Distribution and dispersal of legacy sediment and contamination from historical gold mining at Hill End, New South Wales, Australia

Mine workings and mullock on Hawkins Hill, Hill End, 2014

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Declaration

I hereby declare that this thesis has not been previously submitted to any other institution or university for a higher degree. Except where otherwise acknowledged, this thesis is comprised entirely of my own work.

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Acronyms and abbreviations

Al – Aluminium

As – Arsenic

Au - Gold

Cr – Chromium

Cu – Copper

EDXRF – Energy Dispersive X-ray Fluorescence

EILs – Ecological investigation levels

EF – Emission factor

Fe – Iron

hhXRF = hand held XRF

HILs – Health investigation levels

Hg – Mercury

ISQG – Interim sediment quality guideline

Li – Lithium

MAM – Minimal Age Model

Mn – Manganese

OSL – Optically stimulated luminescence

Pb – Lead

pOSL – portable optically stimulated luminescence

RPD = relative percent difference.

RSD = relative standard deviation

Sc – Scandium

SD = standard deviation

SE = standard error

Ti – Titanium

Wavelength Dispersive X-ray Fluorescence

XRF – X-ray Fluorescence

XRD – X-ray Diffraction

Zn – Zinc

< LOD – less than detectable limit

Abstract

The gold rushes in the 19th century impacted landscapes throughout the world through vegetation clearance, disturbance of soil and sediment and the release of metals (e.g. mercury and arsenic) into the environment. Legacy sediment episodically produced from anthropogenic activities such as gold mining is now stored in modern landscapes and can contain high concentrations of metals. In Australia, the little research into the environmental impacts of historical gold mining has generally focused on metal contamination and there has been limited research into long-term geomorphological changes in landscapes associated with gold mining processes such as the impact of large scale legacy sediment production. This study explored the long-term environmental impacts of historical gold mining at Hill End, New South Wales, Australia, by investigating the dispersal of legacy sediment as well as spatial patterns and temporal trends of mercury, arsenic, lead, copper and zinc contamination. Soil and sediment metal contamination was analysed using X-ray fluorescence (XRF) and a direct mercury analyser. Optically stimulated luminescence (OSL) and excess ^{210}Pb were used to constrain temporal patterns of contamination and sedimentation. Hill End has high hillslope-channel and longitudinal connectivity and there are few places where legacy sediment storage occurs within the catchment. In the uplands of Hill End, legacy sediment is stored in finely laminated sequences in tailings dams. There was no sediment stored in the steep gorges of Hill End and sediment was stored with cobbles and gravel in occasional mid-channel and bank attached bars in the lower reaches of the system. The majority of samples contained little to no metal enrichment and high levels of metal contamination were mainly restricted to artificial depocentres such as tailings dams and in spoil adjacent to stamper batteries and cyanide tanks. Chemostratigraphy and sediment dating in Chappell's Dam revealed that metal contamination peaked during the height of gold mining (c. 1871-1880). It declined shortly after the cessation of ore processing in the adjacent stamper battery, coinciding with the decline of gold mining in the region. Peak metal concentrations of mercury (44.58 mg kg^{-1}) and arsenic (221.0 mg kg^{-1}) found in Chappell's Dam are well above ANZECC sediment quality guidelines and could pose a risk to local aquatic ecosystems. Understanding the fate of legacy sediment and metal contaminated sediment in a highly connected system such as Hill End will shed light on the larger scale impacts of historical gold mining in Australia and can be used to inform management strategies for derelict and active mines.

1.0 Introduction

1.1 Legacy sediment

Anthropogenic activities have caused geomorphic and hydrologic adjustments in landscapes throughout the world for thousands of years. Intensive land-use practices such as mining, agriculture and land clearing lead to accelerated rates of erosion in peopled landscapes and caused the mobilisation of large volumes of soil and sediment. This sediment, broadly termed legacy sediment, has been mobilised by anthropogenic land-use which has altered pre-human environments and is currently stored within modern landscapes (James, 2013; Jefferson et al., 2013; Niemitz et al., 2013). Legacy sediment has been generated through various types of anthropogenic activities such as mining, agriculture, land clearing and urbanisation (Prosser et al., 2001; Walling, 2006; Syvitski and Kettner, 2011; James, 2013). The release of metal and metalloids (hereafter referred to as 'metals') contaminants such as arsenic (As), mercury (Hg), lead (Pb), copper (Cu) and zinc (Zn), and other pollutants such as phosphorus (P) and nitrogen (N), is associated with the production of legacy sediment from mining and agricultural activities. If produced in high concentrations, these contaminants pose significant problems for ecosystems and human populations (Niemitz et al., 2013; Singer et al., 2013).

Production of legacy sediment has accelerated since the colonisation of the New World (Syvitski and Kettner, 2011). In particular, places such as Australia, New Zealand, North America and South Africa suffered intensive forms of anthropogenic land-use as European agricultural and industrial practices were introduced in the absence of appropriate soil conservation practices. Consequently, large volumes of legacy sediment have been generated in these landscapes, often in conjunction with the release of environmental contaminants.

Gold mining during the gold rushes of the 19th century was arguably one of the most intensive forms of anthropogenic land-use leading to environmental disturbance in human history. Legacy sediment generated by historical gold mining has impaired modern environments around the world through increased sediment delivery to fluvial systems and heavy metal contamination within catchments (e.g. Pavlowsky et al., 2010; Chakraborti et al., 2013; Singer et al., 2013; Lecce and Pavlowsky, 2014). Analysis of the distribution and geochemical properties of legacy sediment can be used to determine the extent and degree of the environmental impacts caused by historical gold mining, the risks associated with further disturbance in the landscape, and the potential for landscape recovery following major disturbance. This thesis aims to fill a significant knowledge gap by investigating the character, distribution and contaminant load of legacy sediment associated with historical gold mining at Hill End, New South Wales (NSW), in the heartland of the first Australian gold fields.

1.2 Gold mining during the 19th century gold rushes

The gold rushes of the 19th century affected many parts of the New World including North America (from c. 1799), Australia (from c. 1851) and New Zealand (from c. 1852). A lack of environmental regulation during the gold rush period meant that natural resources were exploited in and around gold fields. Vegetation was cleared to make way for mining activities and to supply timber for new infrastructure. Vast quantities of soil and sediment were disturbed during mining processes. Rocks and sediment were processed using machines, chemicals and races, while mine tailings and metals were released into the environment, and natural drainage patterns in catchments were altered to supply water for mining and ore-processing operations (Stone and Mackinnon, 1976; Drinkwater, 1982; Lacerda, 1997; Mayne, 2003; Hill, 2011; Frost, 2013). As such, numerous studies have investigated the legacy effects of historical gold mining around the world (e.g. North America (Pavlowsky et al., 2010; Lecce et al., 2011; Singer et al., 2013), Australia (Bycroft et al., 1982; Dhindsa et al., 2003; Churchill et al., 2004) and South Africa (Naicker et al., 2003; Bakatula et al., 2011; Lusilao-Makiese et al., 2013). In particular there has been a focus on hazards to ecosystems and human populations through the presence of metals in legacy sediment. However, there is a geographical bias evident in the literature with the majority of research focusing on gold fields in North America and comparatively little research in Australia and New Zealand.

1.2.1 Historical gold mining in Australia

Australian landscapes have been greatly affected by vegetation clearance and resource development that accompanied European settlement since 1788, but few historical activities were more intense and are likely to have had such significant environmental impacts as the gold rushes in Australia from c. 1851 to c. 1900. The gold rush began in Australia with the discovery of payable gold in Ophir, near Hill End in NSW, in 1851. During the gold rushes many migrants arrived in Australia and large populations travelled to the gold fields, leading to the establishment of new towns and villages throughout eastern Australia. The first gold fields in Australia were established in central NSW and included Ophir, Hargraves, Hill End, Tambaroora, Gulgong, Bathurst and Sofala (Figure 1.1). Gold fields were also quickly established in Victoria and Queensland and populations at the more popular gold fields such as Ballarat, Bendigo and Hill End increased rapidly making them some of the most populated inland towns in Australia. The discovery of gold greatly contributed to the Australian population, which tripled from 430,000 in 1851 to 1.7 million people in 1871 (Wells, 2007).

