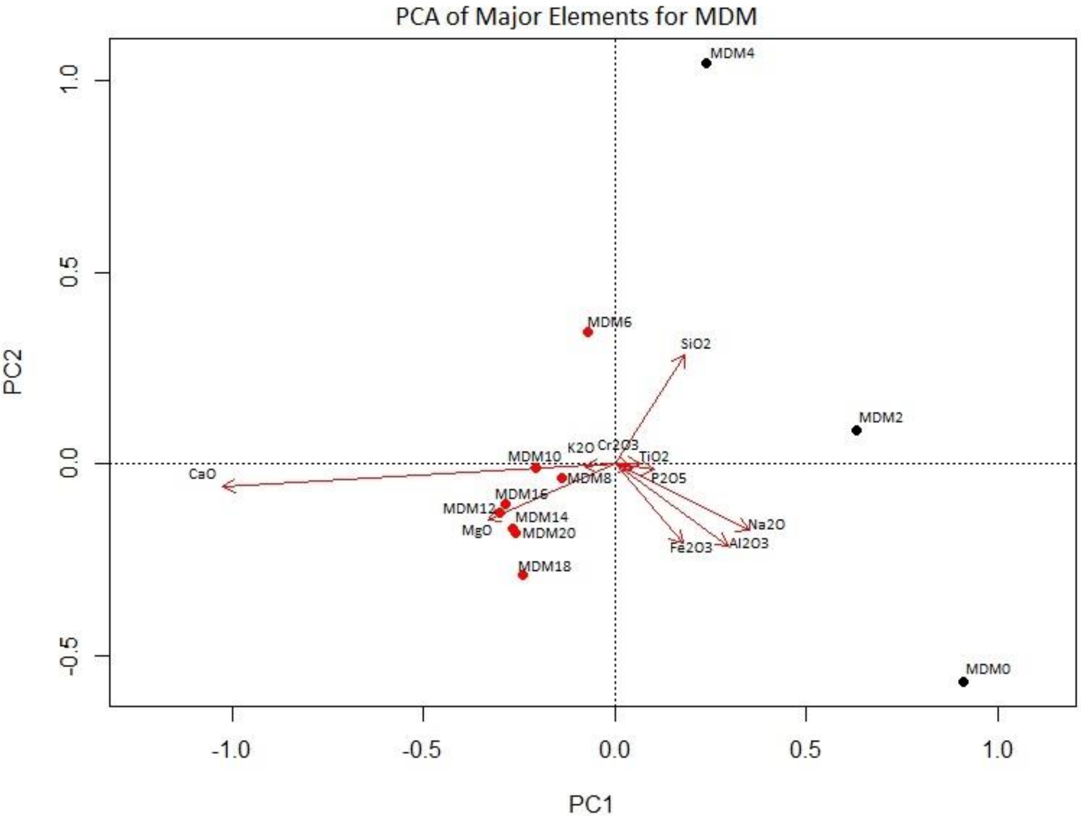


Figure 4.13: PCA of MDM major elements

4.6. Site HBP

4.6.1. Sediment Properties

Once again, no radiometric dates were available for site HBP and therefore a visual correlation was made between radiometric dates for site CM and depth points for site HBP. The sediment accumulation rate for site HBP was calculated to be approximately 1 cm accumulation every 5 years and therefore represents an approximately 65 year sediment record. The zone presented in *Figure 4.14* span the following dates. Zone HBP0 spans from 1953 to 1958, Zone HBP1 spans from 1958 to 1998 and Zone HBP2 spans from 1998 to 2018. The point of interest of 1988 is correlated to approximately 6 cm in depth on the y-axis of *Figure 4.14*. There are evident fluctuations across the zones although Zone HBP0 shows very little change over the period of 5 years. There is however some fluctuation evident in terms of grain size distribution with fluctuations presented at every 2 years across the zone. The time period is too small for any notable changes in sediment grain size but could indicate seasonal variations. The regular fluctuations of sediment grain size are evident across the sediment record although the time interval is not constant.

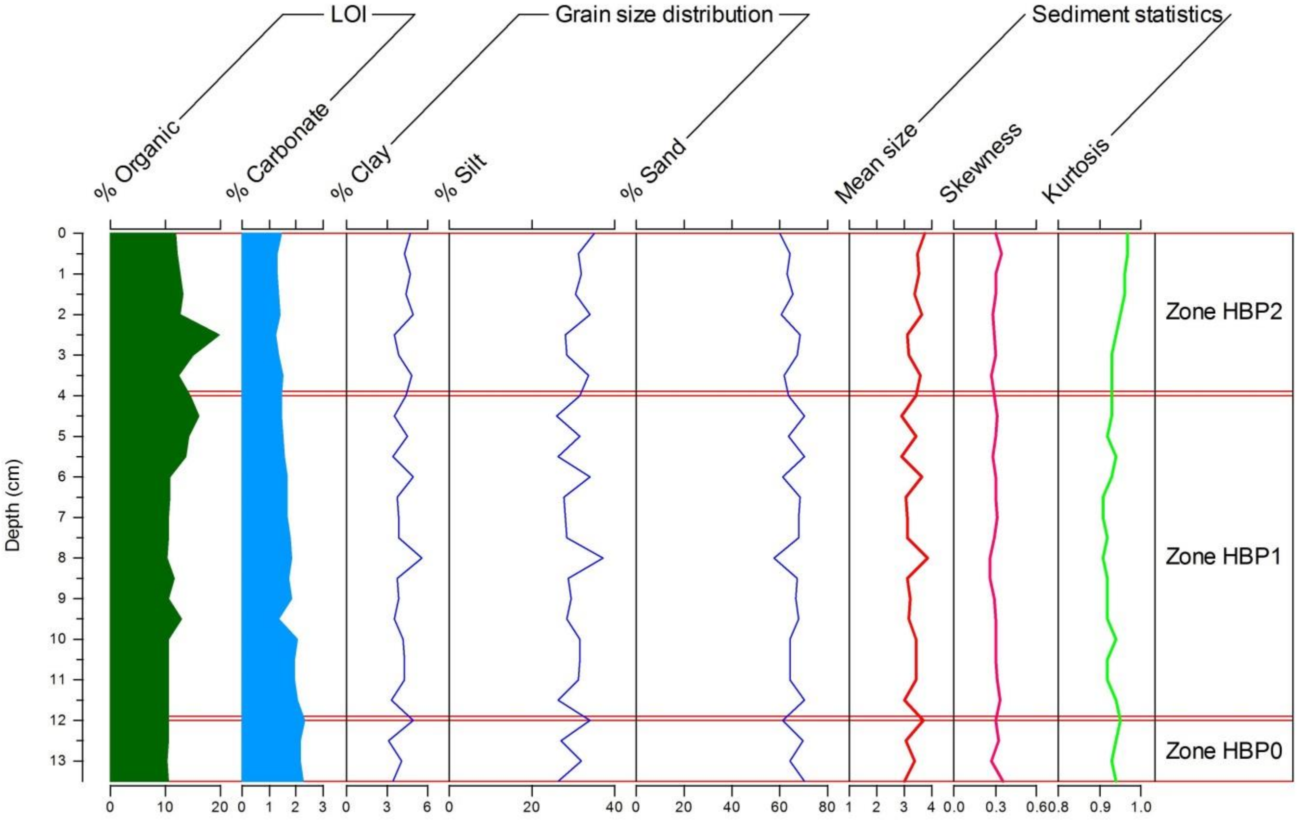


Figure 4.14: HBP stratigraphic plot for LOI and grain size distribution

Zone HBP1 represents a span of approximately 40 years in which there are multiple fluctuations with regard to both LOI data and sediment grain size data. There is a noticeable peak in %Organic with a dip in %Carbonate at 9.5 cm (1970). The %Organic increases at 6 cm (1988) from 10 % to 15 % strengthening the appeal of 1988 as a point of interest across all four sites. Although there are multiple fluctuations in sediment grain size throughout Zone HBP1, at 8 cm (1978) there is a substantial peak in %Clay and %Silt with a dip in %Sand showing that there are more smaller grains present. Zone HBP2 is once again a fairly dynamic zone as it is near the surface and has more recent sediment in its composition. There is a slight decrease in %Carbonate with a sharp and substantial peak in %Organic at 2.5 cm (2006) of almost 10 %. It is also observed at this point of 2.5 cm that there is an increase in %Sand with a decrease in %Clay and %Silt representing a composition of larger sediment grains.

4.6.2. Major Elemental Composition

The composition of major elements for site HBP (*Figure 4.15*) was split into two zones as determined through cluster analysis using CONISS. Zone HBP0 (*Figure 4.14*) was excluded as it was beyond the scope of the samples analysed for major elements as the samples only reached 12 cm in depth. The dates for the samples and zones are the same as those presented in *4.6.1. Sediment Properties*. The composition of major elements in *Figure 4.15* show commonalities with all three sites however the level of change or fluctuations is more similar to site TPE. There are very few changes that occur throughout Zone HBP1 as most of the major elements remain fairly constant with composition levels similar to site TPE. There are however slight decreases in CaO and Na_2O approaching 4 cm or 1998. The point at which both CaO and Na_2O begin to decrease is approximately 6 cm or 1988.

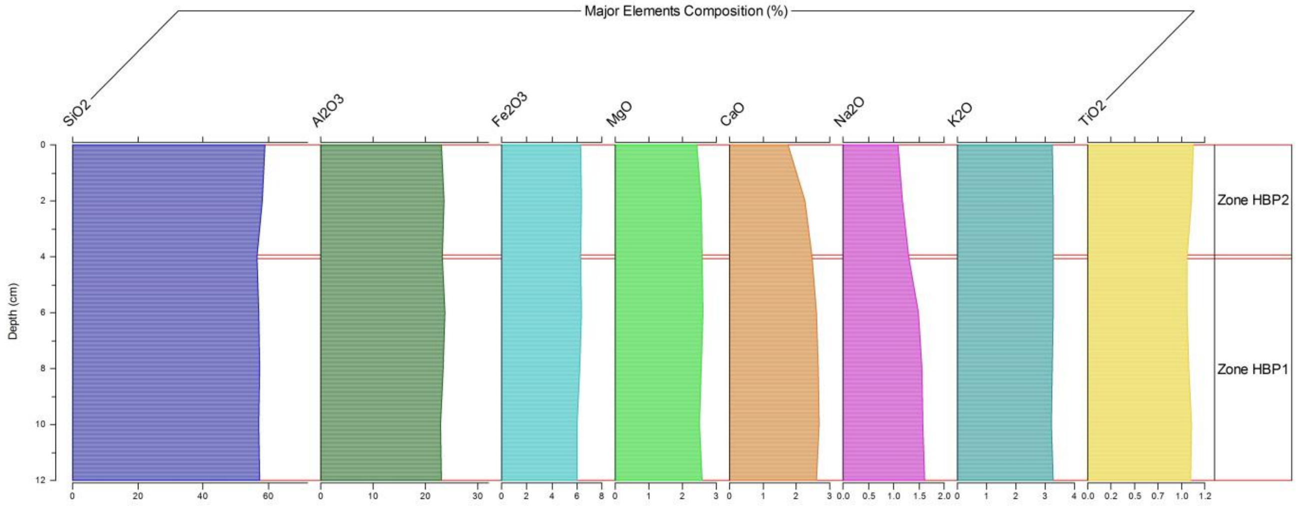


Figure 4.15: HBP stratigraphic plot for major elements

Zone HBP2 represents little variation in the major elements which compose more of the sediments but does show change with respect to CaO and Na_2O. Both CaO and Na^{2}O continue a decreasing trend from 4 cm (1998) through to 0 cm (2018). There is a slight increase in SiO_2 and in TiO_2 towards 2018.

4.6.3. PCA for Major Elements

The zones presented in *Figure 4.15* were determined through the clustering method CONISS and are consistent with the clustered sample points of the principle components bi-plot presented in *Figure 4.16*. Two zones were determined using clustering. Both Zone HBP1 (the samples in red in *Figure 4.16*) and Zone HBP2 (The samples in black in *Figure 4.16*) show very weak clustering meaning that individual samples have affiliations to separate major elements. The samples comprising Zone HBP1 are confined to quadrant 3 and 4 with sample HBP8 representing a strong affinity to Na_2O. Samples HBP10 and HBP12 have sufficient affiliation with Na_2O while HBP6 and HBP4 are affiliated to MgO and Al_2O_3. These affiliations do not sufficiently aid in explaining the observations made in *4.6.2. Major Elemental Composition*.

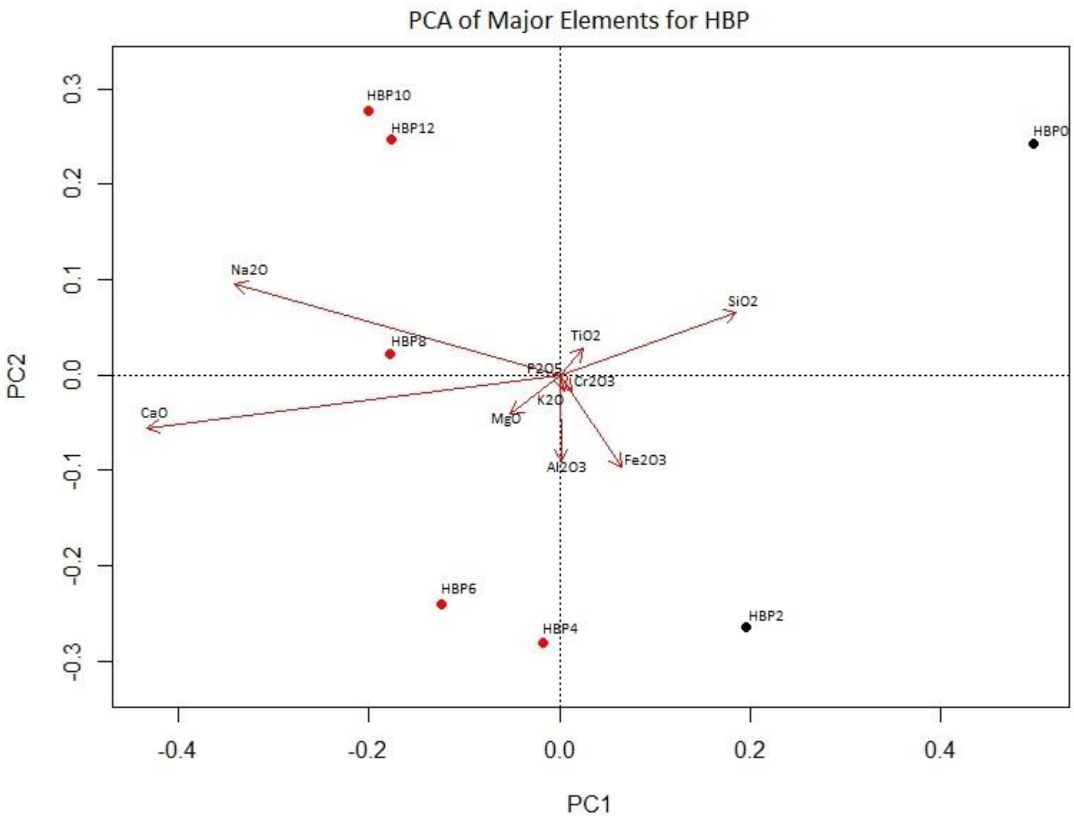


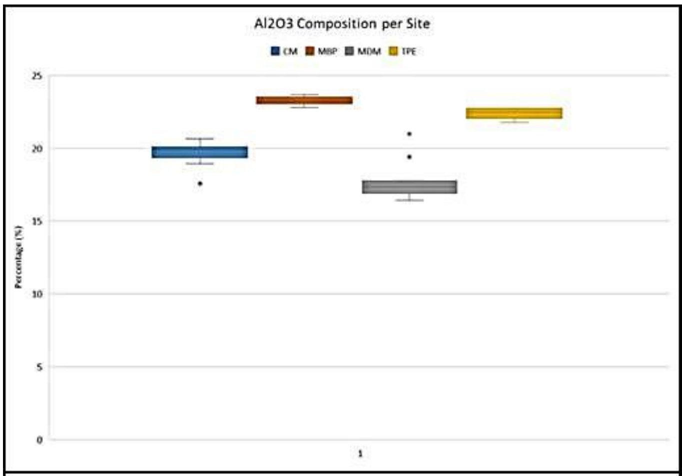
Figure 4.16: PCA for HBP major elements

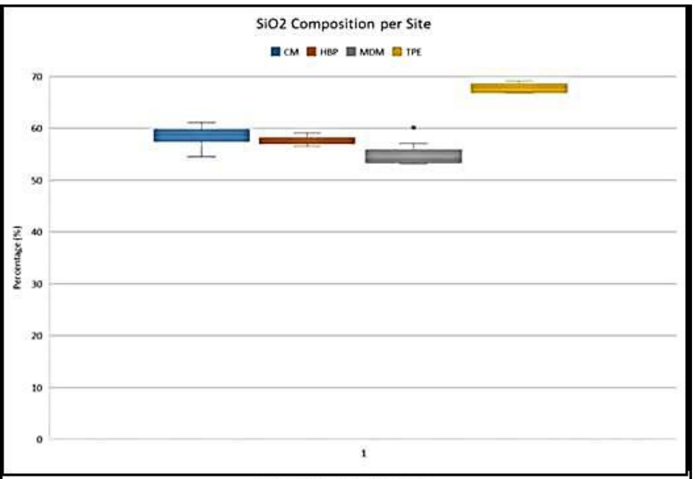
Zone HBP2, which comprises of samples HBP0 and HBP2, shows a weak clustering within one quadrant as the samples are split over quadrant 1 and 2. Sample HBP0 has a fairly strong affinity to SiO_2 which aids in explaining the increase in SiO_2 composition up to 2018. Sample HBP0 also has a very weak affiliation to both CaO and Na_2O. Sample HBP2 has a strong affinity to Fe_2O_3 in quadrant 2. There is very little aid given by *Figure 4.16* as to explaining the relationships that samples and therefore depth points have to particular changes in major element compositions.