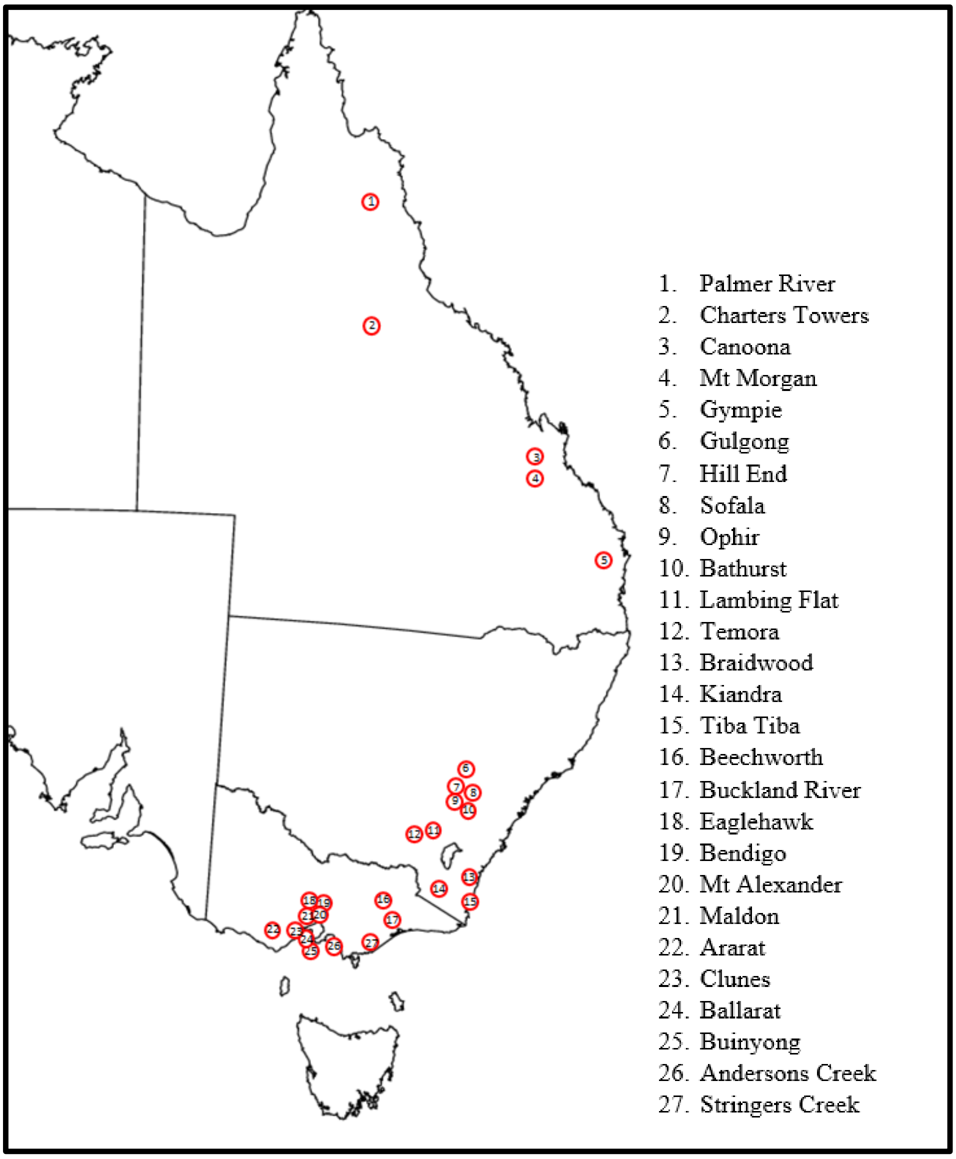

Figure 1.1: Major gold fields in eastern Australia during the gold rush (c. 1851-1900). Note: Gold mining in Western Australia began in the late 1890s. Figure adapted from Victorian Cultural Collaboration (2014).

Widespread clearance of vegetation and soil disturbance occurred during the gold rushes in Australia (Frost, 2013). Large swathes of Eucalyptus forest and woodland were cleared for mining activities and to provide timber for communities living in and around mining camps (Drinkwater, 1982). Evidence of this can be seen in drawings, paintings and early photographs of the gold rush settlements and surrounding landscapes (Figure 1.2).

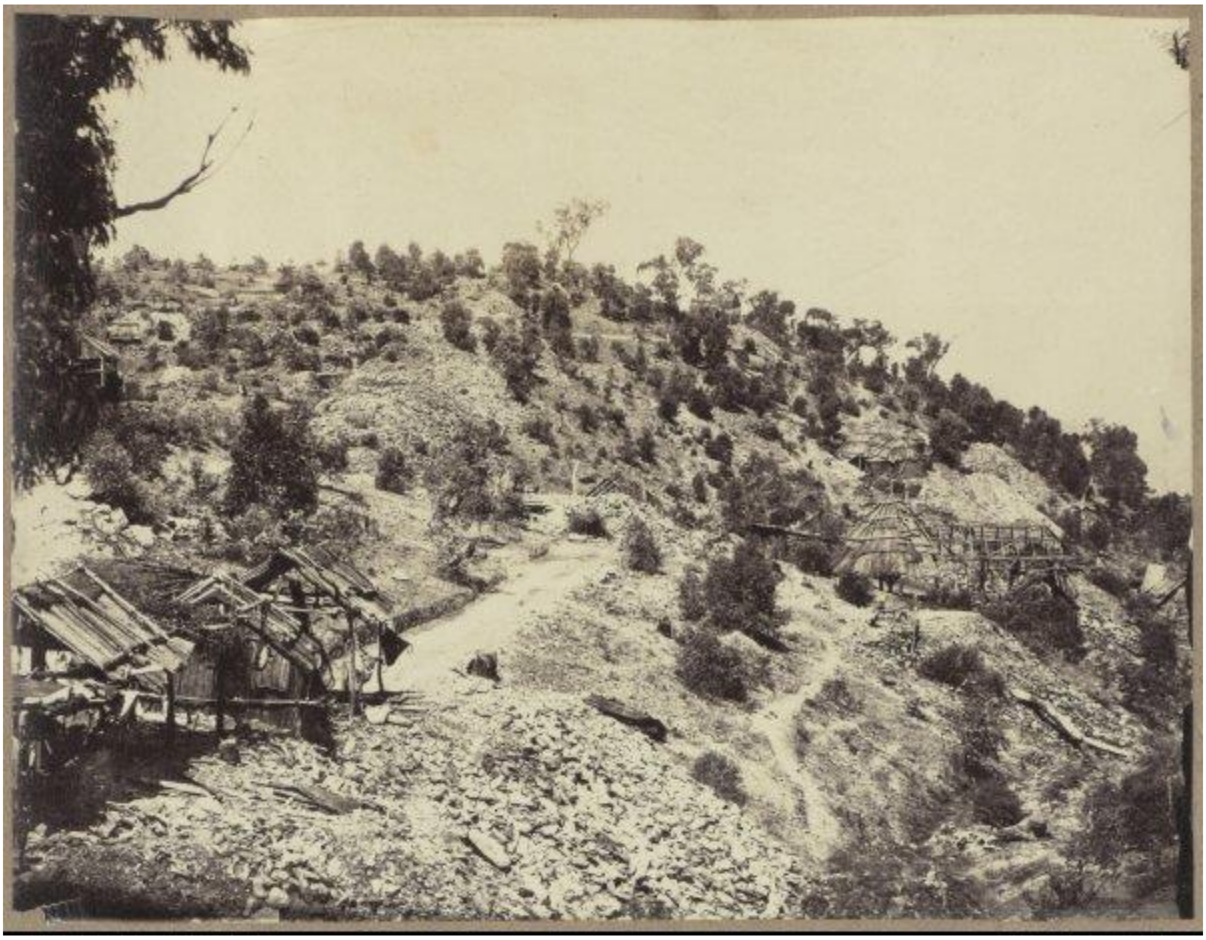

Figure 1.2: Hillslope at Hakwins Hill with bare soil from vegetation clearance and mullock from reef mining, 1872. American & Australasian Photographic Company, National Library of Australia (photograph identification number: vn4728576)

There were very limited legislative environmental constraints placed on gold mining operations during the 19th century Australian gold rush. Mining reports suggest that if environmental degradation at a gold field was very severe then mining operations would cease, however there are few known instances of this occurring (Parks Victoria, 2012). Remediation of landscapes following gold mining was not required, which exacerbated the impacts of historical gold mining due to erosion of hillslopes and gullies continuing long after gold mining ceased (Scott, 2001; Lottermoser, 2010).

A lack of environmental regulations meant that vegetation clearance and the disturbance of soil and sediment occurred in conjunction with the liberal release of metals into the environment from gold mining and ore-processing (Lottermoser, 2010). Liquid Hg was used to recover Au during sluicing and from the processing of gold-bearing ore (Alpers et al., 2005). Hg contamination is one of the most significant environmental issues that has arisen from gold mining (Müezzinogˇlu, 2003), however other metals released by historical gold mining can also cause significant environmental harm. For example, Zn dust was used to extract gold following treatment with Hg when tailings containing gold were dissolved using cyanide solution (Novotny, 2004). At some gold fields, As was released into the environment following the excavation and subsequent roasting and crushing of gold -bearing ores containing naturally high concentrations of As. These metals were often lost to the environment in the form of mine tailings, where they are likely to have been bound to sediment (Bycroft et al., 1982; Lacerda and Salomons, 1998). Tailings were left on-site without treatment where they were susceptible to erosion and leaching, causing contamination on hillslopes and in aquatic systems (Lacerda and Salomons, 1998). High concentrations of these metals are toxic to humans and other organisms and can cause significant environmental harm (Lacerda and Salomons, 1998).

1.2.2 The need for research at Australian gold fields

There has been limited research into the specific environmental impacts created by historical gold mining in Australia (Frost, 2013). Studies have found elevated concentrations of Hg and As in soil and sediment at several Australian gold fields in Victoria and Queensland (Bycroft et al., 1982; Dhindsa et al., 2003; Churchill et al., 2004; Sultan and Dowling, 2006a; Sultan and Dowling, 2006b; Sultan, 2007), however there has been limited research into legacy sediment containing As and Hg contamination in NSW. Since historical goldmining occurred in NSW at the same time and used the same technology as goldmining operations in Victoria and Queensland, it is probable that goldfields and their catchments in NSW also contain contaminated legacy sediment.

It is known that historical gold mining and agriculture contributed to increased soil erosion and sediment delivery in the 19th century in Australia (Prosser et al., 2001; Scott, 2001), however research into these environmental impacts has mostly focused on the contribution of agriculture to these processes. Previous sediment studies have demonstrated the importance of understanding the factors leading to soil erosion and sediment transport in river systems in

Australia following European settlement (e.g. Wallbrink et al., 1998; Olley and Scott, 2002), and so a detailed investigation of environmental impacts associated with historical gold mining is required and warranted. Sediment and contamination from historical goldmining is likely to have been mixed and moved downstream and influenced geomorphological and ecological conditions.

1.2.3 The Hill End goldfield

Hill End was part of the first major goldfield in NSW and Australia during the goldrush. During its peak in gold mining activity (c. 1870-1874) it had an estimated population of 8,000 people, making it one of the most populous inland towns in Australia at the time. Mining began in Hill End in 1851 and it produced approximately 56 tonnes of gold through a combination of alluvial and reef mining. The majority of mining activity had ceased at the end of the east Australian goldrush by the late 1890s, however small scale mining continued at Hill End until midway through the 20th century. Hill End is now primarily a cultural heritage site and popular tourist destination managed by NSW National Parks and Wildlife, and the historical goldfields are currently being re-examined for further gold extraction with newer mining technqiues by a mining company, Hill End Gold Pty Ltd.

The goldrush caused significant landscape disturbance at Hill End by mobilising large volumes of rock, soil and sediment and altering natural drainage patterns to enable water supply for mining operations. Gold mining activities at Hill End also made liberal use of heavy metals (Drinkwater, 1982) and large volumes of heavy metals are likely to have been released into the environment. Sediment and tailings with contamination from metals were likely mobilised from hillslopes and other areas before entering drainage systems and being washed through the landscape. These contaminants may be found in abundance in sediment deposits at Hill End given the intensive mining operations and multiple ore processing facilities that operated there during the gold rush.

Hill End is an ideal place to investigate how historical mining activities impacted landscapes in an Australian context, however an investigation into the local and downstream impacts of historical goldmining has never been undertaken until now. Understanding the history and environmental impacts caused by goldmining at Hill End will provide valuable information for concerned stakeholders in the region and can provide evidence for a broader understanding of landscape response to historical mining and potential future trajectories of change. Information derived from Hill End can also be used to inform future management strategies for derelict mine sites in Australia and elsewhere around the world.

1.3 Aims and hypotheses

This thesis will explore the major environmental impacts of historical goldmining at Hill End by investigating the spatial distribution and geochemical properties of legacy sediment and soil disturbed by mining activities and their current depositional setting in the landscape.

The aims of this research are to:

1 Assess the character and spatial distribution of mining materials and metal contamination that reside in the landscape.
2 Identify the primary locations of legacy sediment in the landscape and its geochemical signature.
3 Determine whether metal contamination is specifically associated with legacy sediment and the timeframe of peak contamination associated with mining.
4 Develop a conceptual geomorphic model that describes the main biophysical processes and the role of catchment sediment connectivity responsible for transport and deposition of legacy sediment and historical mining pollutants.

The overarching hypothesis of this research is that while the liberation of rock, soil and sediment from hillslopes and mining activities introduced legacy sediment and associated metal contamination into the landscape, the legacy sediment and pollutants now exist primarily in discrete depocentres within the catchment due to the operation of hydrological and geomorphic processes. Legacy sediment is likely to be stored in natural depocentres (e.g. floodplain pockets, bars, and benches) as well as artificial depocentres (e.g. dams) and that chemostratigraphy in these depocentres could reveal a detailed record of environmental impacts over time.

The aims of the research will be addressed by investigating historical records and using multiple types of soil and sediment analyses to determine the location and geochemical properties of legacy sediment in Hill End and to interpret the impacts of historical goldmining on the landscape. X-ray fluorescence (XRF) and a direct mercury analyser (DMA) will be used to determine concentrations of metals in sediment, X-ray diffraction (XRD) will be used to determine mineralogy, and optically stimulated luminescence (OSL) and excess lead-210

(^{210}Pb) will be used to interpret the different depositional environments of legacy sediment and the timing of peak contamination.

1.4 Thesis structure

This chapter introduced the importance of legacy sediment and gave a brief outline of environmental impacts created by historical goldmining in Australia and the need for further research. Chapter 2 is a literature review that explores recent research on legacy sediment, the types of landscape disturbance created by historical goldmining, and the way that legacy sediment investigations are being used to assess long term environmental impacts of historical goldmining. Chapter 3 describes the regional setting, anthropogenic history and the study area of Hill End. Chapter 4 describes the sampling strategy and analytical methods used in this research. Chapters 5 and 6 describe the results of this research, including the character and distribution of legacy sediment, the spatial distribution of metals and temporal patterns of contamination from goldmining at Hill End. Chapter 7 provides a discussion of the major findings of this research and their broader significance and presents a conceptual geomorphic model of legacy sediment, contamination and sediment connectivity in catchments. The final chapter of this thesis summarises the major findings and their implications in the context of the aims and hypothesis of this research.

2.0 Legacy sediment and historical gold mining

2.1 Introduction

This chapter is a literature review that explores the concept and use of the term legacy sediment and discusses how legacy sediment relates to environmental impacts created by anthropogenic land-use. The review will then use scientific literature, historical records and photographs to review the various forms of landscape disturbance created by historical gold mining and discuss how an understanding of legacy sediment can be used to assess long-term environmental impacts of gold mining.

2.2 Legacy sediment in the environment

A burgeoning interest in understanding complex interactions between humans and the environment has led to a focus of anthropogenic geomorphology in recent years (Szabó, 2010; Jefferson et al., 2013). Intensive forms of anthropogenic land-use such as mining, agriculture, land clearing, urbanisation and water diversion can cause geomorphic adjustments in landscapes (Prosser et al., 2001; Walling, 2006; Syvitski and Kettner, 2011; James, 2013). A primary form of geomorphic change caused by these types of anthropogenic land-use involves the rapid mobilisation of large volumes of sediment. This sediment, termed legacy sediment, is released, transported and deposited on hillslopes and fluvial systems in catchments and can contain harmful concentrations of pollutants causing long-term problems for ecosystems and human populations. The term legacy sediment has become synonymous with investigations of human disturbance to environments since it first entered the literature in a water quality and sediment transfer investigation by Novotny (2004). Legacy sediment has since emerged in various investigations regarding pollution (Singer et al., 2013), geomorphology (Voli et al., 2013) and ecological processes (Hupp et al., 2009). The majority of this legacy sediment research has been conducted in North America, however studies outside North America are becoming more frequent and add to the knowledge base of human-landscape interactions globally.

2.2.1 Defining legacy sediment

There have been a few definitions of legacy sediment presented since it first emerged in the literature and several of these definitions are relatively narrow and geographically constrained. Walter et al. (2007) developed one of the earliest definitions of legacy sediment and restricted its definition to:

"Sediment that was eroded from upland hill slopes after the arrival of early Colonial American settlers and during centuries of intensive land uses…" (Walter et al., 2007 p. 16).

This definition and subsequent definitions (e.g. Niemitz et al., 2013) have limited the geographical domain of legacy sediment to within North America. This interpretation has recently been contested in the literature because anthropogenically generated sedimentary deposits have been generated throughout the world for thousands of years (Syvitski and Kettner, 2011) and sedimentary deposits with similar characteristics to the ones described by Walter et al. (2007) and Niemitz et al. (2013) have been found throughout Asia, Australia and Europe (James, 2010; James, 2013).

Anthropogenically generated sedimentary deposits outside North America are increasingly being referred to as legacy sediment (e.g. Hale et al., 2010; Liang et al., 2014), which has led to the development of a more general definition that reflects these emerging uses of the term. James (2013) argues that based on the current use of the term outside North America, a sedimentary deposit could be classified as legacy sediment if it is clear that the deposit is associated with processes that have been substantially accelerated by anthropogenic activities. James (2013) suggests the term legacy sediment should refer more broadly to:

"*...sedimentary deposits generated episodically by human activities*." (James, 2013 p. 4).

This is the most general and flexible definition of legacy sediment in the literature and represents a step forward on previous interpretations of legacy sediment, with an acknowledgement of the fact that human activities have contributed to increased sediment fluxes and other landscape changes globally.