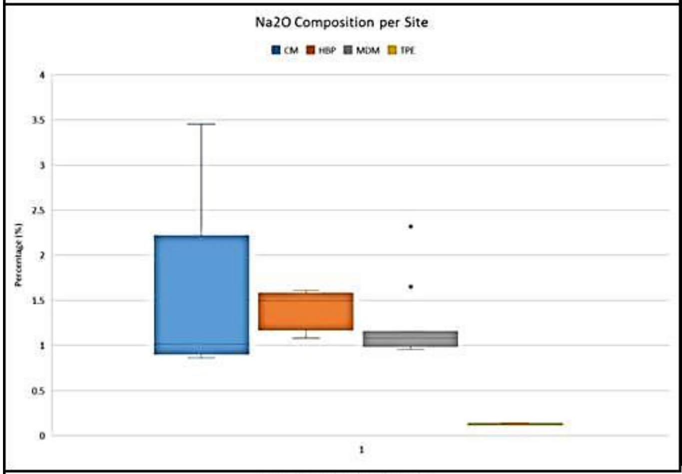
4.7. Regional Synthesis

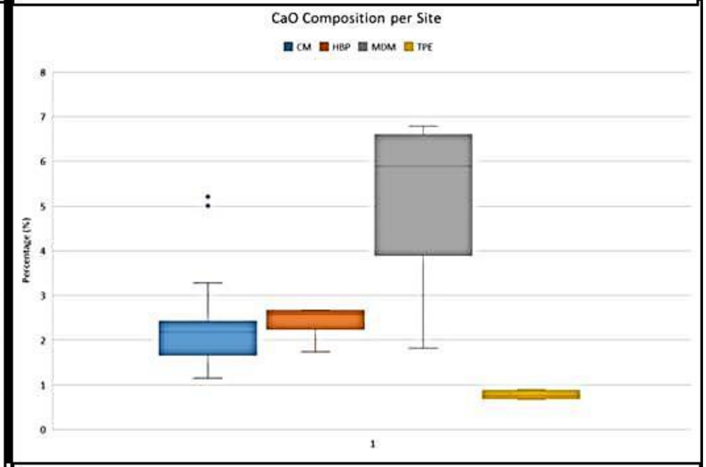
A regional synthesis is presented here concerning the comparisons between sites which provides a better understanding of the relationships between sites and therefore in the region as a whole. All four sites have similarities and differences but it is those similarities that could possibly provide a better understanding of the area as a whole.

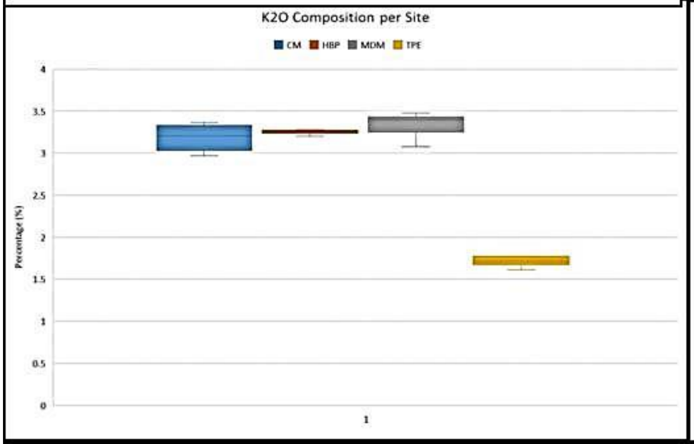
The composition of major elements per site is a good indicator for observing and understanding the differences between sites and therefore pans. There are very evident differences between sites when considering the composition of major elements. These are presented in *Figure 4.17* which compares the averages of selected major elements between sites. Sites HBP and TPE have the highest concentration of Al_2O_3 out of any sites by approximately 3 %. Site TPE also has the highest level of SiO_2 composition by approximately 8 % over site CM. For major elements such as Na_2O, CaO, Fe_2O_3 and MgO, site TPE has the lowest concentrations compared to the other three sites. Site MDM has a higher concentration of CaO and MgO than the other three sites by at least by 3 % and 1.5 % respectively. Site CM has the highest Fe_2O_3 concentration compared to the other three sites by at least 1 %. For the majority of major elements in *Figure 4.17* there is a clear similarity between the sites of CM, MDM and HBP. These include SiO_2, Na_2O, Fe_2O_3, MgO and CaO. This possibly represents a link or relationship between these three sites and therefore pans as they maintain very similar major element characteristics. This could be caused by similarities in sediment sources surrounding the pans.

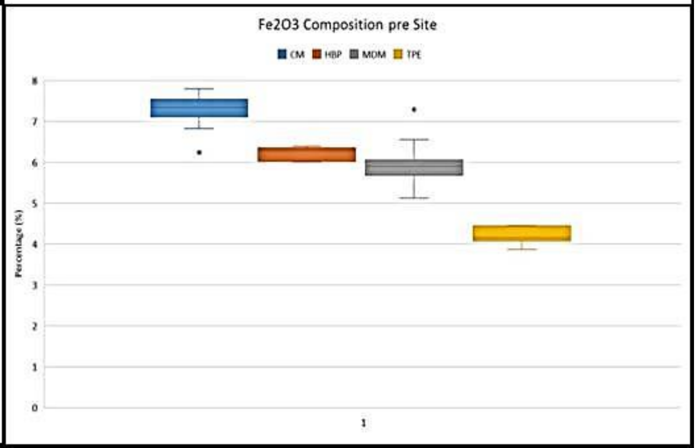

Al2O3 Composition per Site
CM
MBP
MDM
TPE
Percentage (%)
0
5
10
15
20
25
1


SiO2 Composition per Site
CM
HBP
MDM
TPE
Percentage (%)
0
10
20
30
40
50
60
70
1


Na2O Composition per Site
CM
HBP
MDM
TPE
Percentage (%)
0
0.5
1
1.5
2
2.5
3
3.5
4
1


CaO Composition per Site
CM
HBP
MDM
TPE
Percentage (%)
0
1
2
3
4
5
6
7
8
1


K2O Composition per Site
CM
HBP
MDM
TPE
Percentage (%)
0
0.5
1
1.5
2
2.5
3
3.5
4
1


Fe2O3 Composition pre Site
CM
HBP
MDM
TPE
Percentage (%)
0
1
2
3
4
5
6
7
8
1

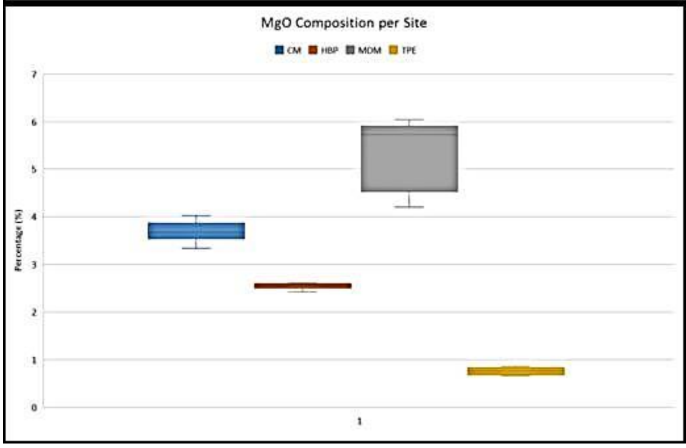

MgO Composition per Site
CM
HBP
MDM
TPE
Percentage (%)
0
1
2
3
4
5
6
7
1

Figure 4.17: Averages of selected major elemental compositions between all four sites.

More linkages can be made between the sites when considering the points of interest or events identified throughout the sediment and major element analysis. Such events or interest points include the changes that occurred in approximately 1988 where sites CM, MDM and HBP showed substantial increases in organic carbon content and decreases in carbonate content. Site TPE however showed a slight dip in organic carbon content at this same time period. Another commonality between sites CM, MDM and HBP in 1988 was a noticeable decrease in sediment grains classified as sand grains with increases in clay and silt grains. The event identified at 1988 has observed changes across all four sites and therefore should have regional implications. This relates to events of drought and rainfall as this would impact all sites at the same time period. The similarities in bathymetry between sites could aid in understanding sediment dynamics across the region. The bathymetry between CM and MDM shares similarities in terms of depth and possibly shape even though there is a large size variance. The bathymetry between sites could also aid in differentiating pans such as site CM and TPE where there is a substantial depth and size variance. By linking sediment and major elements results with bathymetric results, a better understanding can be made as to the regional relationship between the pans in the MLD.

5. Discussion

5.1. Introduction

The aim of this study was to determine whether the use of proxies such as sediment properties and major elements could show any environmental or climatic changes in the natural fresh water pans of the Mpumalanga Lake District as well as if it could be determined to what extent anthropogenic influence is evident. This was assessed through the sediment record adopting a palaeolimnological approach. A thorough attempt to achieve the research objectives (**1.2 Aims & Objectives**) concerning the physical characteristics of the pans and environmental, climatic and anthropogenic influences on the pans will be made throughout the discussion chapter.

With the aid of a knowledge base in the literature review (**2. Literature Review**), an attempt will be made as to bridge any research gaps that have emerged. Through the use of bathymetry results, sediment characteristics and major elements results, a discussion will be presented with the aim of achieving the research objectives. This discussion will include an analysis of the presence of the pans of the MLD, inferences determined through the use of sediment and major elements results, and an attempt to determine environmental and climatic change. After which a discussion will be presented in which a regional synthesis will be presented with an attempt to understand the anthropogenic influence on the MLD.

5.2. Mpumalanga Lake District

5.2.1. The Lake Chrissie Problem

The Lake Chrissie problem is largely based on the study conducted by Wellington (1943) which seeks to determine why pans occur in the Mpumalanga Lake District and to understand their characteristics and functioning as pans. A major aim concerning this research project was to better understand the physical characteristics of the pans in the MLD. This aim builds upon the problems outlined by Wellington (1943) by taking a new approach in understanding these pans through the application of bathymetric analysis as well as sediment properties.

Pans in the global and general sense are found within dry arid regions (Goudie and Thomas, 1985; Goudie and Wells, 1995). This however is not the case when considering the pans of the MLD as the area is more temperate with a mean annual rainfall of approximately 900 mm (Schulze, 1997). This only places greater interest in the MLD region as the presence of pans here is very uncommon in the global sense. Although the originating occurrence of these pans in the MLD is difficult to determine, a better understanding can be made as to their characteristics and physical functioning. Wellington (1943) proposed that these pans were once part of a larger river system and were once joined in surface channel flow. This may very well be the case as there is evidence of low lying areas in the generally level topography between certain pans such as between the sites of HBP and MDM. This linkage was previously possible as HBP was located at a higher elevation (1671 m.asl) than MDM (1667 m.asl). Unfortunately this evidence is disappearing with more and more anthropogenic influence in the form of roads, farmlands and farm barriers. These pans are therefore not continuously connected currently and only through intense precipitation events could they form surface flow connections. One of the ways in which any possible linkages between pans can be identified was through examining any physiochemical characteristics in common. A similar approach was taken by Russell (2008) although through the use of hydrochemical characteristics such as salinity. It was determined that the differences between the pans outweighed the similarities and that therefore these possible linkages were not necessarily true. These differences between the pans are evident through many characteristics, not only physical morphology based. This promotes the uniqueness of the pans given their close proximity.

The majority of the pans located within the MLD have an elongated shape generally elongated from North to South. This is visually evident through an overview of the pans such as in *Figure 3.1* and *Figure 3.5*. This elongation was also identified by Wellington (1943) who attributed these shapes to two major factors which were the occurrence of sandstone and dolerite geological compositions and the strong prevailing North-westerly winds during winter months. This is true for the MLD as wind patterns across the region follow an Easterly direction in the summer months and a North-westerly direction in the winter months when wind speeds are the highest and most constant (Tyson *et al*., 1988). Strong and constant winds have strong influence in shaping shallow pans with large areas such as Chrissiesmeer (site CM) (Wellington, 1943; Goudie and Wells, 1995). The wind drives wave action and therefore the movement of sediments which build up in the form of lunettes or sandy deposits on the opposite shoreline to the direction from which the wind is blown from (Goudie and Wells, 1995). The wind action is more influential during the winter months as this is a drier period resulting in a decrease in the water table level and therefore the water level in the pans are lower exposing more shallow sediments causing a stronger erosive behaviour. Wind action also has the ability to remove or transport precipitated mineral deposits brought about by extended drier conditions (Russell, 2008). This could be linked to a process of refreshing of the pans where precipitated solutes are removed. A similar process could be brought about by intense rainfall events which would flush the solute concentration from the pans. Therefore the characteristics of these pans in terms of shape are down to wind direction and strength as well as underlying geology and geomorphology which vary in composition across the region. Although this may aid in understanding the physical characteristics of these pans, in order to obtain a more conclusive understanding, a bathymetric approach is considered.

5.2.2. Bathymetry of Mpumalanga Lake District Pans

The use of a bathymetric approach to understanding the physical characteristics of the pans in the MLD is made here. The sizes of the pans across the MLD vary greatly in terms of size and depth with variations in limnology as well. The research previously conducted on the pans of the MLD focussed on various physical and ecological aspects at the surface and the adjacent landscape (Hutchinson *et al*., 1932; Wellington, 1943; De Klerk *et al*., 2012; Ferreira *et al*. 2012; Foster *et al*., 2015). To this point there has been no research conducted on the pans of the MLD which is concerned with a bathymetric analysis to determine the physical characteristics of these pans.

A bathymetric approach highlights the differences between the selected pans in terms of physical characteristics with Chrissiesmeer being identified as the largest pan within the MLD and one of the largest pans in South Africa which correlates to findings by Wellington (1943). There is a vast difference in size between Chrissiesmeer and the other selected study site pans. It was determined that Chrissiesmeer covered an approximate area of 9.59 km^2 while Magdalenasmeer only covered an area of 1.76 km^2. This highlights the difference in pan sizes and this variation can be identified across a range of pans in the MLD (*Figure 3.5*). The depth of these pans also varies with some being very shallow, such as Hendrik Beukes Pan with its deepest point at only 0.4 m deep, and some pans being substantially deeper, such as Tweelingspan East with its deepest point at approximately 2.4 m. The range of different pan types such as open, salt, grass and reed pans in the MLD could suggest substantial variations in the depth of pans however only through bathymetric analysis can depth variations be accurately understood.