2.2.2 Legacy sediment and sediment flux in catchments

Anthropogenic land-use, poor soil conservation practices and the resulting generation of legacy sediment can influence rates of sediment delivery in catchments and alter patterns of (dis)connectivity between different landscape units. Linking anthropogenically induced upland erosion with downstream delivery, transport and export (i.e. flux) of sediment has been an important research frontier in geomorphology for many years. Identifying the spatial patterns and characteristics of legacy sediment deposits can help to quantify these linkages (Knox, 2006). Understanding patterns of sediment (dis)connectivity between landscape units in catchments is also an important research frontier for geomorphology (Fryirs, 2013), and identifying spatial patterns of legacy sediment can provide evidence for changes in (dis)connectivity due to anthropogenic land-use.

Throughout the world, anthropogenic activities have led to a significant increase in sediment delivery in catchments (Knox, 2006), with some devastating effects on infrastructure, communities and environments through the formation of sediment slugs and aggradation in fluvial systems (Yu et al., 2012). Increases in sediment delivery are especially pronounced in catchments dominated by mining and agriculture, and investigating the relationships between these activities and changes to sediment delivery can provide information on the history, magnitude and frequency of environmental impacts created by anthropogenic land-use. For example, in separate studies Knox (2006) and Lecce and Pavlowsky (2014) linked periods of intensive upland erosion created by mining and agriculture with increased sediment delivery through temporal analysis of legacy sediment deposits. Knox (2006) and Lecce and Pavlowsky (2014) also found that increased sediment delivery had resulted in the burial of pre-settlement floodplains and was impairing modern environments. Walling (1983) noted that the majority of sediment mobilised by anthropogenic land-use usually does not reach the basin outlet, but is stored on floodplains and lower hillslopes in the drainage system. Therefore, the presence of legacy sediment in a catchment and its spatial distribution can provide information on the history of changes to sediment delivery in catchments due to anthropogenic land-use and how these changes impact modern environments.

Anthropogenic land-use can alter lateral, longitudinal and vertical patterns of sediment (dis)connectivity between different landscape units through the modification of sediment sources and by the removal and/or creation of barriers (i.e. sediment sinks) in catchments (Fryirs, 2013). Dams are a primary example of major barriers in catchments that trap and store sediment, causing upstream-downstream disconnectivity. Conversely, the removal of barriers can create upstream-downstream and/or slope-channel connectivity that will facilitate sediment transport (Walling, 2006; Fryirs, 2013). Locating sites where legacy sediment has accumulated such as at barriers or floodplains downstream of areas with intensive anthropogenic land-use can help to identify and quantify (dis)connectivity in catchments. For example, the construction of tens of thousands of milldams on mid-Atlantic streams in North America following European colonisation created upstream-downstream disconnectivity and resulted in the creation of massive legacy sediment stores that buried pre-settlement wetlands and formed fill terraces (Walter and Merritts, 2008). By locating blockages and legacy sediment storage sites, Walter and Merritts (2008) were able to understand patterns of (dis)connectivity along the mid-Atlantic streams. Legacy sediment can therefore play a crucial role in understanding patterns of (dis)connectivity between different landscape units and this information can be used to interpret how anthropogenic land-use has impacted landscapes.

2.2.3 Association between legacy sediment and pollution

The majority of studies linking legacy sediment and pollution have arisen from North America and found the source of pollution to be from mining and agriculture land-use during the 19th and 20th centuries (Müezzinogˇlu, 2003; Foulds et al., 2013; Niemitz et al., 2013; Singer et al., 2013; Lecce and Pavlowsky, 2014). This is due to poor land management strategies and limited regulations for the release of pollutants into the environment during the historical period. The transport of pollutants is intimately linked with sediment transport; pollutants adsorb onto sediment particles which are then deposited within river channels and on floodplains resulting in the contamination of fluvial systems downstream of the pollution source (Prosser et al., 2001; Coulthard and Macklin, 2003). Analysis of the geochemical properties of legacy sediment has revealed elevated concentrations of Hg, As, Cu and Pb in

Gold mining land-use areas and elevated concentrations of As, P and N in agriculture land-use areas (Coulthard and Macklin, 2003; Smith et al., 2003; Pavlowsky et al., 2010; Niemitz et al., 2013; Singer et al., 2013; Lecce and Pavlowsky, 2014). The contamination of legacy sediment can be detrimental to aquatic ecosystems and can and cause health problems for human populations (Paerl, 1999; Alloway, 2013; Niemitz et al., 2013; Lecce and Pavlowsky, 2014).

Although anthropogenic land-use can contribute to the pollution of legacy sediment, elements can be elevated in legacy sediment due to natural processes (Smith et al., 2003). For example, metals can naturally occur in the environment if the parent material of soil or sediment has high contents of metals and through natural geomorphological and pedogenic processes (Sultan, 2007; Alloway, 2013). It is important to discern whether pollutants found in legacy sediment are anthropogenic or natural in origin when investigating the environmental impact of anthropogenic land-use on landscapes.

Recent research has attempted to constrain the extent of legacy sediment contamination in catchments through geochemical analysis of legacy sediment and modelling. Geochemical signatures of legacy sediment deposits are being used as tracers to document historical pollution trends in catchments affected by intensive anthropogenic land-use (Niemitz et al., 2013; Lecce and Pavlowsky, 2014). Modelling approaches provide information on legacy sediment transport pathways and possible locations of contamination hot spots in catchments (Coulthard and Macklin, 2003). Contaminated legacy sediment deposits can act as diffuse sources of contamination when particles are remobilised through erosion, posing chronic as well as acute contamination issues downstream of the original pollution source (Coulthard and Macklin, 2003; Niemitz et al., 2013; Singer et al., 2013).

Investigating the spatial and temporal properties of legacy sediment can reveal where, when and the rate at which sediment has been liberated from, transported through and deposited in landscapes. The geochemical properties of legacy sediment reveal whether anthropogenic land-use has environmental contamination occurs and legacy sediment and if this contamination poses a risks to ecological health and human populations. Anthropogenic land-use continues to generate legacy sediment, with global estimates of around 15 ± 0.5 Gt yr^{-1} of sediment being removed or mobilised in environments annually (Syvitski and Kettner, 2011). Assessment of legacy sediment and associated pollution is therefore important for an understanding of past, present and future environmental impacts due to anthropogenic activities and can be used to inform environmental management strategies for monitoring and rehabilitation of degraded landscapes.

2.3 Historical gold mining

Few human activities types had more intense and widespread environmental impacts than gold mining during the 19th and 20th century gold rushes. Goldfields throughout the world experienced extensive vegetation clearance and soil disturbance leading to vast amounts of sediment being liberated from hillslopes and deposited into fluvial systems (Porcella et al., 1997; Hornberger et al., 1999; Scott, 2001; Alpers et al., 2005; Sultan, 2007; Lecce et al., 2011; Singer et al., 2013). This landscape disturbance occurred in conjunction with the liberal release of pollutants into the environment, including Hg, Cu, As and Pb from the excavation and processing of ore resulting in the contamination of legacy sediment (Stone and Mackinnon, 1976; Bycroft et al., 1982; Lacerda, 1997; Lacerda and Salomons, 1998; Hornberger et al., 1999; Scott, 2001; Churchill et al., 2004; Alpers et al., 2005; Lecce et al., 2011; Frost, 2013; Singer et al., 2013). The majority of literature on legacy sediment related to historical gold mining has arisen from studies of North American goldfields (e.g. James, 2004; Pavlowsky et al., 2010; Lecce et al., 2011; Singer et al., 2013), and there has been limited research into the legacy sediment and historical gold mining in other countries heavily impacted by the gold rushes, such as Australia and New Zealand.

2.3.1 Types of gold mining

Alluvial and reef mining were the two main types of mining during the 19th century gold rushes. Alluvial mining refers to the mining of alluvial gold, that is gold particles that have been transported by water and found in alluvium (Ritchie and Hooker, 1997). Reef mining refers to the mining of gold bearing quartz veins ('reefs') beneath the surface (Ritchie and Hooker, 1997). It was common for alluvial and reef mining to occur simultaneously on goldfields and both forms of gold mining impacted the environment in different ways.

Alluvial mining consisted of washing water over sand, silt and gravel (washdirt) to recover gold particles (Ritchie and Hooker, 1997). There were several alluvial mining methods used during the gold rush including panning, sluicing and hydraulic mining (Stone and Mackinnon, 1976). Panning consisted of washing water over washdirt in a pan and letting the heavier gold particles settle to the bottom of the pan (Bell and Donnelly, 2006). Sluicing saw washdirt and water washed down a sluice box where the heavier gold particles would collect behind riffles while the remainder of the washdirt would flow over the riffles and be discharged downstream (Bell and Donnelly, 2006). Hydraulic mining consisted of spraying large volumes of alluvium with high pressure water cannons to dislodge it from banks and floodplains where it would then be sluiced (Stone and Mackinnon, 1976). With the exception of hydraulic mining, individual alluvial mining operations caused relatively little disturbance to the environment, however the combined impact of many alluvial mining operations in a localised area saw significant impacts to goldfield environments. Alluvial mining often resulted in severe degradation of fluvial systems through the disturbance of large volumes of sediment (Figure 2.1).

Figure 2.1: Alluvial mining at Home Rule, NSW 1872. Large volumes of sediment have been removed from the channel bed and banks and piled next to sluice boxes in preparation for sluicing. American & Australasian Photographic Company, State Library of NSW (photograph identification number: a2822198).

Reef mining required hand tools, jackhammers and explosives to excavate deep shafts in search of gold-bearing reefs beneath the surface (Drinkwater, 1982). Reef mining often took place on hillslopes which required terraces to be built and vegetation removed to make level, clear ground for the construction of buildings to store mining equipment and gold-bearing ore (Hodge, 1965). Unwanted rock and soil excavated from mine shafts was piled downslope or adjacent to mine shafts in mullock heaps. Many reef mining operations operating within a localised area could cause substantial landscape disturbance (Figure 2.2). The legacy of environmental degradation created by reef mining can still be seen at goldfields, where evidence of past land clearance and large mullock heaps created through the disturbance of large volumes of rock and soil still remain on the surface.

Figure 2.2: Cleared land and mine heads of reef mines at Hawkins Hill, Hill End, NSW 1872. Hillslope has been terraced and cleared to enable reef mining. Mullock heaps have been created downslope of reef mines forming scree slopes. American & Australasian Photographic Company, State Library of NSW (photograph identification number: a2825333)

2.3.2 Landscape disturbance from historical gold mining

Historical gold mining caused various types of landscape disturbance including land clearing, erosion, mobilisation of soil and sediment, and alterations to natural drainage patterns (Garden, 2001). The impacts of these forms of landscape disturbance are not restricted to individual goldfields, they can have a catchment scale impact on sediment delivery and contamination of fluvial systems. The long-term impacts of landscape disturbance from historical gold mining have been the subject of many recent legacy sediment investigations (Table 2.1). These studies demonstrate the importance of legacy sediment in understanding how mining and other intensive forms of anthropogenic land-use over the past few centuries have impacted the natural environment.

Table 2.1: Review of studies investigating legacy sediment

Location	Land-use	Pollutants present in legacy sediment	Where legacy sediment has accumulated	Downstream sedimentation rate	Environmental impacts identified through analysing legacy sediment	References
Yellow Breeches Creek, Pennsylvania, USA	Agriculture, mining and mill dams	Nutrients: excess P Metals: Pb and Cu elevated above background concentrations.	Behind abandoned milldams and downstream floodplains	N/A	There are thousands of similar legacy sediment sites in the eastern U.S.A. and these sites could be an unaccounted-for source of nutrients and metals to downstream estuaries in this region. Source of pollutants was likely fertiliser runoff, other agricultural amendments and leaded gasoline.	Niemitz et al. (2013)
Gold Hill mining district, North Carolina, USA	Gold mining and agriculture	Metals: 21% of floodplain samples elevated above probable effect concentrations (PEC) guidelines for Hg and Cu. Pb, Zn elevated above background	Floodplains.	Peak mining period 2.7 cm y^{-1} and long-term average rate 0.9 cm y^{-1}.	Threat of harmful biological effects from metal contamination limited to headwaters of the catchment closest to the goldfields as contamination downstream was diluted by uncontaminated sediment.	Pavlowsky et al. (2010), Lecce et al. (2011) and Lecce and Pavlowsky (2014)
Cid mining district, North Carolina, USA	Gold mining and agriculture	Metals: Hg, Cu, Pb and Zn elevated above background.	Floodplains and terraces	Since mining in the 19^{th} Century, sedimentation rate ranges from 0.3-0.9 cm y^{-1} compared to Holocene sedimentation rates of 0.02-0.65 cm y^{-1}.	Relatively little threat to ecological and human health as no samples exceeded PECfor Hg and only 1-5% of samples exceeded PEC for Cu, Zn and Pb.	Lecce et al. (2011)
Upper Mississippi Valley, USA	Agriculture and mining	N/A	Floodplains, banks and terraces	Sedimentation rate increased by an order of magnitude from Holocene rates of 0.02 cm yr^{-1} in catchments < 700 km^2 and 0.09 mm yr^{-1} in catchments > 170,000 km^2 from Anthropogenic land-use. Average sedimentation rate during	Anthropogenic land-use in the past 200 years has produced greater impacts on floodplain sedimentation and morphology than any natural environmental changes in the past 10,000 years.	Knox (2006)

Table 2.1: Review of studies investigating legacy sediment

Location	Land-use	Pollutants present in legacy sediment	Where legacy sediment has accumulated	Downstream sedimentation rate	Environmental impacts identified through analysing legacy sediment	References
				the period of agricultural and mining in the past 200 years ranged from 0.2 and 2 cm yr^{-1}.		
Sierra Nevada, California, USA	Au mining	Metals: Hg was elevated above background	Alluvial fans, terraces and floodplains	N/A	Large volumes of sediment-adsorbed Hg is being remobilised through flood events and transported downstream to lowlands posing risks to ecological and human health.	Singer et al. (2013)
Mid-Atlantic Piedmont, USA	Mining, agriculture and water storage	N/A	Floodplains and in-filled milldams	No sedimentation rate given but the peak sedimentation rate occurred between 1840 and 1880.	Anthropogenic land-use and the construction of thousands of milldams post-European settlement has increased sedimentation in valleys which has caused geomorphic adjustments in the landscape and buried pre-settlement wetlands	Walter and Merritts (2008) and Merritts et al. (2011)
River Swale, England	Lead mining	Metals: Pb elevated well above background.	Alluvial fans and floodplains	N/A	Contaminated sediments pose hazards to environmental health and human populations. These sediments can be are remobilised and transported downstream. >70% of contaminated sediments remain within the river catchment despite abandonment over 100 years ago.	Coulthard and Macklin (2003) and Foulds et al. (2013)
Tributaries of Chesapeake Bay, USA: Difficult Run, Little Conestoga Creek and Linganore	Land clearing, urbanisation, agriculture, mill dams	N/A	Floodplains	Floodplains have experienced ~1-2 m of aggradation of legacy sediment since anthropogenic land-use in the study area. Current sedimentation rates varied between and within tributaries due to different characteristics of each catchment. Lowest rate: 0.03-1.4 cm yr^{-1}. Highest rate: 0.13-2.9 cm yr^{-1}.	Increased sediment load from upland erosion and remobilisation of legacy sediment deposits through milldam removal has increased suspended sediment and is having detrimental effects to the Chesapeake Bay ecosystem. Channel incision and overbank deposition of floodplains has created hydrologic disconnectivity on floodplains. Sediment load remains high from past anthropogenic land-use despite soil conservation practices.	Schenk and Hupp (2009) and Schenk et al. (2013)

Table 2.1: Review of studies investigating legacy sediment

Location	Land-use	Pollutants present in legacy sediment	Where legacy sediment has accumulated	Downstream sedimentation rate	Environmental impacts identified through analysing legacy sediment	References
Creek						
Blue River catchment, Wisconsin, USA: Blue River and Big Spring Branch	Agriculture and mining	Metals: Pb and Zn elevated above background on floodplains.	Floodplains	Blue River pre-mining period (1830-1900) 0-0.98 cm yr^{-1}, mining period (1900-1920) 0-1.58 cm yr^{-1} and post-mining period (1920-1997) 0.35-2.25 cm yr^{-1}; Big Spring Branch Pre-mining period 0.13-0.80, mining period 0-0.58 cm yr^{-1} and post-mining period 0-0.47 cm yr^{-1}.	Source of pollutants was from mining activities.	Lecce and Pavlowsky (2001)
North Georgia, USA	Gold mining	Metals: Hg elevated two orders of magnitude above background.	Floodplains and point bars	No sedimentation rates were given, however some sites have experienced > 200 cm of aggradation.	Hg-contaminated legacy sediment exceeds health standards and guidelines and may pose a risk to aquatic and terrestrial organisms, however the bioavailability and environmental hazard posed by the Hg-tainted legacy sediment has not been determined.	Leigh (1994) and Leigh (1997)
Lerderderg River, Australia	Gold mining	Metals: Hg concentrations elevated above background	Floodplains	N/A	Elevated Hg concentrations found in some fish species. Elevated Hg concentrations in sediments found in sediment adjacent to mine tailings and downstream of major Au mining operations.	Bycroft (1982)
Gympie, Australia	Gold mining	Metals: Hg was elevated above background	Dams	N/A	Hg could be transported downstream to Mary River which is used for fishing. Hg could bioaccumulate in fish resulting in health problems for humans.	Dhindsa et al. (2003)

Land clearing was essential for historical gold mining to provide timber and to make room for gold mining operations. Timber was used in vast quantities to line mine shafts, build mine huts and for fuel in boilers and stamper batteries. There was also a high demand for timber during the gold rush for communities living in and around goldfields for building, heating and cooking (Frost, 2013). Timber yards were common throughout goldfields to supply mining operations and communities with vast quantities of timber (Figure 2.3). Goldfields were often described as 'moonscapes' due to their lack of vegetation and the large volume of disturbed rock, soil and sediment strewn throughout the landscape (Garden, 2001).