Another physical characteristic explored is the characteristics of the bottom of the pans as this was assumed to vary between types of pans. Through bathymetric analysis, an understanding can be made as to the bottom characteristics such as gradient of slope and bottom sediment characteristics. It was observed that Magdalenasmeer had gentle then sharp gradient decrease from the shoreline leading to a flat bottom comprised of thick sediment deposits and sandstone beds which protrude around the edges of the pan. This was the assumed common form of the pans on the MLD however Tweelingspan East proved otherwise as it presented a steep gradient immediately from the shoreline with the bottom comprising of more silt and clay like sediments. Chrissiesmeer also presented a variety of gradients and bottom characteristics although overall it seems to follow the assumed common pattern of gradient for pans of the area with a gentle gradient from the shoreline. This pan had multiple deep points towards the South with shallow sediments towards the North showing evidence of wind action and sediment build up.

Overall there is no clear and common pattern between the physical characteristics of the pans in the MLD with large amounts of variation apparent. The differences between the four studied sites are assumed to reflect the overall variation across the MLD. The variation between pans in the MLD cannot be simplified to a single causal process. With understanding the physical characteristics of these pans, it is also important to understand the properties of their sediments as this could infer environmental changes which may influence the characteristics and functioning of these pans.

5.3. Sediment Inferences

5.3.1. Sediment Properties

Through the understanding of the sediment properties determined from the studied sites, it can be possible to present inferences which can aid in better explaining the changes and conditions which influence the function and characteristics of these pans in the MLD. A dated sediment record of 129 years was analysed in order to understand physical and geochemical changes within the sediments of Chrissiesmeer. Chrissiesmeer was used to provide a comprehensive sediment record due to its influence and size. Changes in sediment properties could provide information on periods of change in environmental and climatic conditions in the past which could possibly be used to determine trends for future change (Birks and Birks, 2006, Bennion *et al*., 2010). Sediment properties such as organic carbon and carbonate content as well as changes in sediment grain sizes therefore become a proxy for inferring a possible change in conditions (Birks and Birks, 2006, Bennion *et al*., 2010).

With respect to the site of Chrissiesmeer, the sediment properties show definite fluctuations throughout the sediment record over the last 129 years. Although there are definite fluctuations, there do not seem to be clear trends presented. There is an evident increase in organic carbon content over the last 30 years, evident in Zone CM3 and Zone CM4 (*Figure 4.5*), which is on the continued rise beginning from 1988. This indicates a higher level of productivity in Chrissiesmeer although with an increase in carbonate content as well, there is a higher level of precipitated calcium carbonate (Dean, 1999). The higher level of productivity could be down to the direct inputs of sewage from the town of Chrissiesmeer but could also possibly be as a result of atmospheric deposition of nitrogen and sulphur as a result of nearby power production and industry (Josipovic *et al*., 2011). It is however difficult to distinguish between natural and anthropogenic inputs. The sudden increase in organic carbon content could also be an indicator of increased moisture availability, although identifying a period of increased rainfall accurately when only considering organic carbon content is difficult (Heiri *et al*., 2001). Multiple influences can be attributed to the increase in organics and carbonates and therefore these proxies have to be discussed in conjunction with the analysis of sediment grain sizes.

Fluctuations in sediment grain size are evident throughout the sediment record of Chrissiesmeer which as a proxy present inferences on the climatic variability during this record. There are multiple instances of a sharp decrease in sand sized sediment grains which generally infer drier climatic conditions or even a drying out period (Peng *et al*., 2005). These drying out periods could be assumed to be possible drought periods. Evidence of increased precipitation is seen throughout the sediment record as well specifically in Zone CM2, and between Zone CM3 and Zone CM4. There is an increase in possible precipitation evident in the early 2000s which correlates to the increase in organics and carbonate. This is due to the dissolution of minerals from surrounding sediments. The general trend for the sediment grain sizes across the sediment record is that the size distributions tends to fluctuate instead of presenting a gradient trend which therefore shows no evidence of climatic trend changes over time for Chrissiesmeer.

The other sites of Tweelingspan East, Magdalenasmeer and Hendrik Beukes Pan show similarities and differences to Chrissiesmeer. In terms of Tweelingspan East, there are no evident fluctuations in organic carbon content and carbonate content with only increasing trends being evident throughout the recent sediment record. The trends throughout this sediment record do not reflect the changes and trends with respect to Chrissiesmeer. This increasing trend in organics and carbonate do not necessarily infer that there is a trend in increasing precipitation as this would be observed across the sites. There are no trends in sediment grain sizes throughout the sediment record of Tweelingspan with only decadal fluctuations evident which I assumed to be a more stable variation over time than what is evident in the other sites.

Site Magdalenasmeer represents changes more similar to Chrissiesmeer throughout the sediment record. There is a substantial increase in organics at the same time period as Chrissiesmeer of 1988. This increase represents a higher level of lake productivity and possibly an increase in precipitation (Dean, 1999; Heiri *et al*., 2001). However as stated previously, this is not entirely the case as many other direct and indirect factors could influence a sudden increase in organics such as direct inputs of sewage and runoff from farmlands both containing high levels of nitrogen and phosphorous. A difference between the two sites however is evident with respect to the sediment grain size distribution as Magdalenasmeer shows evidence of an increase in smaller sediment particles which suggests a drying out period and which then contradicts the evidence in Chrissiesmeer at the same time period of the late 1990s and early 2000s. The presence of smaller sediment particles is due to sediment being blown in and transported within the pans area by wind. Once again annual to decadal fluctuations tend to dominate the sediment record which are assumed to be the norm for the area.

The site of Hendrik Beukes Pan shares similarities to both Chrissiesmeer and Magdalenaspan although due its depth of no more than 0.4 m, it was assumed that this pan dries up on a seasonal basis with the lack of sufficient rainfall during the winter months in the MLD. There is a definite increase in organics at the same time period as these two sites of 1988. This is of interest as this increase seems to be a common indicator across multiple sites in the MLD and will be discussed later on in more depth. The fluctuations with regard to sediment grain size analysis tend to follow a similar trend to the other sites with patterns of decadal fluctuations with sharp decreases in larger sediment grain sizes which indicate drier periods. These are possible events where the pan had dried up completely allowing wind erosion to take place (Wellington, 1943). Wind action plays a large role in redistributing sediments and can introduce finer sediments from the surrounds.

The fluctuations and or trends evident in the sediment properties of all four sites present inferences about the past conditions influencing the pans throughout the sediment record of up to 129 years ago. These inferences include multiple possible drying up periods and periods of increased precipitation but are not as clear cut as there are many other influences, direct and indirect, that could cause that changes observed. Through the use of observed changes in major elements, a better understanding can be made as to whether there are any industrial signals present throughout the sediment record.

5.3.2. Major Element Inferences

The use of major elements is another proxy which provides inferences on possible contamination and therefore a regional industrial signal. Major elements are naturally occurring so therefore only definite changes in their composition and concentration could infer change or an influencing factor such as atmospheric deposition, acid mine drainage from mining or other industrial contaminant inputs. Although these major elemental inferences cannot necessarily be attributed to contamination sources directly, they do provide some clarity as to sediment supply and accumulation from different sources. Certain major elements such as iron, aluminium and potassium could be proxies for external stressors such as anthropogenic influence. Industrial inputs such as fallout derived or runoff derived could be represented but sudden changes in the compositions of these elements. Although they are naturally occurring, these sudden changes could infer a contamination source. It is however very difficult with the data provided to distinguish between naturally occurring and anthropogenic derived sources. Changes in calcium and sodium are stronger proxies for changes in natural sources and how sediment sources change particularly when considering environmental condition changes such as changes in precipitation.

The site of Chrissiesmeer had the longest sediment record therefore changes would ideally be evident throughout this record. A general decreasing trend in calcium throughout the sediment record with an increase in sodium over the last 40 years could possibly relate to an external stressor but more likely infer changes with regard to geological reason or sediment supply and most probably changes in precipitation. There is an evident increase over the sediment record for both aluminium and iron which cold infer change over time with regard to increased industrial activity (Popovic *et al*., 2001; Rowe *et al*., 2002). Changes in iron content may reflect changes in industrial activity and mining in the area (Geldenhuis & Bell, 1998; Bell *et al*., 2001). The increases in aluminium, iron and titanium could be as a result of increased intensive mining and other industry in the area which has seen intensification over the last 50 years throughout the Mpumalanga Highveld (Chamber of Mines, 2017). There is also an increase in coal prospecting in sites bordering other pans within the MLD. Evident dips in aluminium, iron, magnesium, sodium and titanium at the date 2004 could infer an event of some kind such as a flood event which would cause mixing of sediments and possibly transportation. This event correlates to the increase of organics and increase in larger sediment grains during the early 2000s in Chrissiesmeer which suggest an increase in precipitation.

With respect to the other three sites of TPE, MDM and HBP, changes in concentration and composition of major elements are compared to Chrissiesmeer. In terms of Tweelingspan East, the composition of major elements stays very stable over the sediment record with the only changes being evident in the slight increase trend in magnesium, calcium and sodium beginning from approximately 1978. The changes observed in the sediment record of Tweelingspan East were not as identifiable as those in Chrissiesmeer. This could be due to the vast differences in terms of physical characteristics and bathymetry.

The site of Magdalenasmeer seems to be a more dynamic site compared to Tweelingspan East with respect to the composition of major elements. There is a similar pattern to Chrissiesmeer with the general decrease in calcium over the sediment record and a substantial increase in sodium over the last 30 years. It was suggested that with regard to Chrissiesmeer that these changes in calcium and sodium were possibly related to geological reasons and/or changes in sediment inputs but having similar changes being evident across two sites suggests that it is more complex than previously assumed. The site of Hendrik Beukes Pan reflects a similar change with respect to calcium, in carbonate form, however sodium shows a decrease over the last 30 years and this strengthens the inference that the relationship between these pans is more complex and dynamic than initially suggested. There are sharp increases evident in aluminium, iron and titanium after a dip at 1988 which again strengthens the inference that there is an environmental or climatic event at this stage which is influential enough to cause a complete change in trends. This event could cause the introduction and accumulation of new sediments which could explain the sharp trend changes. These major elements of aluminium, iron and titanium are most closely related to an industrial signal in terms of mining and other industry contamination (Geldenhuis & Bell, 1998; Bell *et al*., 2001). However the decreases evident in magnesium and calcium at the same time period around 1988 suggest that there are no direct inputs of contaminants relating to mining operations (Popovic *et al*., 2001; Rowe *et al*., 2002). If this truly is evidence of an industrial signal then it would have been introduced into the local environment through atmospheric depositional processes or possibly driven and introduced by strong continuous winds (Ghose and Majee, 2001; Josipovic *et al*., 2011). This is possible in the summer months as wind blows in an Easterly direction blowing the emissions produced across the Highveld towards the MLD region (Tyson *et al*., 1988).

The findings presented and the inferences discussed throughout this section provide information as to the characteristics and functioning of the pans in the MLD throughout the sediment record in the hope that a regional industrial signal or indicator may be identified. Although there is possible evidence of this signal or indicator within these pans, it varies between sites and presents itself in various major elements throughout the sediment record at different stages and therefore cannot be considered a clear regional industrial signal. These pans are far more dynamic and unique therefore the inferences are difficult to justify across a regional scale encompassing the entire MLD.

5.4. Local Environmental Change

5.4.1. Environmental and Climatic Events

The events or points of interest identified throughout **4. Results** and **5. Discussion** are markers for possible environmental or climatic change as these events have been identified to not follow the general trend throughout the sediment record. The identified events concern specific dates in which there has been a notable change of pattern in sediment properties and major element compositions.

With regard to sediment grain size distributions there are identified points of interest which have a greater level of change over the decadal or seasonal patterns often present. One event is 1960 in Chrissiesmeer where there is a definite decrease in larger sediment particles which correlates to drier conditions and possible exposure of bottom lake sediments to erosive processes (Peng *et al*., 2005). Similar events include 1934 in site Magdalenasmeer and 1978 in site Hendrik Beukes Pan. Both events show the same substantial decrease in larger sediment particles. Other events include 2006 in site Hendrik Beukes Pan, 1998 in site Chrissiesmeer and 1973 in site Tweelingspan East which all represent an increase in the size of sediment particles which is attributed to an event of increased precipitation (Peng *et al*., 2005). Tweelingspan East however only represented small changes in sediment grain size distribution and this is attributed to its depth which was beyond 2 m. This depth was much more than the other three sites and therefore it is inferred that Tweelingspan East did not have any drying out events of note.

A major point of interest which concerns three of the four sites was the event at 1988 which was evident in Chrissiesmeer, Magdalenaspan and Hendrik Beukes Pan. All three sites represented substantial increases in organic carbon content along with an increase in carbonate which is interesting as there should be an inverse relationship between the two sediment properties according to Dean (1999). As this is not the case here, this adds more interest to the event at 1988. The increase in organic carbon content could possibly reflect an increase in precipitation however this is not the only possibility as changes in organics in fresh water bodies are more complex when considering productivity and direct inputs of nitrogen and phosphorous (Shuman, 2003). In addition to sediment properties, 1988 also shows changes in major elements such as presenting a point of change from which sodium decreases across these three sites. As sodium concentrations are derived from the related geology surrounding the pans, it could be suggested that there is a change in source geology material or the supply of sodium containing sediments. This could possibly relate as well to the levels of salinity in the pans which through increased precipitation would become slightly diluted. The brackish nature for these pans suggests that sources of water input influence the salinity derived from the underlying and surrounding geology more than what was initially assumed (Goudie and Thomas, 1985). This brackish water also suggests that evaporation and precipitation inputs must play a role in the characteristics of the pans. Precipitation and groundwater inputs have a stronger influence on the levels of salinity, pH, major elements and other sediment properties than previously thought.

More commonalities surrounding the event at 1988 include dips in aluminium, iron and magnesium covering a short time period on only approximately 4 years. These dips are most prevalent in site Magdalenasmeer and strengthen the possibility that there is a significant precipitation event at this time period. A sudden change in major elements of that nature most likely has environmental or climatic stressors affecting the site and therefore the whole of the MLD.

5.4.2. Environmental and Climatic Change

From the identified events above in *5.4.1. Environmental and Climatic Events*, it should be possible to determine or make a better understanding of any environmental or climatic change that has taken place across the sediment record. The substantial increases in organics across the sites could possibly represent increases in precipitation which spans over the last approximately 30 years. This increased precipitation is an assumed general trend and there will still be seasonal and annual variations apparent. When considering the size of sediment particles it is also evident that there is a large variation in possible environmental and climatic events over the sediment record. There is no clear trend in the grain size distribution across all the sites and therefore only small periods of environmental and climatic change can be identified. These periods are more events than actual change as there is clear decadal and annual variation within these sites when considering sediment grain sizes.

The point of interest at 1988 shows some form of environmental and climatic change although this is only assumed and there is no clear evidence for the change being linked to climate. In terms of major elements, there could be an association between increases in concentrations from wet atmospheric deposition and increased precipitation particularly during the summer months (De Klerk *et al*., 2012). De Klerk *et al*. (2012) do suggest that there is a relationship between an increase in metals found in the sediments of the MLD through wet atmospheric deposition during the summer months and this was indicated by a strong seasonal variation. This however is difficult to quantify and prove without the analysis of rain water for the presence of any metal contaminants. It therefore seems that there is more evidence for seasonal variations in climatic change rather than change evident throughout the sediment record.