Figure 2.3: Timber yard at Hill End, NSW. Timber yards were common throughout goldfields during the gold rush. American & Australasian Photographic Company, State Library of NSW (photograph identification number: a2822659).

Erosion was a significant environmental problem caused by gold mining and its associated practices during the gold rushes. Land clearing accelerated rates of sheet and gully erosion throughout goldfields (Leigh, 1994; Prosser et al., 2001; Mukundan et al., 2011). This erosion increased sediment supply in catchments and contributed to the formation of sediment waves and slugs throughout the world (Nicholas et al., 1995; James, 2010). Erosion was also an ongoing problem on the goldfields after mining ceased due to a lack of vegetation to stabilise hillslopes, gullies and channel banks (Scott, 2001).

As a result of mining activities and erosion, large volumes of soil and sediment were mobilised from hillslopes and fluvial systems. Alluvial mining saw sediment from channel beds, banks and floodplains excavated, washed through pans and sluices and discharged downstream (Figure 2.1; Ritchie and Hooker, 1997)). Reef mining saw soil and rock excavated from mine shafts and dumped in mullock heaps throughout goldfields where it was subject to erosion (Ritchie and Hooker, 1997; Scott, 2001; Frost, 2013) (Figures 2.2 and 2.3). The disturbance of soil and sediment accelerated rates of erosion on goldfields increasing sediment delivery to fluvial systems and contributed to the generation of large volumes of legacy sediment (Garden, 2001).

Historical gold mining and ore-processing operations relied on a steady water supply which required alterations to natural drainage patterns at goldfields. Alluvial mining practices diverted water to allow miners to excavate sediment from channel beds, banks and floodplains and to provide water for hydraulic mining and sluicing (Figure 2.1). Large volumes of sediment were discharged downstream from alluvial mining activities altering sediment budgets and forms of lateral connectivity whilst impairing water quality and contaminating fluvial systems (James, 2010). Ore processing required small dams (Figure 2.4) to provide water for the day to day running of ore-processing facilities (Frost, 2013). The construction of numerous dams within a localised area could trap large volumes of sediment and create upstream-downstream disconnectivity in fluvial systems (Walter and Merritts, 2008). The diversion of water and disturbance of sediment from gold mining activities created significant degradation to fluvial systems (Scott, 2001).

Figure 2.4: Pullen and Rawsthorne's ore-processing stamper battery and dam at Hill End, NSW. The water supply for the stamper battery can be seen in the foreground and the stamper battery and large timber stores can be seen in the background. American & Australasian Photographic Company, State Library of NSW (photograph identification number: a282481)

2.3.3 Environmental pollution from historical gold mining activities

Historical goldfields throughout the world often contain elevated concentrations of heavy metals in soils and sediment including Hg, As, Cu, Pb and Zn (Bycroft et al., 1982; Ringwood, 1994; Singer et al., 2013; Lecce and Pavlowsky, 2014). Depending on the geology of the region, soil and sediment can be naturally enriched or anthropogenically enriched in these metals due to pollution from gold processing activities (Sultan, 2007; Alloway, 2013). At goldfields where soil and sediments are already naturally enriched in metals from the local geology, the excavation of soil and sediment from the subsurface can exacerbate this contamination.

During the 19th century gold rushes, gold processing techniques for alluvial and reef gold varied, however the use of Hg was common in gold processing. When processing alluvial gold, Hg was commonly used to 'wet' the gold, forming amalgams which enabled concentration and extraction of gold from washdirt (Lacerda, 1997; Strode et al., 2009). Miners attempted to retain Hg during this process, however the loss of Hg into the environment was inevitable (Lacerda, 1997). The processing of reef gold also used Hg to form amalgams, however there were several preparation steps required before Hg was used. Figure 2.5 illustrates the reef gold processing steps, starting with ore being excavated from reef mines and sent to stamper batteries where it was crushed into fine particles (Gojak and Allen, 2000). At some goldfields like Hill End, the ore was roasted in roasting pits before being crushed (Gojak and Allen, 2000). Once the ore was crushed it was washed over Cu wash plates coated in Hg to form an amalgam to extract gold particles (Lacerda, 1997). The amalgam was then heated up using a retort to separate the gold from the Hg. The waste products from this process (tailings) were dumped in the landscape or discharged into fluvial systems (Gojak and Allen, 2000). Tailings piled in the landscape were subject to erosion and leaching that led to the contamination of adjacent soil, sediment and fluvial systems (Bell and Donnelly, 2006). In the late 19th and early 20th century, cyanide was also was used to assist with the extraction process.

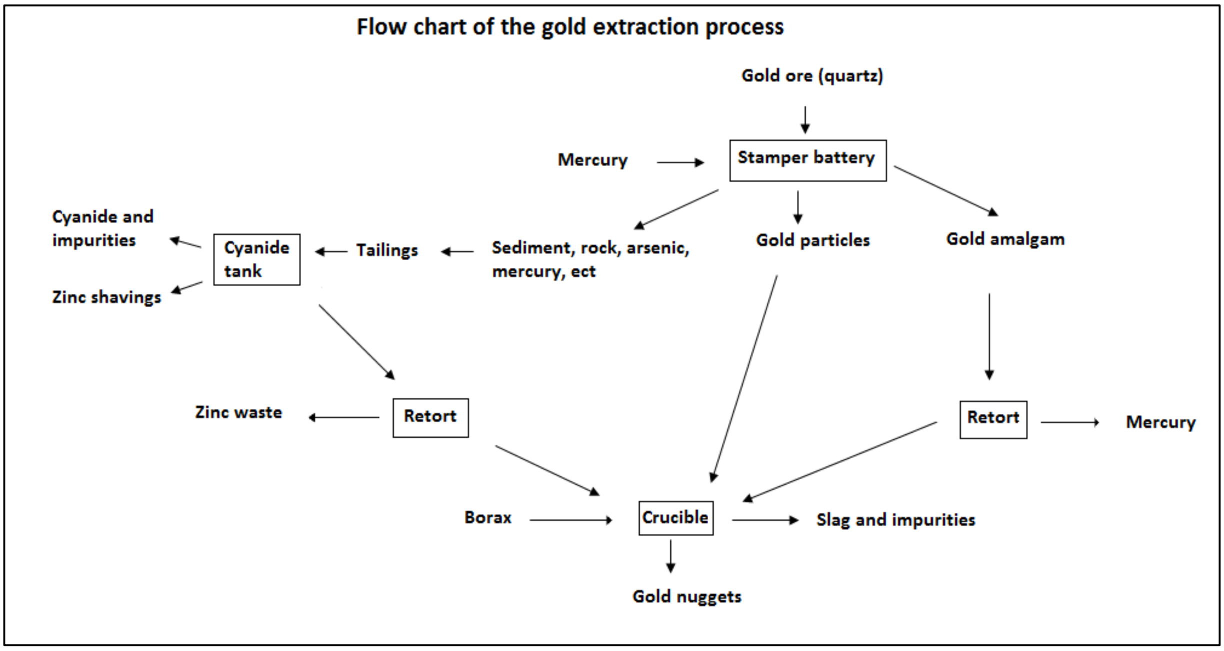

Figure 2.5: A flow chart of the gold extraction process and products used in historical gold mining. The words surrounded by a box represent a mechanism of the process and the words with no box represent outputs and inputs of the process. The outputs of the gold extraction process that contained heavy metals were either deposited into tailings or were dumped into the landscape.

As a result of the mining and processing activities, Hg, As, Cu, Pb and Zn are key metals found in legacy sediment generated by historical gold mining. The literature generally focuses on Hg contamination at historical goldfields due to its toxic properties to humans, however high concentrations of As, Cu, Pb and Zn can also cause human health problems and it can be difficult to determine if these metals are enriched due to natural or anthropogenic processes.

Hg is a metal pollutant which is extremely hazardous to human and environmental health (Lacerda, 1997; Porcella et al.,1997; Lacerda and Salomons, 1998). Hg was sometimes naturally enriched in soil and sediment at historical goldfields due to the geology of the region (Donovan et al., 2013), however Hg contamination is often attributed to the use of Hg in gold processing (Porcella et al., 1997; Hornberger et al., 1999; Hylander and Meili, 2003; Churchill et al., 2004). Müezzinoglu (2003) argues that Hg contamination has been the most significant environmental impact from gold mining. Large volumes of Hg were released into the environment during the gold rushes, with approximately 1-2 kg of Hg released into the environment for every 1 kg of ore processed (Lacerda, 1997). For example, over 815 T of Hg are estimated to have been lost to the environment during the historical period at the Bendigo goldfields in Victoria, Australia (Lacerda, 1997). It is known that Hg can have long residence times in the environment and that it can leach out of tailings down hillslopes and into adjacent fluvial systems (Bycroft et al., 1982; Lacerda and Salomons, 1998), however the extent of Hg contamination at many historic goldfields is not known. Hg contamination is dependent on a variety of environmental factors, not least of which is the initial amount of Hg released into the environment (Lacerda and Salomons, 1998) and, consequently, the extent of Hg contamination at historic goldfields requires detailed assessment.