5.5. Regional Synthesis

A regional synthesis is presented here with the aim of identifying any signals for anthropogenic influence of the pans of the MLD. Across all four sites there is a definite indication of seasonal variation patterns which could be linked with regional environmental change. These seasonal variation patterns however do not give any indication of a regional industrial signal which could link the anthropogenic influence. De Klerk *et al*. (2012) and Foster *et al*., (2015) do however claim that anthropogenic influence can be evident in seasonal variation patterns within the slight changes which are evident in the metals identified in the sediments of the pans in the MLD. Therefore through the use of major elements as a proxy for anthropogenic influence with respect to industrial contamination, there are evident changes throughout the sediment record. These changes could represent an industrial signal but it is difficult to distinguish between natural and anthropogenic sources.

The increases in aluminium, iron, magnesium and titanium over the past 30 years could be an indication of industrial contamination which then serves as an industrial signal however this could be linked to changes in sediment supply. This change was evident for Magdalenasmeer. However only one site does not provide a comprehensive indication of a regional signal. Ideally all four sites are required to provide an indication of a regional industrial signal and therefore suggest an anthropogenic influence. The sites of Chrissiesmeer, Tweelingspan East and Hendrik Beukes Pan do show increases in aluminium, iron, magnesium and titanium over the last 30 to 40 years. This could however be due to changes in sediment supply and to distinguish between environmental and anthropogenic sources is difficult. These trends correlate to those observed in Magdalenasmeer and therefore represent a more comprehensive indication of a regional industrial signal. In order to provide a clear indication of anthropogenic influence across the whole of the MLD, the analysis of more sites would be required in possible future research concerning this research project.

A major topic throughout this research project is the uniqueness for the pans in the MLD. How unique are these pans in the larger context? When considering the global context, it is difficult to justify whether these systems are truly unique as there would need to be a large scale comparison of similar systems from different regions. The uniqueness of the pans in the MLD therefore does not lie in a larger context but rather between pans within the MLD. Differences between pans which are in close proximity to one another are notable which therefore enhances the claim that these systems are unique. They may share the same underlying geology and follow similar hydrogeology systems yet they could be mistaken for being located 100 km apart. This also encourages the assumption that these systems are impacted very differently by regional climatic changes such as drought or prolonged precipitation.

5.6. Future Research Trajectories

This research project as a whole is by no means complete in terms of what else could be studied in order to better our understanding of the characteristics and functioning of fresh water ecosystems as unique as the Mpumalanga Lake District. There is need to firstly address the present research gaps for the study area specifically and then to expand upon this project in terms of a global aspect. Multiple limitations hindered this research such as funding and access to sites therefore this project could have been more extensive incorporating more sites as to gain a better understanding of the whole Mpumalanga Lake District. Further research into sources of contamination would be required and perhaps an approach must be taken that looks into specific trace elements, such as copper, zinc, chromium, nickel and cobalt, rather than major elements so as to determine a more extensive composition of contamination.

A possible approach that could be taken in order to expand upon this research would be to compare the MLD pans to those located in other parts of South Africa such as those in the North-West Province and even further throughout Southern Africa. This would provide new dynamics such as regional landscape and environmental differences. Seasonal regimes of precipitation and drying up events could be compared. Although this is more of a pilot study making use of a palaeolimnological approach, there is promise for more studies which incorporate the same approach in other areas of South Africa. This would bridge the gap in research that is required.

6. Conclusion

6.1. Introduction

Endorheic pans are known to be closed systems which are unstable and have varying water chemistry and geochemistry (Goudie and Well, 1995; Janecke *et al*., 2003). This means that they have a strong seasonal variation and are influenced greatly by climatic and environmental events (Janecke *et al*., 2003). This tends to often have impacts on the functioning of these pans in terms of ecology and may impact the pans physical characteristics. This is certainly the case when considering the pans located in the Mpumalanga Lake District however the influencing factors which cause changes to these pans are much more complex than initially presented. The uniqueness and complexity of these pans presents more challenges than solutions and understanding.

Although these pans relate in many aspects, they differ entirely when considering bathymetry, limnology and sediment properties. The differences between pans were unexpected considering the close proximity to each other such as the pans of Chrissiesmeer and Tweelingspan East. Due to the uniqueness of these pans and the variety of differences between pans, it is difficult to identify a regional industrial signal which can be considered as evidence of anthropogenic influence which is what this research project was aiming to achieve.

6.2. Achievement of Study Objectives

This dissertation set out objectives in order to achieve a comprehensive understanding of the pans of the Mpumalanga Lake District. These included to understand the physical morphology characteristics of the pans, to understand the possibility of anthropogenic influence across the MLD and if that can be identified as a regional industrial signal, to determine changes in sediment composition over time (temporal scale), and to possibly determine environmental and climatic change with regard to the last approximately 130 years. A major aim of this research project was also to present a pilot palaeolimnological research project that is the first of its kind based specifically on the MLD region in the hopes that this may lay the ground work for future research in the region.

The initial assumption was that the pans of the MLD were similar in physical characteristics and function. This however was proven not to be the case as it was determined that there was great variability between sites in terms of their bathymetry and limnology as well as their sediment properties. Although there were some similarities, the variations in physiochemical characteristics were present throughout the sediment record. Evidence of changes in sediment grain size between sites indicated that some pans such as Magdalenasmeer and Hendrik Beukes Pan show seasonal patterns of drying up while Tweelingspan East did not show this seasonal record indicating a more stable record in terms of seasonal variability. This was unexpected when considering the proximity of these pans to each other. The pans of the MLD are far more unique and variable than what was initially assumed. This therefore represents a sufficient achievement of the objective concerning the physical lake morphology of the pans in the MLD.

The objectives concerning the determination of the extent that anthropogenic influence has had in the MLD over a temporal scale were far more difficult to achieve due to the high variability between pans. This variability however does represent the differences between pans in terms of major elements. Due to the proximity of the pans, it was initially assumed that there would be little variation between the pans as they would represent the same levels of contamination. This however was not entirely the case. Although there are similarities between sites throughout the sediment record, there are variations between sites which are more dependent on environmental factors rather than the introduction of contaminants. In terms of the temporal aspect, it was initially assumed that there was a gradual change over the past 100 years when mining was introduced to the Mpumalanga Highveld region. This was not evident as the majority of changes in major elements and metals were determined to only occur over the last 30 to 40 years. There was however a general increase in metals such as iron and aluminium which suggest possible contamination associated with industrial activities. This therefore provides an indication as to a regional industrial signal in the MLD.

The last objective concerned the determination of possible environmental and climatic changes. It was initially assumed that there would be evidence for regional climatic changes with the frequency and severity of climatic events increasing. It was however determined that the regional environment and climate are far more complex and show great seasonal and decadal variability rather than a clear increasing or decreasing trend. These were inferences based predominantly on sediment proxies. Determinations were made however to a number of possible climatic events such as periods of increased precipitation and drying out periods. Therefore the objective was partially achieved but much more research would be required as to fully determine any changes in regional climate as these inferences are not proof of change.

The assessment of how unique these pans in the MLD are to one another is a difficult assessment to quantify as there in no set guideline for uniqueness. Therefore these pans are a very interesting case as they vary significantly in certain aspects such as physical morphology yet some have similar water quality results. There is an assumption that due to the significant differences in geochemical and physical properties , that these pans of the MLD are impacted differently by any external stressor, natural or anthropogenic, regardless of their close proximity.

The ability of this research project to be a pilot project in the field of palaeolimnology in the specific region of the MLD was put to the test throughout the project and with the proposal of the aforementioned aims. Although no conclusive indicators of an anthropogenically sourced industrial signal were obtained, proxies allowed for assumptions to be made as to possibilities of evident contamination. With possibly more work on sediment analysis, specifically trace elements, the use of a palaeolimnological approach in the region may be highly successful. This project needs to be viewed as a whole as a pilot study in the field of palaeolimnology in the MLD and not as a specific project to identify key sources of contamination from mining in the area.

6.3. Synthesis

Throughout this dissertation there has been a theme of the uniqueness and variability of the pans located in the Mpumalanga Lake District. This is true when considering the determined observations. These pans vary in multiple aspects but share one major similarity which is their proximity to one another. This only enhances the uniqueness of these pans. When considering the extensive industrial activity taking place across the Mpumalanga Highveld, it is important to understand the impact this has had and will have on such a unique location. South Africa already suffers from a lack of large fresh water sources due to anthropogenic influence and cannot afford to lose more. The evidence of changes in major elements over the last 30 to 40 years provides a regional industrial signal for the Mpumalanga Lake District which is on the increase. This regional industrial signal reflects the anthropogenic influence that has intensified in the region during recent history.