Despite the growing body of literature on legacy sediment generated by historical gold mining, further research is still needed in catchments throughout the world. For example, in Australia the timing and methods used for historical gold mining were similar to North America, however the majority of legacy sediment research in Australia has focused on pastoralism, not historical gold mining (Frost, 2013). Initial geochemical investigations in Australia have shown similar results to North American studies; legacy sediment has been found with elevated concentrations of Hg at and downstream of goldfields (Bycroft et al., 1982; Dhindsa et al., 2003; Churchill et al., 2004). Further research is needed to constrain the extent of pollution and to explore the impact of increased sediment delivery from the generation of large volumes of legacy sediment from historical gold mining in places such as Australia.

2.4 Summary

This chapter has outlined the importance of legacy sediment and associated pollution created by anthropogenic activities, in particular, historical gold mining. Understanding the character and spatial patterns of legacy sediment and contamination in the landscape can lead to an improved understanding of long-term environmental impacts of gold mining. The next two chapters describe the study area and the multidisciplinary research approach that has been used to investigate environmental impacts of historical gold mining at Hill End, NSW.

3.0 Regional setting and landscape of Hill End

3.1 Introduction

Hill End is located in central New South Wales and was selected as the focus of this research because it was a bustling boom-town at the heart of one of Australia's largest historical goldfields. There has been little research into the long-term environmental impacts of historical gold mining in NSW, and Hill End provides an ideal location to investigate the impacts of mining on the landscape due to the large volume of publically available historical records, historical photographs and contemporary accounts from the gold rush period in Hill End, and its preservation as a cultural heritage site. This chapter describes the environmental setting of Hill End, including a history of catchment land-use, and identifies and justifies the selection of the key study sites for this research.

3.2 Environmental setting

The village of Hill End is situated on an undulating plateau surrounded by steep hills with narrow ridges and valleys (Figure 3.1). The Hill End catchment is drained by Hill End Creek and its tributaries which are typically narrow drainage lines with steep gradients. The majority of gold mining in the Hill End region took place on the hillslopes in the upper parts of the catchment in the form of reef mining, however alluvial mining was also widespread in the region and occurred primarily within the drainage lines and on floodplain pockets near the town, and also in the lower reaches of Hill End Creek and the Turon River.

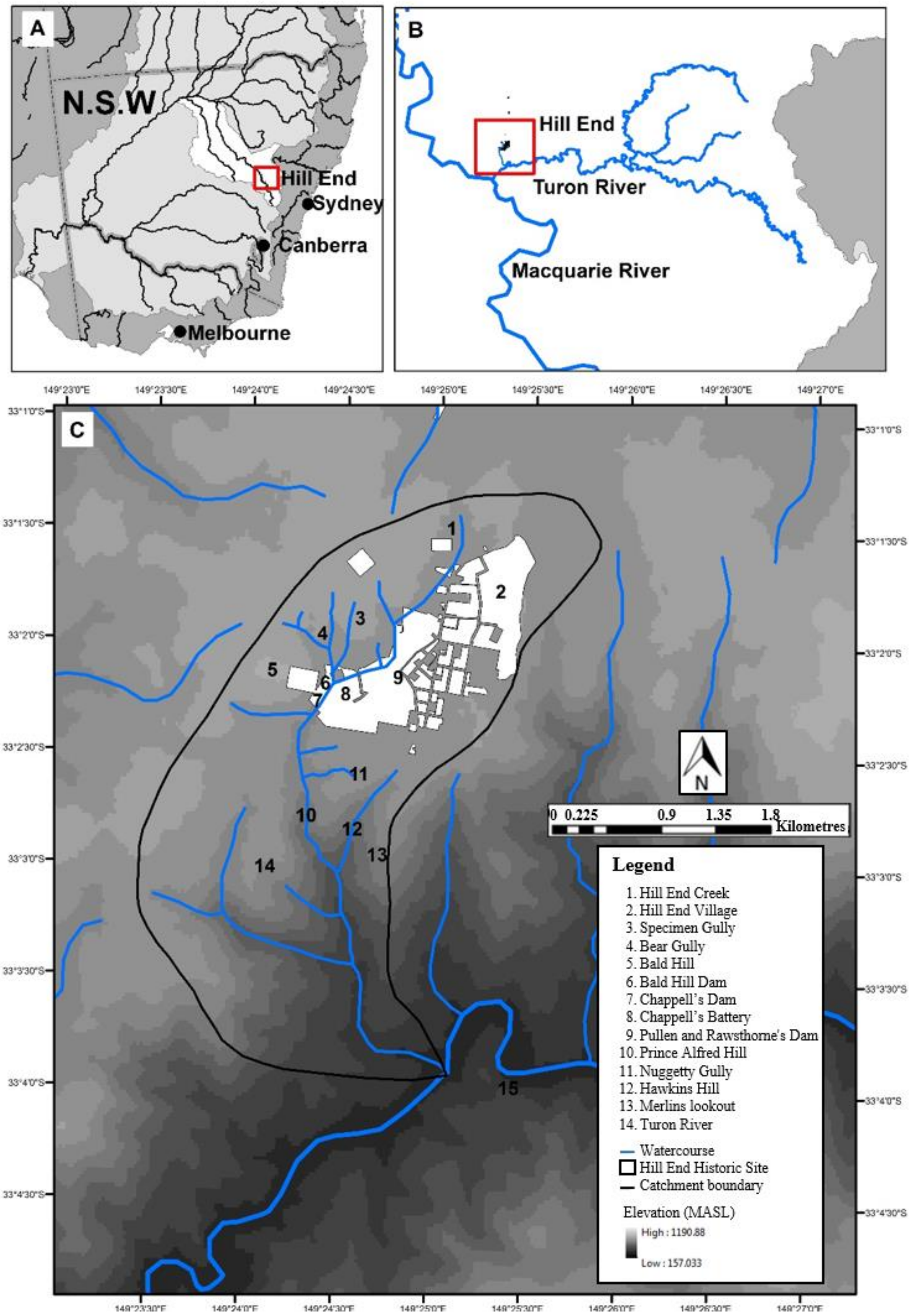

Figure 3.1: Hill End catchment map illustrating the location of key sites in this research.

3.2.1 Hill End catchment

The Hill End catchment drains through Hill End Creek into the Turon River and then into the Macquarie River (Figure 3.1). The Macquarie River is a major source of water for agriculture in the Murray-Darling Basin and feeds the Macquarie Marshes, a large Ramsar wetland of international ecological significance (Kingsford and Thomas, 1995; Brock, 1998; Ralph et al., Submitted). Hill End Creek has an ephemeral flow regime and has several tributaries including Nuggetty Gully, Bear Gully, Specimen Gully, Insolvent Gully, Solvent Gully, Sawpit Gully and Brewery Gully. Hill End Creek is known as Oakey Creek after its junction with Nuggetty Gully (for the purposes of this thesis, Hill End Creek and Oakey Creek will be named together as 'Hill End Creek').

The upper reach of Hill End Creek drains through a partly confined valley near the village of Hill End before entering the abandoned gold diggings west of the village where the channel converges with Specimen Gully and Bear Gully (Figure 3.2A). This upstream reach of Hill End Creek is a sediment storage zone and channel width ranges from 1-3 m and the bed material is predominantly comprised of sand and silt. In this reach, Hill End Creek was dammed at several locations during the gold rush, and while the abandoned dams have mostly infilled with sediment, most of the dam walls have been breached unintentionally due to erosion or removed intentionally following the peak period of gold mining. The main dams along Hill End Creek were Pullen and Rawsthorne's Dam and three dams used by Thomas Chappell for his stamper battery complex known as Chappell's Dam, Bald Hill Dam and the third dam is unnamed. Currently on-ground evidence only exists for Pullen and Rawsthorne's Dam, Chappell's Dam and Bald Hill Dam (Figure 3.1 and Figure 3.2B).

Downstream of Chappell's Dam, Hill End Creek becomes confined by bedrock and is a sediment transport zone where there is little accommodation space for sediment to accumulate due to valley confinement (Figure 3.2C). Channel width ranges from 5-10 m and the bed material is predominantly comprised of silts and clays, however there is limited bed material as the channel has been incised to bedrock. Downstream of Kitties Falls, the major knickpoint in the catchment, channel gradient increases greatly and the bed material consists of poorly sorted boulders and cobbles (Figure 3.2D). Valley width increases slightly and gradient decreases in the lower reaches of Hill End Creek, and as a result the bed material begins to fine and consists of poorly sorted small boulders and cobbles (Figure 3.2E). Accommodation space increases slightly and there are several large vegetated mid-channel bars along this reach.