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Appendix 1: Bathymetry Data

CM Bathymetry Data																											
Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth
1	-26.32613	30.20833	-0.8	81	-26.34377	30.20975	-1	161	-26.32948	30.21889	-1.2	241	-26.32091	30.21871	-1	321	-26.30273	30.21581	-0.8	Edge	-26.31130	30.21639	0	Edge	-26.33690	30.22672	0
2	-26.32630	30.20865	-0.5	82	-26.34426	30.20976	-1.1	162	-26.32965	30.21935	-1.2	242	-26.32091	30.21911	-1.1	322	-26.30203	30.21547	-0.9	Edge	-26.31068	30.21697	0	Edge	-26.33813	30.22636	0
3	-26.32650	30.20902	-0.9	83	-26.34454	30.20978	-1.2	163	-26.32975	30.21962	-1.3	243	-26.32093	30.21954	-1	323	-26.30181	30.21532	-0.9	Edge	-26.30994	30.21700	0	Edge	-26.33940	30.22590	0
4	-26.32665	30.20929	-0.8	84	-26.34528	30.20990	-0.9	164	-26.32984	30.21995	-1.2	244	-26.32093	30.21995	-1.1	324	-26.30157	30.21522	-0.8	Edge	-26.30900	30.21725	0	Edge	-26.34097	30.22525	0
5	-26.32690	30.20982	-0.9	85	-26.34555	30.20990	-1.1	165	-26.33002	30.22049	-1.3	245	-26.32093	30.22022	-1.1	325	-26.30129	30.21519	-0.7	Edge	-26.30860	30.21660	0	Edge	-26.34225	30.22447	0
6	-26.32752	30.21080	-0.9	86	-26.34640	30.21000	-1.1	166	-26.33014	30.22072	-1.2	246	-26.32091	30.22081	-1.1	326	-26.30103	30.21508	-0.8	Edge	-26.30824	30.21538	0	Edge	-26.34324	30.22375	0
7	-26.32811	30.21179	-1	87	-26.34706	30.20998	-1.2	167	-26.33024	30.22096	-1.2	247	-26.32094	30.22104	-1.2	327	-26.30073	30.21490	-0.5	Edge	-26.30779	30.21438	0	Edge	-26.34450	30.22249	0
8	-26.32885	30.21284	-1	88	-26.34747	30.20997	-1	168	-26.33034	30.22113	-1.2	248	-26.32098	30.22139	-1.2	328	-26.30059	30.21481	-0.7	Edge	-26.30697	30.21359	0	Edge	-26.34479	30.22184	0
9	-26.32978	30.21419	-1	89	-26.34801	30.20998	-1.1	169	-26.33054	30.22144	-1.3	249	-26.32102	30.22179	-1.2	329	-26.30042	30.21471	-0.9	Edge	-26.30603	30.21312	0	Edge	-26.34602	30.22068	0
10	-26.33082	30.21573	-1	90	-26.34864	30.20983	-0.8	170	-26.33076	30.22180	-1.1	250	-26.32103	30.22202	-1.1	330	-26.30006	30.21426	-0.8	Edge	-26.30489	30.21302	0	Edge	-26.34679	30.21940	0
11	-26.33210	30.21712	-1	91	-26.34863	30.20925	-0.6	171	-26.33091	30.22217	-1.2	251	-26.32100	30.22258	-1.1	331	-26.29996	30.21407	-0.9	Edge	-26.30370	30.21312	0	Edge	-26.34760	30.21832	0
12	-26.33357	30.21804	-1	92	-26.34847	30.20911	-0.8	172	-26.33105	30.22244	-1.1	252	-26.32097	30.22300	-1.1	332	-26.29986	30.21371	-0.9	Edge	-26.30248	30.21347	0	Edge	-26.34864	30.21710	0
13	-26.33499	30.21881	-1	93	-26.34827	30.20872	-1	173	-26.33132	30.22291	-1.2	253	-26.32094	30.22330	-1	333	-26.29957	30.21312	-1	Edge	-26.30175	30.21374	0	Edge	-26.34893	30.21611	0
14	-26.33595	30.21937	-1	94	-26.34805	30.20831	-0.9	174	-26.33142	30.22312	-1.1	254	-26.32093	30.22367	-1.3	334	-26.29953	30.21296	-0.8	Edge	-26.30103	30.21360	0	Edge	-26.34888	30.21546	0
15	-26.33756	30.22027	-1.2	95	-26.34796	30.20770	-0.9	175	-26.33156	30.22344	-1	255	-26.32090	30.22394	-1.1	335	-26.29932	30.21248	-0.8	Edge	-26.30065	30.21290	0	Edge	-26.34864	30.21459	0
16	-26.33839	30.22075	-1	96	-26.34765	30.20752	-1.1	176	-26.33162	30.22370	-1.1	256	-26.32086	30.22440	-1	336	-26.29902	30.21199	-0.7	Edge	-26.30030	30.21169	0	Edge	-26.34857	30.21376	0
17	-26.33914	30.22118	-1.3	97	-26.34739	30.20960	-1.1	177	-26.33165	30.22383	-1	257	-26.32087	30.22468	-1	337	-26.29841	30.21120	-0.7	Edge	-26.30012	30.21072	0	Edge	-26.34893	30.21240	0
18	-26.33966	30.22145	-1.1	98	-26.34720	30.20641	-0.9	178	-26.33175	30.22423	-1.1	258	-26.32087	30.22484	-1	338	-26.29853	30.21045	-0.8	Edge	-26.30001	30.20990	0	Edge	-26.34902	30.21104	0
19	-26.34045	30.22197	-1	99	-26.34695	30.20585	-1	179	-26.33186	30.22470	-1.1	259	-26.32088	30.22557	-1	339	-26.29884	30.20973	-0.8	Edge	-26.30018	30.20880	0	Edge	-26.34918	30.20988	0
20	-26.34127	30.22223	-1.1	100	-26.34651	30.20514	-0.9	180	-26.33187	30.22499	-1	260	-26.32089	30.22594	-0.9	340	-26.29900	30.20940	-0.5	Edge	-26.30061	30.20720	0	Edge	-26.34968	30.20862	0
21	-26.34222	30.22274	-1.1	101	-26.34624	30.20460	-1	181	-26.33185	30.22530	-0.9	261	-26.32032	30.22556	-0.9	341	-26.29877	30.20926	-0.8	Edge	-26.30109	30.20560	0	Edge	-26.34984	30.20729	0
22	-26.34267	30.22307	-0.7	102	-26.34587	30.20372	-0.9	182	-26.33185	30.22589	-0.9	262	-26.31976	30.22484	-0.9	342	-26.29859	30.20919	-0.7	Edge	-26.30157	30.20443	0	Edge	-26.34989	30.20613	0
23	-26.34278	30.22316	-0.8	103	-26.34550	30.20253	-1.1	183	-26.33187	30.22612	-0.9	263	-26.31940	30.22444	-1.1	343	-26.29831	30.20904	-0.7	Edge	-26.30163	30.20347	0	Edge	-26.34986	30.20529	0
24	-26.34290	30.22324	-0.6	104	-26.34547	30.20173	-0.9	184	-26.33189	30.22638	-0.8	264	-26.31928	30.22422	-1	344	-26.29822	30.20903	-0.6	Edge	-26.30091	30.20254	0	Edge	-26.34957	30.20411	0
25	-26.34272	30.22297	-0.8	105	-26.34552	30.20160	-0.5	185	-26.33162	30.22623	-0.7	265	-26.31902	30.22391	-0.9	345	-26.29809	30.20934	-0.6	Edge	-26.29991	30.20170	0	Edge	-26.34909	30.20346	0
26	-26.34241	30.22222	-0.8	106	-26.34551	30.20142	-0.4	186	-26.33139	30.22586	-0.9	266	-26.31893	30.22372	-1	346	-26.29805	30.20969	-0.6	Edge	-26.29871	30.20118	0	Edge	-26.34838	30.20301	0
27	-26.34224	30.22186	-1.1	107	-26.34451	30.20183	-0.9	187	-26.33105	30.22536	-0.9	267	-26.31875	30.22343	-0.9	347	-26.29804	30.21021	-0.6	Edge	-26.29771	30.20128	0	Edge	-26.34795	30.20222	0
28	-26.34207	30.22148	-1.1	108	-26.34380	30.20184	-1	188	-26.33095	30.22522	-1	268	-26.31850	30.22291	-1	348	-26.29802	30.21052	-0.5	Edge	-26.29674	30.20179	0	Edge	-26.34766	30.20157	0
29	-26.34186	30.22103	-1.1	109	-26.34341	30.20176	-0.9	189	-26.33077	30.22503	-0.9	269	-26.31800	30.22214	-1	349	-26.29804	30.21122	-0.6	Edge	-26.29582	30.20273	0	Edge	-26.34767	30.20104	0
30	-26.34155	30.22045	-1	110	-26.34311	30.20177	-1	190	-26.33044	30.22466	-1	270	-26.31781	30.22189	-1.1	350	-26.29807	30.21140	-0.7	Edge	-26.29522	30.20366	0	Edge	-26.34696	30.20050	0
31	-26.34129	30.22013	-1.1	111	-26.34250	30.20172	-0.9	191	-26.33017	30.22441	-1.1	271	-26.31764	30.22164	-1	351	-26.29786	30.21243	-0.6	Edge	-26.29549	30.20461	0	Edge	-26.34632	30.20001	0
32	-26.34116	30.21966	-1.1	112	-26.34184	30.20169	-0.9	192	-26.33007	30.22432	-1	272	-26.31698	30.22050	-1	352	-26.29796	30.21263	-0.6	Edge	-26.29606	30.20512	0	Edge	-26.34533	30.19970	0
33	-26.34094	30.21909	-1	113	-26.33912	30.20348	-0.9	193	-26.32970	30.22382	-1	273	-26.31667	30.22002	-1	353	-26.29837	30.21366	-0.8	Edge	-26.29628	30.20569	0	Edge	-26.34444	30.19934	0
34	-26.34080	30.21875	-1	114	-26.33879	30.20415	-0.8	194	-26.32948	30.22360	-1.1	274	-26.31652	30.21922	-0.9	354	-26.29887	30.21471	-0.8	Edge	-26.29596	30.20651	0	Edge	-26.34351	30.19909	0
35	-26.34062	30.21833	-1.2	115	-26.33804	30.20559	-0.9	195	-26.32927	30.22334	-1.1	275	-26.31633	30.21940	-0.9	355	-26.29974	30.21561	-0.9	Edge	-26.29598	30.20743	0	Edge	-26.34263	30.19902	0
36	-26.34047	30.21797	-1.2	116	-26.33726	30.20674	-0.6	196	-26.32907	30.22305	-1	276	-26.31610	30.21896	-1	356	-26.30043	30.21622	-1	Edge	-26.29565	30.20791	0				
37	-26.34027	30.21751	-1.2	117	-26.33695	30.20732	-0.5	197	-26.32892	30.22275	-1	277	-26.31580	30.21854	-1	357	-26.30122	30.21663	-0.9	Edge	-26.29587	30.20860	0				
38	-26.34016	30.21722	-1.3	118	-26.33597	30.20808	-0.8	198	-26.32877	30.22249	-1.1	278	-26.31544	30.21805	-0.9	358	-26.30298	30.21811	-0.9	Edge	-26.29573	30.21010	0				
39	-26.33994	30.21673	-1.3	119	-26.33420	30.20834	-0.7	199	-26.32865	30.22223	-1.1	279	-26.31483	30.21738	-0.8	359	-26.30369	30.21873	-0.9	Edge	-26.29539	30.21095	0				
40	-26.33964	30.21609	-1.1	120	-26.33274	30.20784	-0.8	200	-26.32853	30.22200	-1.1	280	-26.31440	30.21751	-0.9	360	-26.30468	30.21922	-1	Edge	-26.29481	30.21055	0				
41	-26.33954	30.21587	-1.2	121	-26.33162	30.20712	-0.8	201	-26.32832	30.22161	-1.1	281	-26.31402	30.21818	-0.9	Edge	-26.34177	30.19910	0	Edge	-26.29429	30.20978	0				
42	-26.33931	30.21525	-1.3	122	-26.33067	30.20673	-0.8	202	-26.32824	30.22144	-1.2	282	-26.31344	30.21922	-0.9	Edge	-26.34091	30.19970	0	Edge	-26.29378	30.20948	0				
43	-26.33907	30.21477	-1.2	123	-26.32904	30.20662	-0.8	203	-26.32816	30.22128	-1	283	-26.31282	30.21994	-0.9	Edge	-26.33999	30.20022	0	Edge	-26.29317	30.21009	0				
44	-26.33887	30.21429	-1.1	124	-26.32865	30.20648	-0.7	204	-26.32800	30.22105	-1	284	-26.31194	30.22024	-1	Edge	-26.33895	30.20141	0	Edge	-26.29212	30.21123	0				
45	-26.33868	30.21382	-1.3	125	-26.32787	30.20653	-0.7	205	-26.32790	30.22089	-1.2	285	-26.31161	30.22133	-1	Edge	-26.33819	30.20237	0	Edge	-26.29255	30.21212	0				
46	-26.33849	30.21333	-1.2	126	-26.32708	30.20660	-0.4	206	-26.32767	30.22058	-1.3	286	-26.31128	30.22184	-0.9	Edge	-26.33763	30.20418	0	Edge	-26.29326	30.21325	0				
47	-26.33834	30.21293	-1.3	127	-26.32723	30.20730	-0.8	207	-26.32755	30.22038	-1.1	287	-26.31112	30.22236	-1	Edge	-26.33688	30.20656	0	Edge	-26.29383	30.21410	0				
48	-26.33822	30.21264	-1.3	128	-26.32730	30.20797	-0.9	208	-26.32740	30.22018	-1.2	288	-26.31081	30.22336	-0.9	Edge	-26.33624	30.20745	0	Edge	-26.29392	30.21481	0				
49	-26.33816	30.21243	-1.1	129	-26.32746	30.20889	-1	209	-26.32725	30.21999	-1.1	289	-26.31059	30.22313	-1	Edge	-26.33526	30.20775	0	Edge	-26.29468	30.21523	0				
50	-26.33806	30.21217	-1.2	130	-26.32755	30.20923	-0.9	210	-26.32700	30.21966	-1.3	290	-26.31053	30.22267	-1	Edge	-26.33440	30.20804	0	Edge	-26.29600	30.21590	0				
51	-26.33789	30.21159	-1.2	131	-26.32764	30.20957	-1	211	-26.32668	30.21919	-1.1	291	-26.31050	30.22173	-1.1	Edge	-26.33390	30.20781	0	Edge	-26.29653	30.21622	0				
52	-26.33780	30.21138	-1.3	132	-26.32788	30.21072	-1	212	-26.32660	30.21911	-1	292	-26.31048	30.22150	-1.2	Edge	-26.33272	30.20677	0	Edge	-26.29725	30.21692	0				
53	-26.33768	30.21110	-1.1	133	-26.32793	30.21099	-1.1	213	-26.32632	30.21888	-1.2	293	-26.31046	30.22136	-1	Edge	-26.33158	30.20596	0	Edge	-26.29790	30.21873	0				
54	-26.33758	30.21080	-1.1	134	-26.32801	30.21150	-1	214	-26.32617	30.21875	-1.1	294	-26.31038	30.22095	-1.1	Edge	-26.33028	30.20557	0	Edge	-26.29870	30.21934	0				
55	-26.33741	30.21052	-0.9	135	-26.32806	30.21175	-1.1	215	-26.32592	30.21834	-1.1	295	-26.31030	30.22056	-1	Edge	-26.32882	30.20570	0	Edge	-26.30005	30.21993	0				
56	-26.33729	30.21025	-1.1	136	-26.32816	30.21222	-1.1	216	-26.32577	30.21819	-1.2	296	-26.31025	30.22026	-1	Edge	-26.32742	30.20591	0	Edge	-26.30159	30.22101	0				
57	-26.33712	30.20993	-1.1	137	-26.32824	30.21255	-1.2	217	-26.32561	30.21801	-1.2	297	-26.31011	30.21963	-1.1	Edge	-26.32577	30.20648	0	Edge	-26.30253	30.22129	0				
58	-26.33694	30.20960	-1.2	138	-26.32837	30.21297	-1	218	-26.32541	30.21785	-1.1	298	-26.31006	30.21927	-1	Edge	-26.32402	30.20752	0	Edge	-26.30328	30.22135	0				
59	-26.33690	30.20924	-1.1	139	-26.32841	30.21312	-1.1	219	-26.32501	30.21750	-1	299	-26.30998	30.21883	-0.9	Edge	-26.32258	30.20866	0	Edge	-26.30412	30.22183	0				
60	-26.33679	30.20866	-1	140	-26.32844	30.21336	-1.2	220	-26.32487	30.21735	-0.9	300	-26.30992	30.21842	-0.8	Edge	-26.32189	30.20936	0	Edge	-26.30570	30.22238	0				
61	-26.33671	30.20842	-1.1	141	-26.32849	30.21359	-1.2	221	-26.32457	30.21699	-1	301	-26.30934	30.21851	-0.9	Edge	-26.32146	30.21017	0	Edge	-26.30723	30.22287	0				
62	-26.33657	30.20786	-0.9	142	-26.32853	30.21377	-1.3	222	-26.32434	30.21672	-0.9	302	-26.30896	30.21855	-0.9	Edge	-26.32085	30.21104	0	Edge	-26.30846	30.22340	0				
63	-26.33590	30.20775	-0.7	143	-26.32858	30.21398	-1.1	223	-26.32414	30.21653	-1	303	-26.30836	30.21860	-0.9	Edge	-26.32078	30.21197	0	Edge	-26.30975	30.22427	0				
64	-26.33705	30.20784	-0.7	144	-26.32868	30.21439	-1.1	224	-26.32346	30.21591	-1.3	304	-26.30792	30.21866	-0.9	Edge	-26.32075	30.21276	0	Edge	-26.31119	30.22517	0				
65	-26.33728	30.20790	-1	145	-26.32871	30.21461	-1	225	-26.32317	30.21572	-1	305	-26.30764	30.21874	-1	Edge	-26.32063	30.21385	0	Edge	-26.31268	30.22602	0				
66	-26.33756	30.20802	-1.1	146	-26.32874	30.21484	-1.1	226	-26.32294	30.21560	-1.1	306	-26.30721	30.21879	-1	Edge	-26.32042	30.21495	0	Edge	-26.31405	30.22660	0				
67	-26.33785	30.20808	-1	147	-26.32879	30.21521	-1.2	227	-26.32271	30.21550	-1	307	-26.30612	30.21903	-1	Edge	-26.32023	30.21564	0	Edge	-26.31506	30.22703	0				
68	-26.33825	30.20823	-1.1	148	-26.32883	30.21554	-1.1	228	-26.32260	30.21541	-0.9	308	-26.30565	30.21919	-1.1	Edge	-26.31998	30.21624	0	Edge	-26.31656	30.22728	0				
69	-26.33863	30.20836	-1.1	149	-26.32886	30.21598	-1	229	-26.32235	30.21528	-1	309	-26.30540	30.21925	-1.3	Edge	-26.31960	30.21664	0	Edge	-26.31811	30.22761	0				
70	-26.33946	30.20864	-1.2	150	-26.32886	30.21621	-1.2	230	-26.32190	30.21510	-0.9	310	-26.30530	30.21929	-1	Edge	-26.31914	30.21676	0	Edge	-26.31943	30.22784	0				
71	-26.33999	30.20887	-1.2	151	-26.32887	30.21647	-1.1	231	-26.32144	30.21502	-1	311	-26.30501	30.21942	-1.1	Edge	-26.31853	30.21660	0	Edge	-26.32121	30.22813	0				
72	-26.34055	30.20906	-1.1	152	-26.32889	30.21665	-1.2	232	-26.32102	30.21504	-0.9	312	-26.30467	30.21952	-1	Edge	-26.31766	30.21659	0	Edge	-26.32287	30.22815	0				
73	-26.34089	30.20919	-1.2	153	-26.32894	30.21705	-1.1	233	-26.32086	30.21566	-0.9	313	-26.30446	30.21962	-1	Edge	-26.31701	30.21674	0	Edge	-26.32487	30.22826	0				
74	-26.34168	30.20939	-1.1	154	-26.32898	30.21721	-1.2	234	-26.32089	30.21587	-1.2	314	-26.30394	30.21979	-0.9	Edge	-26.31648	30.21713	0	Edge	-26.32720	30.22809	0				
75	-26.34203	30.20955	-1.2	155	-26.32905	30.21758	-1.1	235	-26.32090	30.21604	-1	315	-26.30360	30.21908	-0.9	Edge	-26.31567	30.21651	0	Edge	-26.32904	30.22757	0				
76	-26.34227	30.20955	-1	156	-26.32911	30.21787	-1.2	236	-26.32090	30.21665	-1	316	-26.30354	30.21850	-0.9	Edge	-26.31481	30.21577	0	Edge	-26.33059	30.22756	0				
77	-26.34249	30.20957	-1.2	157	-26.32917	30.21806	-1.3	237	-26.32089	30.21679	-1.1	317	-26.30350	30.21816	-0.9	Edge	-26.31416	30.21540	0	Edge	-26.33133	30.22760	0				
78	-26.34287	30.20960	-1.3	158	-26.32926	30.21832	-1.1	238	-26.34089	30.21735	-1	318	-26.30339	30.21755	-0.9	Edge	-26.31333	30.21551	0	Edge	-26.33293	30.22738	0				
79	-26.34322	30.20967	-1.2	159	-26.32933	30.21855	-1.2	239	-26.32091	30.21799	-1.1	319	-26.30309	30.21681	-0.9	Edge	-26.31209	30.21608	0	Edge	-26.33453	30.22723	0				
80	-26.34349	30.20971	-1.1	160	-26.32939	30.21871	-1.3	240	-26.32092	30.21825	-1	320	-26.30279	30.21615	-0.9	Edge	-26.31175	30.21646	0	Edge	-26.33572	30.22703	0				

HBP Bathymetry Data

Label	Rank	Latitude	Longitude	Depth	Label	Rank	Latitude	Longitude	Depth
256	1	-26.39500	30.24713	-0.3	Edge	Edge	-26.38837	30.24726	0
257	2	-26.39484	30.24700	-0.4	Edge	Edge	-26.38883	30.24760	0
258	3	-26.39510	30.24667	-0.4	Edge	Edge	-26.38941	30.24801	0
259	4	-26.39540	30.24659	-0.4	Edge	Edge	-26.39042	30.24840	0
260	5	-26.39581	30.24608	-0.4	Edge	Edge	-26.39132	30.24845	0
261	6	-26.39523	30.24514	-0.4	Edge	Edge	-26.39264	30.24843	0
262	7	-26.39485	30.24467	-0.5	Edge	Edge	-26.39346	30.24842	0
263	8	-26.39446	30.24437	-0.3	Edge	Edge	-26.39389	30.24841	0
264	9	-26.39374	30.24358	-0.4	Edge	Edge	-26.39503	30.24827	0
265	10	-26.39326	30.24297	-0.3	Edge	Edge	-26.39590	30.24807	0
266	11	-26.39302	30.24255	-0.4	Edge	Edge	-26.39751	30.24777	0
267	12	-26.39260	30.24190	-0.4	Edge	Edge	-26.39854	30.24737	0
268	13	-26.39229	30.24156	-0.3	Edge	Edge	-26.39907	30.24717	0
269	14	-26.39200	30.24091	-0.3	Edge	Edge	-26.39986	30.24673	0
270	15	-26.39242	30.24100	-0.3	Edge	Edge	-26.40031	30.24618	0
271	16	-26.39283	30.24084	-0.3	Edge	Edge	-26.40099	30.24570	0
272	17	-26.39339	30.24072	-0.3	Edge	Edge	-26.40109	30.24514	0
273	18	-26.39376	30.24065	-0.3	Edge	Edge	-26.40087	30.24428	0
274	19	-26.39415	30.24075	-0.3	Edge	Edge	-26.40082	30.24352	0
275	20	-26.39480	30.24086	-0.3	Edge	Edge	-26.40083	30.24256	0
276	21	-26.39561	30.24120	-0.3	Edge	Edge	-26.40066	30.24190	0
277	22	-26.39602	30.24119	-0.3	Edge	Edge	-26.40058	30.24115	0
278	23	-26.39614	30.24124	-0.4	Edge	Edge	-26.40041	30.24051	0
279	24	-26.39631	30.24119	-0.3	Edge	Edge	-26.39978	30.23976	0
280	25	-26.39639	30.24115	-0.4	Edge	Edge	-26.39911	30.23891	0
281	26	-26.39668	30.24115	-0.3	Edge	Edge	-26.39822	30.23832	0
282	27	-26.39691	30.24140	-0.3	Edge	Edge	-26.39751	30.23804	0
283	28	-26.39724	30.24228	-0.4	Edge	Edge	-26.39631	30.23837	0
284	29	-26.39733	30.24281	-0.4	Edge	Edge	-26.39567	30.23837	0
285	30	-26.39725	30.24303	-0.4	Edge	Edge	-26.39468	30.23806	0
286	31	-26.39701	30.24324	-0.4	Edge	Edge	-26.39376	30.23785	0
287	32	-26.39672	30.24361	-0.4	Edge	Edge	-26.39265	30.23792	0
288	33	-26.39637	30.24377	-0.4	Edge	Edge	-26.39171	30.23809	0
289	34	-26.39571	30.24435	-0.4	Edge	Edge	-26.39040	30.23839	0
290	35	-26.39533	30.24452	-0.4	Edge	Edge	-26.38949	30.23929	0
291	36	-26.39517	30.24460	-0.4	Edge	Edge	-26.38866	30.24006	0
292	37	-26.39504	30.24486	-0.4	Edge	Edge	-26.38791	30.24092	0
293	38	-26.39494	30.24507	-0.4	Edge	Edge	-26.38712	30.24211	0
294	39	-26.39493	30.24510	-0.4					
295	40	-26.39470	30.24533	-0.4					
296	41	-26.39437	30.24553	-0.4					
297	42	-26.39412	30.24572	-0.3					
298	43	-26.39384	30.24585	-0.3					
299	44	-26.39323	30.24600	-0.4					
300	45	-26.39254	30.24628	-0.3					
301	46	-26.39237	30.24610	-0.4					
302	47	-26.39223	30.24596	-0.4					
303	48	-26.39213	30.24589	-0.3					
304	49	-26.39184	30.24555	-0.4					
305	50	-26.39140	30.24519	-0.4					
306	51	-26.39120	30.24504	-0.3					
307	52	-26.39084	30.24477	-0.3					
308	53	-26.39063	30.24458	-0.3					
309	54	-26.39027	30.24435	-0.3					
310	55	-26.38995	30.24420	-0.3					
311	56	-26.38968	30.24402	-0.3					
312	57	-26.38955	30.24455	-0.3					
313	58	-26.38971	30.24476	-0.3					
314	59	-26.39000	30.24530	-0.3					
315	60	-26.39026	30.24577	-0.4					
316	61	-26.39049	30.24605	-0.3					
317	62	-26.39078	30.24638	-0.3					
318	63	-26.39094	30.24665	-0.3					
319	64	-26.39116	30.24695	-0.3					
320	65	-26.39156	30.24724	-0.3					
321	66	-26.39199	30.24753	-0.3					
322	67	-26.39238	30.24787	-0.3					
323	68	-26.39277	30.24813	-0.3					
324	69	-26.39330	30.24818	-0.36					
325	70	-26.39356	30.24811	-0.35					
326	71	-26.39379	30.24808	-0.37					
Edge	Edge	-26.38653	30.24321	0					
Edge	Edge	-26.38653	30.24411	0					
Edge	Edge	-26.38642	30.24471	0					
Edge	Edge	-26.38631	30.24533	0					
Edge	Edge	-26.38658	30.24567	0					
Edge	Edge	-26.38701	30.24619	0					
Edge	Edge	-26.38798	30.24680	0					

MDM Bathymetry Data															
Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth
30	-26.3773	30.28106	-1	110	-26.3756	30.29145	-1.2	190	-26.3785	30.28187	-1.2	Edge	-26.38551	30.29037	0
31	-26.3774	30.28141	-1.1	111	-26.3755	30.2912	-1.3	191	-26.3788	30.28214	-1.2	Edge	-26.38667	30.28916	0
32	-26.3772	30.28171	-1.2	112	-26.3754	30.29064	-1.2	192	-26.379	30.28248	-1.2	Edge	-26.38735	30.28815	0
33	-26.3771	30.28195	-1	113	-26.3753	30.29024	-1.2	193	-26.3794	30.28295	-1.2	Edge	-26.38768	30.28764	0
34	-26.3769	30.2822	-1	114	-26.3752	30.28994	-1.3	194	-26.3796	30.28327	-1.2	Edge	-26.38809	30.28665	0
35	-26.3767	30.28257	-1.3	115	-26.3751	30.28954	-1.2	195	-26.3798	30.28356	-1.2	Edge	-26.38816	30.28559	0
36	-26.3765	30.28278	-1.1	116	-26.375	30.28926	-1.3	196	-26.38	30.28398	-1.3	Edge	-26.38780	30.28455	0
37	-26.3763	30.28312	-1.3	117	-26.3748	30.28876	-1.4	197	-26.3801	30.28418	-1.2	Edge	-26.38745	30.28424	0
38	-26.376	30.28349	-1.3	118	-26.3747	30.28837	-1.3	198	-26.3803	30.28449	-1.2	Edge	-26.38707	30.28405	0
39	-26.3758	30.28379	-1.3	119	-26.3746	30.28806	-1.2	199	-26.3805	30.28501	-1.3	Edge	-26.38673	30.28407	0
40	-26.3755	30.28432	-1.2	120	-26.3744	30.28764	-1.3	200	-26.3807	30.28529	-1.4	Edge	-26.38631	30.28424	0
41	-26.3753	30.28471	-1.3	121	-26.3741	30.28726	-1.3	201	-26.3808	30.28551	-1.2	Edge	-26.38593	30.28431	0
42	-26.3751	30.28521	-1.3	122	-26.3739	30.28661	-1.3	202	-26.3811	30.28601	-1.2	Edge	-26.38563	30.28428	0
43	-26.3749	30.28547	-1.2	123	-26.3738	30.28625	-1.2	203	-26.3812	30.28635	-1.3	Edge	-26.38530	30.28410	0
44	-26.3748	30.28579	-1.3	124	-26.3735	30.28549	-1.2	204	-26.3814	30.28674	-1.2	Edge	-26.38490	30.28406	0
45	-26.3746	30.28609	-1.3	125	-26.3733	30.28504	-1.2	205	-26.3816	30.28693	-1.3	Edge	-26.38428	30.28372	0
46	-26.3742	30.28657	-1.3	126	-26.3733	30.28482	-1.1	206	-26.3817	30.28718	-1.2	Edge	-26.38389	30.28343	0
47	-26.3741	30.28687	-1.3	127	-26.3732	30.28463	-1.3	207	-26.382	30.28764	-1.3	Edge	-26.38363	30.28299	0
48	-26.374	30.28716	-1.3	128	-26.3731	30.28444	-1.2	208	-26.3822	30.28806	-1.3	Edge	-26.38320	30.28266	0
49	-26.3738	30.28748	-1.2	129	-26.373	30.2842	-0.9	209	-26.3824	30.28839	-1.3	Edge	-26.38275	30.28241	0
50	-26.3736	30.28774	-1.3	130	-26.373	30.2841	-0.5	210	-26.3827	30.28902	-1.3	Edge	-26.38229	30.28174	0
51	-26.3734	30.28817	-1.3	131	-26.3731	30.2842	-0.7	211	-26.3829	30.28933	-1.2	Edge	-26.38174	30.28106	0
52	-26.3732	30.2884	-1.3	132	-26.3733	30.28432	-1.2	212	-26.383	30.28967	-1.2	Edge	-26.38125	30.28057	0
53	-26.3731	30.28879	-1.3	133	-26.3736	30.2847	-1.2	213	-26.3832	30.28993	-1.2	Edge	-26.38068	30.28026	0
54	-26.3729	30.28921	-1.2	134	-26.3738	30.28496	-1.1	214	-26.3833	30.2901	-1.3	Edge	-26.37992	30.28018	0
55	-26.3727	30.28963	-1.3	135	-26.3739	30.28512	-1.2	215	-26.3833	30.29024	-1.2	Edge	-26.37901	30.28021	0
56	-26.3724	30.29001	-1.3	136	-26.3741	30.28535	-1.2	216	-26.3836	30.29066	-1	Edge	-26.37801	30.28032	0
57	-26.3722	30.29068	-1.3	137	-26.3743	30.28559	-1.2	217	-26.3838	30.29049	-1	Edge	-26.37653	30.28072	0
58	-26.372	30.29097	-1.2	138	-26.3745	30.28584	-1.2	218	-26.3839	30.29031	-1.1	Edge	-26.37529	30.28111	0
59	-26.3719	30.29106	-1.1	139	-26.3749	30.28631	-1.3	219	-26.384	30.29007	-1.2	Edge	-26.37449	30.28139	0
60	-26.3719	30.29119	-0.8	140	-26.3751	30.28648	-1.2	220	-26.384	30.28986	-1.2	Edge	-26.37292	30.28259	0
61	-26.3724	30.29155	-0.4	141	-26.3754	30.28683	-1.3	221	-26.3842	30.28955	-1.2	Edge	-26.37257	30.28306	0
62	-26.3725	30.29158	-0.5	142	-26.3757	30.28724	-1.3	222	-26.3842	30.28896	-1.2	Edge	-26.37236	30.28335	0
63	-26.3727	30.2916	-0.8	143	-26.3759	30.28753	-1.3	223	-26.3844	30.28851	-1.2	Edge	-26.37187	30.28376	0
64	-26.373	30.2917	-0.8	144	-26.3762	30.2878	-1.3	224	-26.3845	30.2881	-1.2	Edge	-26.37141	30.28465	0
65	-26.3733	30.2919	-0.6	145	-26.3765	30.28812	-1.3	225	-26.3846	30.28777	-1.2	Edge	-26.37121	30.28538	0
66	-26.3734	30.29177	-0.9	146	-26.3769	30.28856	-1.3	226	-26.3847	30.28742	-1.3	Edge	-26.37113	30.28598	0
67	-26.3733	30.29151	-1.2	147	-26.3773	30.28895	-1.3	227	-26.3848	30.28716	-1.2	Edge	-26.37092	30.28650	0
68	-26.3732	30.29132	-1.3	148	-26.3775	30.28918	-1.3	228	-26.3849	30.28669	-1.2	Edge	-26.37073	30.28716	0
69	-26.3731	30.29101	-1.2	149	-26.3783	30.29	-1.3	229	-26.385	30.28628	-1.2	Edge	-26.37054	30.28809	0
70	-26.373	30.29076	-1.3	150	-26.3787	30.29032	-1.3	230	-26.385	30.28583	-1.2	Edge	-26.37038	30.28878	0
71	-26.3728	30.29043	-1.3	151	-26.3791	30.29061	-1.3	231	-26.3851	30.28549	-1.2				
72	-26.3727	30.29022	-1.3	152	-26.3797	30.29097	-1.3	232	-26.385	30.28519	-1.2				
73	-26.3725	30.28995	-1.3	153	-26.3802	30.29137	-1.3	233	-26.385	30.2847	-1.2				
74	-26.3724	30.28966	-1.3	154	-26.3806	30.29163	-1.3	234	-26.3853	30.28484	-1.1				
75	-26.3722	30.28951	-1.2	155	-26.3812	30.29167	-1.2	235	-26.3856	30.28506	-1.1				
76	-26.3722	30.28938	-1.3	156	-26.3812	30.29132	-1.2	236	-26.3861	30.2853	-1.1				
77	-26.372	30.28908	-1.3	157	-26.3811	30.29086	-1.3	237	-26.3862	30.28541	-1.2				
78	-26.3719	30.28886	-1	158	-26.381	30.29045	-1.3	238	-26.3864	30.28556	-1.2				
79	-26.3718	30.28875	-1.2	159	-26.3809	30.28998	-1.3	239	-26.3866	30.28575	-1.2				
80	-26.3717	30.28858	-0.8	160	-26.3808	30.28967	-1.3	240	-26.3867	30.28593	-1.2				
81	-26.3716	30.28847	-0.8	161	-26.3807	30.28928	-1.3	241	-26.3868	30.28603	-1.3				
82	-26.3716	30.28838	-0.8	162	-26.3806	30.28892	-1.3	242	-26.387	30.28617	-1.2				
83	-26.3715	30.28835	-0.6	163	-26.3805	30.28852	-1.3	243	-26.3871	30.28625	-1.2				
84	-26.3716	30.28828	-0.3	164	-26.3805	30.28816	-1.3	244	-26.3873	30.2861	-0.8				
85	-26.3714	30.28821	-0.4	165	-26.3804	30.28765	-1.3	245	-26.3873	30.28597	-0.7				
86	-26.3716	30.28842	-0.6	166	-26.3803	30.2873	-1.3	246	-26.3874	30.28582	-0.7				
87	-26.3716	30.28848	-0.8	167	-26.3802	30.28691	-1.3	247	-26.3873	30.28578	-0.6				
88	-26.3718	30.28871	-0.9	168	-26.3801	30.28654	-1.3	248	-26.387	30.28564	-1.1				
89	-26.3719	30.28872	-1.1	169	-26.3799	30.28604	-1.3	249	-26.3866	30.28571	-1.2				
90	-26.372	30.28855	-1.3	170	-26.3798	30.28571	-1.3	250	-26.3861	30.28574	-1.3				
91	-26.372	30.28833	-1.2	171	-26.3797	30.28544	-1.3	251	-26.3857	30.28555	-1.3				
92	-26.3721	30.28841	-1	172	-26.3796	30.28507	-1.3	252	-26.3846	30.28545	-1.3				
93	-26.3723	30.28853	-1.2	173	-26.3794	30.28475	-1.3	253	-26.3843	30.28538	-1.3				
94	-26.3725	30.28885	-1.2	174	-26.3792	30.28441	-1.3	254	-26.3841	30.28542	-1.2				
95	-26.3727	30.28905	-1.2	175	-26.3789	30.28386	-1.3	255	-26.3838	30.2855	-1.3				
96	-26.3729	30.28934	-1.2	176	-26.3786	30.28323	-1.3	Edge	-26.36998	30.28923	0				
97	-26.3732	30.28964	-1.2	177	-26.3785	30.28287	-1.3	Edge	-26.36995	30.28987	0				
98	-26.3734	30.28986	-1.2	178	-26.3784	30.28254	-1.2	Edge	-26.37026	30.29048	0				
99	-26.3736	30.29014	-1.2	179	-26.3783	30.28221	-1.1	Edge	-26.37079	30.29108	0				
100	-26.3738	30.29032	-1.2	180	-26.3782	30.28184	-1	Edge	-26.37218	30.29194	0				
101	-26.3742	30.29076	-1.3	181	-26.3783	30.28168	-1.1	Edge	-26.37356	30.29260	0				
102	-26.3745	30.29103	-1.2	182	-26.3782	30.28147	-1.2	Edge	-26.37502	30.29296	0				
103	-26.3749	30.29139	-1.2	183	-26.3781	30.28126	-1.1	Edge	-26.37622	30.29307	0				
104	-26.3752	30.29171	-1.2	184	-26.3778	30.28088	-1.1	Edge	-26.37737	30.29312	0				
105	-26.3754	30.29207	-1.2	185	-26.3777	30.28073	-0.9	Edge	-26.37833	30.29313	0				
106	-26.3756	30.29228	-1.1	186	-26.3777	30.28069	-0.7	Edge	-26.37979	30.29294	0				
107	-26.3756	30.29236	-0.9	187	-26.3778	30.28092	-1.1	Edge	-26.38159	30.29250	0				
108	-26.3758	30.29227	-1	188	-26.3782	30.28155	-1.1	Edge	-26.38298	30.29199	0				
109	-26.3757	30.29187	-1.2	189	-26.3784	30.28175	-1	Edge	-26.38427	30.29129	0				

TPE Bathymetry Data

Label	Latitude	Longitude	Depth	Label	Latitude	Longitude	Depth
1	-26.35812	30.25024	-1.7	81	-26.35595	30.25110	0
2	-26.35807	30.25092	-2.0	82	-26.35541	30.25170	0
3	-26.35807	30.25121	-2.1	83	-26.35517	30.25248	0
4	-26.35806	30.25147	-2.1	84	-26.35513	30.25274	0
5	-26.35807	30.25198	-2.2	85	-26.35503	30.25302	0
6	-26.35806	30.25240	-2.3	86	-26.35501	30.25336	0
7	-26.35805	30.25266	-2.3	87	-26.35504	30.25376	0
8	-26.35801	30.25321	-2.2	88	-26.35504	30.25418	0
9	-26.35800	30.25381	-2.2	89	-26.35502	30.25458	0
10	-26.35807	30.25429	-2.3	90	-26.35506	30.25495	0
11	-26.35816	30.25490	-2.2	91	-26.35511	30.25519	0
12	-26.35825	30.25530	-2.2	92	-26.35534	30.25548	0
13	-26.35839	30.25565	-2.1	93	-26.35561	30.25572	0
14	-26.35849	30.25589	-2.2	94	-26.35586	30.25589	0
15	-26.35859	30.25610	-2.1	95	-26.35622	30.25603	0
16	-26.35863	30.25623	-2.0	96	-26.35662	30.25617	0
17	-26.35863	30.25631	-1.7	97	-26.35703	30.25629	0
18	-26.35842	30.25618	-1.8	98	-26.35794	30.25638	0
19	-26.35806	30.25605	-2.0	99	-26.35848	30.25635	0
20	-26.35762	30.25583	-2.3	100	-26.35916	30.25626	0
21	-26.35724	30.25568	-2.2	101	-26.35991	30.25605	0
22	-26.35694	30.25552	-2.2	102	-26.36033	30.25589	0
23	-26.35644	30.25530	-2.1	103	-26.36075	30.25570	0
24	-26.35602	30.25512	-2.0	104	-26.36103	30.25554	0
25	-26.35580	30.25495	-2.0	105	-26.36141	30.25525	0
26	-26.35550	30.25485	-1.9	106	-26.36168	30.25496	0
27	-26.35535	30.25470	-1.9	107	-26.36181	30.25474	0
28	-26.35520	30.25457	-1.9	108	-26.36185	30.25445	0
29	-26.35514	30.25446	-1.8	109	-26.36176	30.25427	0
30	-26.35555	30.25446	-2.2	110	-26.36176	30.25396	0
31	-26.35588	30.25446	-2.0	111	-26.36178	30.25375	0
32	-26.35623	30.25447	-2.1	112	-26.36170	30.25298	0
33	-26.35680	30.25444	-2.1	113	-26.36157	30.25266	0
34	-26.35728	30.25438	-2.2	114	-26.36150	30.25233	0
35	-26.35769	30.25434	-2.3	115	-26.36135	30.25198	0
36	-26.35817	30.25426	-2.2	116	-26.36128	30.25169	0
37	-26.35862	30.25417	-2.3	117	-26.36129	30.25144	0
38	-26.35919	30.25400	-2.3	118	-26.36113	30.25096	0
39	-26.35999	30.25381	-2.4	119	-26.36101	30.25062	0
40	-26.36019	30.25373	-2.2	120	-26.36082	30.25028	0
41	-26.36073	30.25345	-2.2	121	-26.36054	30.25001	0
42	-26.36120	30.25322	-2.2	122	-26.36026	30.24993	0
43	-26.36147	30.25312	-1.9	123	-26.35980	30.24984	0
44	-26.36117	30.25307	-2.2				
45	-26.36082	30.25298	-2.3				
46	-26.36041	30.25290	-2.2				
47	-26.36002	30.25274	-2.2				
48	-26.35932	30.25256	-2.2				
49	-26.35862	30.25240	-2.3				
50	-26.35807	30.25230	-2.2				
51	-26.35750	30.25220	-2.1				
52	-26.35698	30.25215	-2.2				
53	-26.35658	30.25212	-2.1				
54	-26.35611	30.25200	-2.0				
55	-26.35572	30.25191	-1.9				
56	-26.35557	30.25185	-1.9				
57	-26.35581	30.25174	-2.0				
58	-26.35618	30.25164	-2.0				
59	-26.35690	30.25158	-2.0				
60	-26.35732	30.25150	-2.1				
61	-26.35769	30.25148	-2.1				
62	-26.35794	30.25141	-2.2				
63	-26.35843	30.25141	-2.2				
64	-26.35894	30.25137	-2.2				
65	-26.35943	30.25134	-2.2				
66	-26.36008	30.25122	-2.1				
67	-26.36048	30.25115	-2.2				
68	-26.36079	30.25107	-2.2				
69	-26.36104	30.25101	-1.4				
70	-26.36064	30.25103	-2.1				
71	-26.36024	30.25076	-2.1				
72	-26.35977	30.25043	-2.0				
73	-26.35940	30.25016	-1.8				
74	-26.35946	30.24987	0				
75	-26.35894	30.24991	0				
76	-26.35844	30.24992	0				
77	-26.35785	30.25000	0				
78	-26.35730	30.25012	0				
79	-26.35680	30.25033	0				
80	-26.35643	30.25057	0				

Appendix 2: Major Elements Data

CM Majors %																
Sample no.	CM Depth	Age	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	Cr2O3	NiO	LOI	Total
1	CM0	2017	54.55	20.64	7.79	0.13	3.76	2.21	3.45	2.97	0.78	0.23	0.03	0.01	3.35	99.89
2	CM2.5	2016	57.04	19.98	7.58	0.14	3.63	2.3	2.59	3.04	0.82	0.21	0.04	0.01	3	100.38
3	CM5	2013	57.2	20.07	7.55	0.14	3.5	2.09	2.46	3.04	0.84	0.19	0.04	0.01	2.8	99.91
4	CM8	2009	58.19	19.25	7.18	0.13	3.34	1.91	2.18	3.03	0.8	0.16	0.03	0.01	2.96	99.18
5	CM10.5	2005	57.15	20.1	7.73	0.13	3.53	1.59	2.23	3.07	0.79	0.15	0.03	0.01	3.13	99.66
6	CM13	1996	58.71	19.74	7.52	0.14	3.44	1.2	1.53	3.14	0.89	0.13	0.03	0.01	2.97	99.45
7	CM14	1988	60.76	19.95	7.35	0.14	3.58	1.15	1.14	3.27	0.94	0.11	0.03	0.01	1.3	99.73
8	CM15	1979	61.12	20.09	7.27	0.13	3.63	1.2	1.06	3.35	0.96	0.1	0.03	0.01	1.07	100.02
9	CM16	1969	60.91	19.7	7.09	0.13	3.61	1.89	0.94	3.27	0.88	0.09	0.02	0.01	1.35	99.89
10	CM17	1960	59.84	19.91	7.33	0.12	3.73	2.15	0.97	3.32	0.87	0.09	0.03	0.01	1.46	99.83
11	CM18	1949	59.38	20.16	7.39	0.12	3.80	2.21	0.92	3.36	0.88	0.09	0.03	0.01	1.76	100.09
12	CM19	1937	59.00	20.31	7.42	0.12	3.87	2.36	0.90	3.33	0.87	0.10	0.03	0.01	1.53	99.84
13	CM20	1924	58.89	19.77	7.22	0.12	3.87	2.45	0.89	3.37	0.88	0.10	0.03	0.01	1.78	99.37
14	CM21	1910	58.58	18.96	6.82	0.13	4.02	3.28	0.93	3.33	0.87	0.10	0.04	0.01	2.85	99.90
15	CM22	1901	59.13	17.57	6.25	0.13	3.92	5.21	0.89	2.98	0.80	0.10	0.03	0.01	2.86	99.88
16	CM23	1888	58.34	17.60	6.24	0.13	3.92	5.01	0.86	2.99	0.78	0.09	0.03	0.01	3.22	99.21

HBP Majors %															
Sample no.	HBP Depth	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	Cr2O3	NiO	LOI	Total
1	HBP0	59.05	23.07	6.29	0.10	2.43	1.74	1.08	3.24	1.08	0.10	0.03	0.01	1.43	99.66
2	HBP2	58.12	23.51	6.40	0.09	2.55	2.25	1.17	3.28	1.06	0.10	0.04	0.01	1.37	99.95
3	HBP4	56.50	23.17	6.30	0.09	2.57	2.47	1.30	3.26	1.02	0.10	0.03	0.01	1.47	98.28
4	HBP6	57.05	23.68	6.36	0.09	2.61	2.59	1.49	3.26	1.02	0.10	0.03	0.01	1.68	99.96
5	HBP8	57.27	23.36	6.21	0.09	2.56	2.66	1.57	3.24	1.04	0.10	0.03	0.01	1.85	99.98
6	HBP10	57.06	22.79	6.02	0.08	2.50	2.68	1.58	3.20	1.06	0.10	0.03	0.01	2.02	99.11
7	HBP12	57.22	23.11	6.01	0.09	2.59	2.59	1.61	3.27	1.05	0.10	0.03	0.01	2.29	99.97

MDM Majors %															
Sample no.	MDM depth	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	Cr2O3	NiO	LOI	Total
1	MDM0	54.71	20.98	7.29	0.13	4.53	1.82	2.32	3.08	0.92	0.19	0.04	0.01	3.77	99.80
2	MDM2	57.10	19.41	6.55	0.13	4.21	2.69	1.65	3.19	0.96	0.16	0.05	0.01	3.62	99.73
3	MDM4	60.16	16.44	5.12	0.12	4.30	3.90	1.06	3.25	0.87	0.12	0.03	0.01	4.27	99.64
4	MDM6	55.82	16.89	5.46	0.12	5.54	5.18	0.95	3.37	0.81	0.10	0.02	0.01	5.55	99.82
5	MDM8	54.03	17.40	5.79	0.12	6.04	5.54	0.99	3.43	0.80	0.10	0.03	0.01	6.22	100.51
6	MDM10	53.34	16.85	5.68	0.12	5.89	5.89	0.99	3.39	0.78	0.10	0.02	0.01	6.90	99.96
7	MDM12	53.58	17.26	5.82	0.13	5.91	6.72	1.04	3.41	0.80	0.10	0.03	0.01	5.12	99.92
8	MDM14	53.71	17.48	5.93	0.13	5.90	6.57	1.08	3.46	0.81	0.10	0.02	0.01	4.95	100.16
9	MDM16	54.02	17.31	5.89	0.12	5.72	6.78	1.09	3.41	0.81	0.11	0.03	0.01	5.07	100.36
10	MDM18	53.31	17.75	6.06	0.12	5.98	6.44	1.15	3.48	0.84	0.09	0.03	0.01	5.03	100.29
11	MDM20	53.19	17.35	5.94	0.12	5.61	6.60	1.13	3.40	0.81	0.09	0.03	0.01	5.71	99.99

TPE Majors %															
Sample no.	TPE depth	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	Cr2O3	NiO	LOI	Total
1	TPE0	66.92	22.73	4.46	0.07	0.82	0.86	0.14	1.77	0.99	0.10	0.03	0.01	1.16	100.05
2	TPE2	66.76	22.74	4.43	0.07	0.86	0.89	0.13	1.77	0.99	0.10	0.03	0.01	0.98	99.75
3	TPE4	68.29	22.15	4.16	0.05	0.78	0.78	0.12	1.72	0.95	0.10	0.03	0.02	0.91	100.04
4	TPE6	68.02	22.41	4.15	0.04	0.74	0.74	0.12	1.71	0.95	0.11	0.03	0.01	0.87	99.89
5	TPE8	67.74	22.54	4.15	0.04	0.69	0.71	0.12	1.70	0.95	0.11	0.04	0.01	0.85	99.65
6	TPE10	69.13	21.76	3.87	0.04	0.66	0.67	0.12	1.61	0.91	0.14	0.03	0.01	1.01	99.95

Appendix 3: LOI and Grain Size Data

CM Age, LOI and Grain Size Analysis										
Sample nc	depth	age (yrs)	% Organic	% Carbona	% Clay	% Silt	% Sand	Mean size	Skewness	Kurtosis
1	0-0.5	2017	20.103	3.351	2.21	24.25	73.54	3	0.25	1.07
6	2.5-3	2016	16.237	2.999	2.42	21.77	75.81	2.83	0.38	1.06
9	4-4.5	2014	16.007	2.911	2.26	23.85	76.15	2.83	0.37	1.07
11	5-5.5	2013	16.115	2.802	2.86	25.24	71.9	3.08	0.34	1.02
13	6-6.5	2012	16.36	2.872	2.33	21.52	76.15	2.8	0.37	1.06
15	7-7.5	2010	16.09	2.934	3.23	24.38	72.39	3	0.39	1.02
17	8-8.5	2009	15.846	2.957	3.75	28.33	67.92	3.25	0.39	0.94
19	9-9.5	2007	15.438	2.966	2.73	23.31	73.96	2.9	0.37	1.03
22	10.5-11	2005	15.369	3.126	3.24	27.43	69.33	3.2	0.36	0.99
24	11.5-12	2002	14.265	3.312	2.38	22.83	74.79	2.85	0.38	1.02
26	12.5-13	1999	12.471	2.757	2.21	21.5	76.26	2.75	0.38	1.04
27	13-13.5	1996	11.712	2.972	3.7	27.66	68.64	3.16	0.34	0.96
29	14-14.5	1988	2.705	1.3	4.12	30.12	65.76	3.36	0.34	0.97
31	15-15.5	1979	3.111	1.069	3.69	29.41	70.48	3.18	0.31	0.95
32	15.5-16	1974	4.307	1.242	3.33	30.79	65.88	3.19	0.27	0.9
33	16-16.5	1969	3.959	1.347	2.88	29.53	67.59	3.1	0.23	0.92
34	16.5-17	1964	4.111	1.382	3.19	31.07	65.74	3.31	0.28	0.94
35	17-17.5	1960	3.901	1.463	4.47	41.69	53.84	3.92	0.17	0.95
36	17.5-18	1955	4.553	1.482	3.17	29.52	67.04	3.14	0.28	0.9
37	18-18.5	1949	4.961	1.76	3.98	33.9	62.42	3.41	0.22	0.9
38	18.5-19	1943	5.108	1.452	3.42	29.55	67.03	3.14	0.26	0.91
39	19-19.5	1937	5.448	1.526	3.48	27.91	68.61	3.04	0.29	0.92
40	19.5-20	1930	5.493	1.619	2.66	23.83	73.54	2.61	0.35	0.9
41	20-20.5	1924	5.315	1.784	3.63	28.95	67.42	3.01	0.32	0.88
42	20.5-21	1917	5.295	2.069	3.61	31.97	64.32	3.18	0.19	0.89
43	21-21.5	1910	4.969	2.848	3.8	37.8	58.4	3.63	0.13	0.96
44	21.5-22	1906	5.159	3.247	3.1	28.96	67.94	3.13	0.19	0.97
45	22-22.5	1901	4.749	2.863	4.05	29.84	66.11	3.35	0.27	1
46	22.5-23	1894	5.614	3.161	2.74	23.62	73.64	2.93	0.31	1.03
47	23-23.5	1888	5.55	3.219	3.02	24.04	72.94	2.9	0.33	1.01
48	23.5-24	1883	5.492	3.781	2.8	25.36	71.84	2.95	0.26	0.99
49	24-24.5	1878	5.669	3.493	2.62	23.27	74.11	2.83	0.26	1.03
50	24.5-25	1873	5.616	4.272	2.75	22.72	74.53	2.8	0.32	1.01
51	25-25.5	1868	5.767	3.53	3.25	23.56	73.19	2.86	0.32	1.01
52	25.5-26	1863	5.775	3.322	2.86	21.97	75.17	2.7	0.36	1.01
53	26-26.5	1858	5.918	3.47	2.69	21.27	76.04	2.66	0.37	1
54	26.5-27	1853	6.143	3.617	2.08	18.32	79.6	2.32	0.31	1.01
55	27-27.5	1848	6.195	3.59	3.65	29.08	67.27	3.17	0.2	0.97
56	27.5-28	1843	5.96	3.467	2.71	21.61	75.68	2.64	0.3	1
57	28-28.5	1838	8.682	3.588	3.08	23.56	73.36	2.78	0.33	0.96
58	28.5-29	1833	8.666	3.425	4.48	33.85	61.67	3.72	0.37	1
59	29-29.5	1828	8.772	3.39	2.04	16.76	81.2	2.13	0.43	1.02

HBP LOI and Grain Size Analysis

Sample nc	depth	depth	% Organic	% Carbona	% Clay	% Silt	% Sand	Mean size	Skewness	Kurtosis
1	0-0.5	0-0.5	11.898	1.435	4.67	35.24	60.09	3.75	0.31	0.97
2	0.5-1	0.5-1	12.086	1.294	4.33	31.12	64.5	3.48	0.35	0.97
3	1-1.5	1-1.5	12.712	1.292	4.71	32.08	63.21	3.5	0.3	0.96
4	1.5-2	1.5-2	13.221	1.366	4.34	30.39	65.27	3.37	0.31	0.96
5	2-2.5	2-2.5	12.701	1.367	4.98	34.12	60.9	3.64	0.28	0.95
6	2.5-3	2.5-3	19.690	1.237	3.56	28.21	68.23	3.13	0.29	0.94
7	3-3.5	3-3.5	14.983	1.346	3.9	28.57	67.53	3.16	0.3	0.93
8	3.5-4	3.5-4	12.258	1.489	4.84	33.59	61.57	3.56	0.27	0.93
9	4-4.5	4-4.5	14.536	1.466	4.43	31.66	63.91	3.41	0.29	0.93
10	4.5-5	4.5-5	16.079	1.428	3.51	26.02	70.47	2.9	0.32	0.93
11	5-5.5	5-5.5	14.160	1.497	4.5	31.65	63.85	3.42	0.3	0.92
12	5.5-6	5.5-6	13.766	1.578	3.4	26.24	70.36	2.89	0.28	0.94
13	6-6.5	6-6.5	10.716	1.684	4.92	33.93	61.15	3.62	0.3	0.93
14	6.5-7	6.5-7	10.738	1.656	3.74	27.89	68.37	3.06	0.3	0.91
15	7-7.5	7-7.5	10.538	1.680	3.89	28.21	67.9	3.1	0.32	0.91
16	7.5-8	7.5-8	10.560	1.787	3.91	28.36	67.73	3.12	0.29	0.92
17	8-8.5	8-8.5	10.392	1.846	5.62	37.06	57.32	3.82	0.26	0.91
18	8.5-9	8.5-9	11.631	1.730	3.78	28.93	67.29	3.12	0.26	0.92
19	9-9.5	9-9.5	10.589	1.814	3.9	29.48	66.62	3.23	0.29	0.92
20	9.5-10	9.5-10	12.860	1.314	3.52	28.5	67.98	3.14	0.3	0.92
21	10-10.5	10-10.5	10.429	2.017	4.16	31.59	64.25	3.44	0.31	0.94
22	10.5-11	10.5-11	10.616	1.921	4.28	31.41	64.31	3.4	0.3	0.92
23	11-11.5	11-11.5	10.582	1.925	4.29	31.3	64.41	3.4	0.32	0.92
24	11.5-12	11.5-12	10.561	2.017	3.3	26.48	70.22	3.02	0.34	0.94
25	12-12.5	12-12.5	10.428	2.287	4.94	34.06	61	3.66	0.3	0.95
26	12.5-13	12.5-13	10.538	2.152	3.12	27.04	69.84	3.06	0.33	0.94
27	13-13.5	13-13.5	10.389	2.162	4.03	31.77	64.2	3.39	0.27	0.93
28	13.5-14	13.5-14	10.587	2.246	3.48	26.48	70.04	3	0.36	0.94

MDM LOI and Grain Size Analysis

Sample nc	depth	depth	% Organic	% Carbona	% Clay	% Silt	% Sand	Mean size	Skewness	Kurtosis
1	0-0.5	0-0.5	15.173	3.774	1.11	15.35	83.54	2.32	0.34	1.04
3	1-1.5	1-1.5	14.474	3.608	1.32	15.5	83.18	2.11	0.37	1.03
4	1.5-2	1.5-2	14.496	3.688	1.34	14.13	84.53	1.89	0.45	1.1
5	2-2.5	2-2.5	14.447	3.624	1.86	17.99	80.15	2.29	0.43	1.03
6	2.5-3	2.5-3	14.721	3.549	1.89	16.32	81.79	2.12	0.46	1.09
7	3-3.5	3-3.5	14.640	3.513	2.15	18.49	79.36	2.3	0.39	1.03
8	3.5-4	3.5-4	13.546	3.573	2.13	17.25	80.62	2.11	0.4	1.02
9	4-4.5	4-4.5	9.964	4.271	2.41	20.92	76.67	2.5	0.37	0.98
10	4.5-5	4.5-5	8.687	4.809	1.58	16.19	82.13	2.02	0.37	1.04
11	5-5.5	5-5.5	8.271	5.262	1.26	17.38	80.84	2.12	0.18	1
12	5.5-6	5.5-6	8.764	5.300	1.18	16.86	81.51	2.09	0.18	0.99
13	6-6.5	6-6.5	8.992	5.548	1.38	15.53	83.09	2.1	0.3	1.04
14	6.5-7	6.5-7	9.012	5.579	0.83	14.53	84.36	1.92	0.21	0.99
15	7-7.5	7-7.5	9.116	5.721	0.63	13.24	85.96	1.87	0.27	1.03
16	7.5-8	7.5-8	9.257	5.716	0.37	10.19	89.25	1.54	0.32	1.1
17	8-8.5	8-8.5	8.887	6.216	0.66	13.46	85.82	1.92	0.3	1.02
18	8.5-9	8.5-9	8.910	6.322	0.49	12.15	87.22	1.76	0.29	1.02
19	9-9.5	9-9.5	8.800	6.305	0.7	14.39	84.8	1.99	0.27	1.01
20	9.5-10	9.5-10	8.792	6.361	0.61	10.77	88.17	1.79	0.32	1.09
21	10-10.5	10-10.5	8.382	6.903	0.79	11.91	87.3	1.75	0.36	1.09
22	10.5-11	10.5-11	8.368	6.815	0.37	10.01	89.23	1.46	0.3	1.07
23	11-11.5	11-11.5	8.462	6.788	0.59	12.65	86.39	1.73	0.26	1
24	11.5-12	11.5-12	8.381	7.074	0.41	8.76	90.22	1.26	0.32	1.09
25	12-12.5	12-12.5	9.382	5.115	1.44	14.45	84.04	1.94	0.31	1.04
26	12.5-13	12.5-13	9.504	4.989	0.6	9.46	89.5	1.29	0.39	1.12
27	13-13.5	13-13.5	9.407	4.935	0.79	12.24	86.41	1.65	0.27	1.06
28	13.5-14	13.5-14	9.496	5.055	0.89	11.33	87.14	1.55	0.3	1.1
29	14-14.5	14-14.5	9.642	4.949	1.47	12.81	85.53	1.66	0.43	1.09
30	14.5-15	14.5-15	9.903	4.950	0.77	10.63	87.94	1.44	0.31	1.08
31	15-15.5	15-15.5	9.561	5.167	1.29	12.11	86.39	1.62	0.37	1.08
32	15.5-16	15.5-16	9.587	5.130	0.84	9.83	88.16	1.25	0.32	1.08
33	16-16.5	16-16.5	9.786	5.068	1.42	11.77	86.12	1.49	0.36	1.1
34	16.5-17	16.5-17	10.116	4.720	0.78	10.07	88.35	1.29	0.37	1.1
35	17-17.5	17-17.5	9.887	4.469	1.05	11.52	86.8	1.54	0.31	1.08
36	17.5-18	17.5-18	9.956	4.641	1.54	14.99	82.75	1.81	0.26	0.99
37	18-18.5	18-18.5	9.762	5.030	0.91	10.86	87.54	1.35	0.38	1.11
38	18.5-19	18.5-19	9.699	5.190	0.74	9.99	87.41	1.01	0.42	1.06
39	19-19.5	19-19.5	9.627	5.364	0.97	11.29	87.71	1.57	0.34	1.08
40	19.5-20	19.5-20	9.161	5.547	1.4	14.68	83.9	2.02	0.28	1.05
41	20-20.5	20-20.5	8.991	5.715	1.62	15.1	82.92	1.94	0.3	1.05
42	20.5-21	20.5-21	9.100	5.604	1.66	15.58	82.14	1.95	0.24	1.04
43	21-21.5	21-21.5	9.127	5.716	1.77	16.89	81.01	2.16	0.21	1.04
44	21.5-22	21.5-22	8.680	5.825	1.6	14.99	82.32	1.79	0.2	0.98

TPE LOI and Grain Size Analysis										
Sample no.	depth	depth	% Organic	% Carbonate	% Clay	% Silt	% Sand	Mean size	Skewness	Kurtosis
1	0-0.5	0-0.5	23.453	1.157	8.15	45.9	54.63	4.47	0.2	0.94
2	0.5-1	0.5-1	23.356	1.195	7.08	40.81	52.11	4.09	0.18	0.9
3	1-1.5	1-1.5	23.971	1.102	6.44	37.65	55.91	3.83	0.19	0.88
4	1.5-2	1.5-2	23.558	1.035	6.16	35.1	58.74	3.58	0.18	0.85
5	2-2.5	2-2.5	23.376	0.984	7.42	39.01	53.57	3.97	0.17	0.89
6	2.5-3	2.5-3	23.128	0.973	6.68	38.04	55.28	3.84	0.17	0.87
7	3-3.5	3-3.5	22.186	0.899	5.65	35.37	58.98	3.56	0.17	0.87
8	3.5-4	3.5-4	23.022	0.901	5.45	34.69	59.86	3.5	0.17	0.87
9	4-4.5	4-4.5	22.836	0.906	6.35	38.57	55.03	3.82	0.13	0.9
10	4.5-5	4.5-5	22.881	0.835	5.24	32.2	62.56	3.32	0.22	0.85
11	5-5.5	5-5.5	23.283	0.862	5.53	35.49	58.89	3.51	0.12	0.9
12	5.5-6	5.5-6	23.158	0.812	5.92	37.74	56.34	3.72	0.12	0.92
13	6-6.5	6-6.5	23.343	0.868	7.65	43.35	49	4.24	0.16	0.94
14	6.5-7	6.5-7	23.161	0.845	6.86	40.74	52.4	3.98	0.12	0.92
15	7-7.5	7-7.5	22.768	0.812	5.9	35.42	58.68	3.56	0.15	0.88
16	7.5-8	7.5-8	22.527	0.946	4.97	33.92	61.11	3.47	0.17	0.91
17	8-8.5	8-8.5	22.008	0.850	6.98	40.26	52.76	4.02	0.17	0.91
18	8.5-9	8.5-9	20.672	0.924	6.71	37.27	56.02	3.84	0.2	0.89
19	9-9.5	9-9.5	19.946	0.818	6.06	33.98	59.96	3.51	0.2	0.86
20	9.5-10	9.5-10	20.227	0.919	6.04	33.05	60.91	3.49	0.25	0.86
21	10-10.5	10-10.5	19.767	1.008	7.67	41.9	50.43	4.25	0.22	0.89

Appendix 4: YSI Data

CM YSI Data							
No.	Depth	Depth	Temperature ˚C	Dissolved Oxygen %	Dissolved Oxygen mg/L	Conductivity µS/cm	pH
1	0	0	13.9	100	8.37	4936	8.43
2	0.5	0.5	13.7	99	8.21	4915	8.43
3	1	1	13.4	93	7.86	4868	8.42
HBP YSI Data							
No.	Depth	Depth	Temperature ˚C	Dissolved Oxygen %	Dissolved Oxygen mg/L	Conductivity µS/cm	pH
1	0	0	20.8	100.9	7.36	3588	9
2	0.5	0.5	20.8	97	7.09	3587	8.98
MDM YSI Data							
No.	Depth	Depth	Temperature ˚C	Dissolved Oxygen %	Dissolved Oxygen mg/L	Conductivity µS/cm	pH
1	0	0	20.8	106	7.61	4922	8.3
2	0.5	0.5	20.4	99.6	7.31	4872	8.09
3	1	1	19.4	93	6.92	4778	8.06
4	1.5	1.5	19.3	92	6.86	4763	8.08
TPE YSI Data							
No.	Depth	Depth	Temperature ˚C	Dissolved Oxygen %	Dissolved Oxygen mg/L	Conductivity µS/cm	pH
1	0	0	14.8	107.3	8.77	219.7	7.91
2	0.5	0.5	14.8	106.7	8.78	218.4	7.94
3	1	1	14.8	105.5	8.8	216.9	7.98
4	1.5	1.5	14.7	98.2	8.05	216.1	7.95
5	2	2	14.4	85.5	7.16	220.1	7.91

Appendix 5: CM Dating Data

CM Dating Data								
Core CM0	1							
Code 1	Date	2017						
210-Pb	flux = 27	2.8 +/- 8.7	Bq/m^2	/yr				
90% Equ	ilibrium d	epth = 18.8	cm, or	4.66	g/cm^2			
99% Equ	ilibrium d	epth = 24.8	cm, or	9.56	g/cm^2			
Depth	Drymass	Cum Unsupp	Ch	ronolo	gy	Sedimenta	tion	Rate
		Pb-210	Date	Age	Std			% Std
cm	g/cm^2	Bq/m^2	AD	yr	Error	g/cm^2/yr	cm/yr	Error
0	0	8761.6	2017	0				
0.25	0.0113	8736.9	2017	0	2	0.1248	2.002	14.9
2.75	0.1714	8384.2	2016	1	2	0.1172	1.502	15.3
5.25	0.4014	7775.6	2013	4	2	0.0777	0.764	9.4
8.25	0.7306	6856.7	2009	8	2	0.0858	0.751	11
10.75	1.0297	6052.6	2005	12	2	0.0651	0.415	6.3
13.25	1.5151	4557.1	1996	21	2	0.0434	0.191	7
14.25	1.8252	3602	1988	29	2	0.0388	0.102	7.1
15.25	2.2783	2653.2	1979	38	2	0.0567	0.105	9.6
16.25	2.9061	1945.6	1969	48	3	0.0712	0.113	16
17.25	3.5338	1489.7	1960	57	3	0.0755	0.112	16.1
18.25	4.2554	1063.4	1949	68	4	0.0584	0.081	19.7
19.25	4.982	723.1	1937	80	5	0.059	0.079	22.1
20.25	5.7418	477.1	1924	93	7	0.0546	0.07	36
21.25	6.5423	317.8	1910	107	10	0.0705	0.088	47.6
22.25	7.3428	236.3	1901	116	12	0.1037	0.124	71
23.25	8.2079	158.3	1888	129	16	0.0438	0.052	72.3