Figure 3.2: Hill End Creek and the Turon River. (A) The upper reach of Hill End Creek with floodplain pockets at its convergence with Bear Gully 1.6 km downstream (B) Hill End Creek and the infill Bald Hill Dam 1.75 km downstream, (C) the bedrock confined reach of Hill End Creek past the convergence with Brewery Gully 2.3 km downstream, (D) the major knickpoint of Hill End Creek known as Kitties Falls 2.9 km downstream, (E) the lower reach of Hill End Creek 5.5 km downstream, (F) the Turon River 2.6 km downstream of the Hill End Creek confluence.

In the Turon River downstream of Hill End Creek, valley width widens and accommodation space increases greatly. As such in-stream depositional geomorphic units become more frequent, including sandy bank-attached bars and point bars (Figure 3.2F). Channel width ranges from 30 to 40 m in the partly confined Turon River. The Turon River was also impacted by historical gold mining, however the history and location of mining activity along the Turon River is poorly documented compared to Hill End Creek. The Turon River was predominantly an alluvial mining area and alluvial races were established within the channel, and there were numerous stamper batteries operating along its floodplains during the gold rush (Hodge, 1969). The Turon River converges with the Macquarie River approximately 4 km downstream of its junction with Hill End.

3.2.2 Climate and vegetation

Hill End has a subhumid to semiarid climate which is typical of the central west region of NSW. Hill End experiences large variations in minimum and maximum temperatures throughout the year; the average winter temperature range is 0.6 to 12.9 °C and the average summer temperature range is 11.6 to 28.0 °C (Buerau of Meterology, 2014). Average annual rainfall at Hill End is 638 mm, with the majority of this rain falling in the summer months between November and February, while average annual evaporation is 1500 mm (Bureau of Meteorology, 2014)

Vegetation communities in the Hill End region are mostly comprised of dry sclerophyll forest and include several species of Eucalypts including Brittle Gum (*Eucalyptus mannifera sub maculosa*), Red Stringybark (*Eucalyptus macrorhyncha*) and White Box (*Eucalyptus albens*). However, most of the natural vegetation at Hill End was cleared during the gold rush. After the gold rush when major mining activities ceased in Hill End re-vegetation begun to occur. The village of Hill End is currently surrounded by dry sclerophyll forest and within the village deciduous vegetation planted after European settlement is dominant, inclduing English Elm (*Ulmus procera*) and Monterey Pine (*Pinus radiata*) (Conybeare Morrison Group, 2013).

3.2.3 Geology and soils

Hill End (the town) is situated within the Hill End Trough, a depositional basin located within the Lachlan Fold Belt. The Hill End Trough was formed by deep water acid volcanic deposits and marine sedimentation (Jagodzinski and Black, 1999). Within Hill End there are two types of sedimentary formations; the Chesleigh formation (majority of the region) and Cookman formation (western edge of the region). The Chesleigh formation has a lower sedimentary unit and an upper volcaniclastic unit with interbedded greywacke sandstone and siltstones, as well as lithic sandstone and mudstone (Geoscience Australia, 2011). The Cookman formation has interbedded fine to medium grained quartz rich sandstone, siltstone, laminated shale and cherty tuff (Geoscience Australia, 2011).

The gold at Hill End mainly occurs in the Chesleigh formation in quartz veins in a slate and greywacke sequence. These quartz veins generally strike north-south and range from 10-40 cm in width (New South Wales Department of Primary Industries, 2007). The host rocks are interbedded sandstones and shales (New South Wales Department of Primary Industries, 2007). Quartz veins can contain albite, calcite, sericite, ankerite and sulfide minerals including arsenopyrite, pyrite, pyrrhotite, chalcopyrite and galena (Wilde et al., 2004).

Soils in the north, east and west of the Hill End region are generally red and yellow duplex soils, while soils in the south region of Hill End are generally lithosols (Conybeare Morrison Group, 2013). The soil at Hill End is generally sandy loam overlaying clayey subsoil, however due to mining throughout the region much of this topsoil and been eroded and deposited downstream or at the bottom of hillslopes.

3.3 Anthropogenic activities at Hill End

3.3.1 Pre-European history

An indigenous population of Wiradjuri aboriginal people occupied the region for thousands of years prior to European settlement in the Turon River and Macquarie River catchments, including Hill End (Figure 3.3). There is limited evidence of landscape disturbance in Hill End created by the Wiradjuri, however during their occupancy it is thought that the landscape was subject to seasonal burning of grasslands to provide an environment desirable for animals to graze and be hunted (Conybeare Morrison Group, 2013). There is no mention in early accounts of Hill End of the Wiradjuri people having significantly altering the drainage lines or hillslopes of Hill End prior to European settlement in the region.

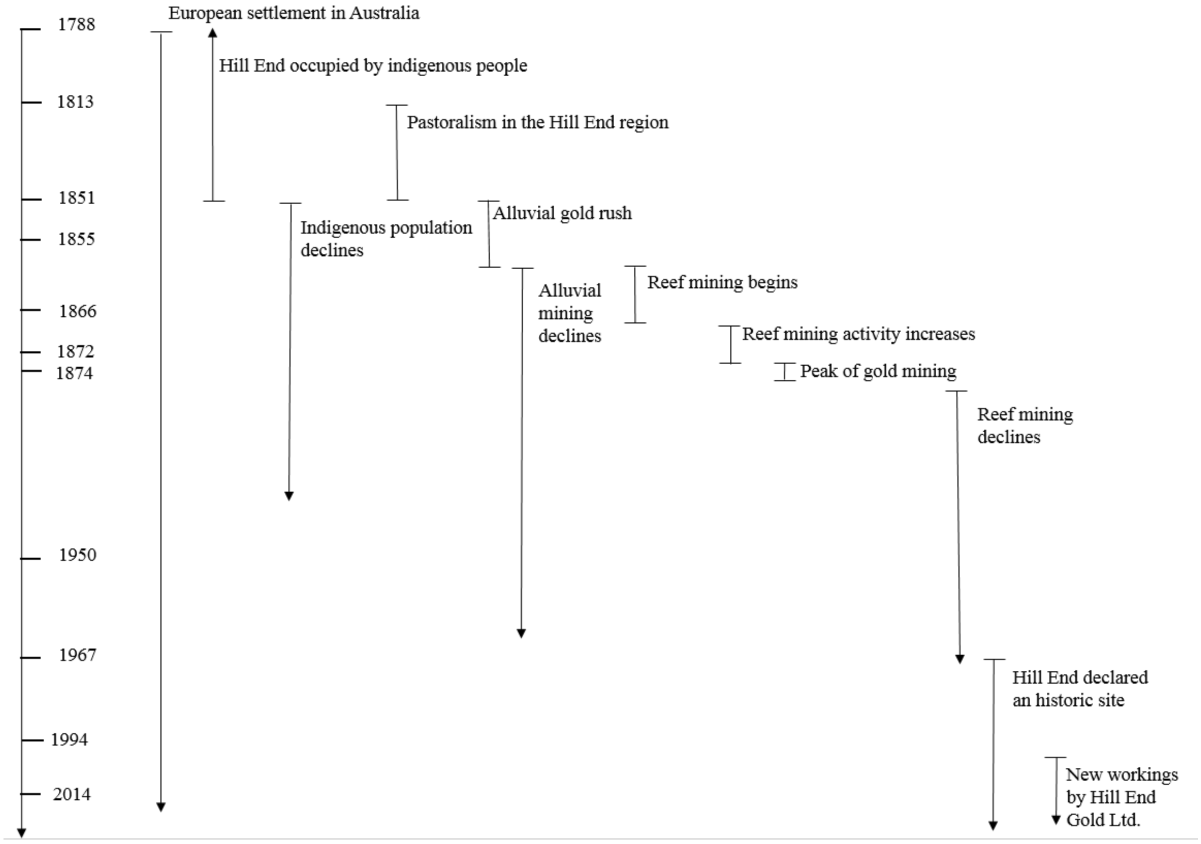

Figure 3.3: Timeline of catchment land-use in Hill End

3.3.2 The anthropogenic landscape

Central NSW opened up for European settlement and pastoralism following the first crossing of the Great Dividing Range in the Blue Mountains in 1813 (Figure 3.3). The Hill End region may have been subject to some European exploration and pastoralism immediately after 1813, however the first notable settlement in and around Hill End did not occur until after gold was first discovered nearby at Ophir in 1851 (Hodge, 1964). Since then, the dominant forms of land-use have been gold mining, logging, pastoralism and urbanisation. As a result, the landscape of Hill End has been significantly impacted by intensive periods of gold mining with widespread land clearing and alteration of the natural drainage patterns. There has been (and still is) extensive gullying throughout Hill End that has resulted in erosion and the mobilisation of large volumes of soil and sediment (Figure 3.4A), especially to the west of the village around abandoned gold diggings. Large piles of mullock consisting of excavated rock, soil and other mine waste from reef mining operations are scattered throughout the landscape and can be found on hillslopes and next to abandoned mine shafts and drives (Figure 3.4B).

There are, however, signs of landscape recovery in and around Hill End such as the re-establishment of native vegetation on hillslopes and in gullies (Figure 3.4C).

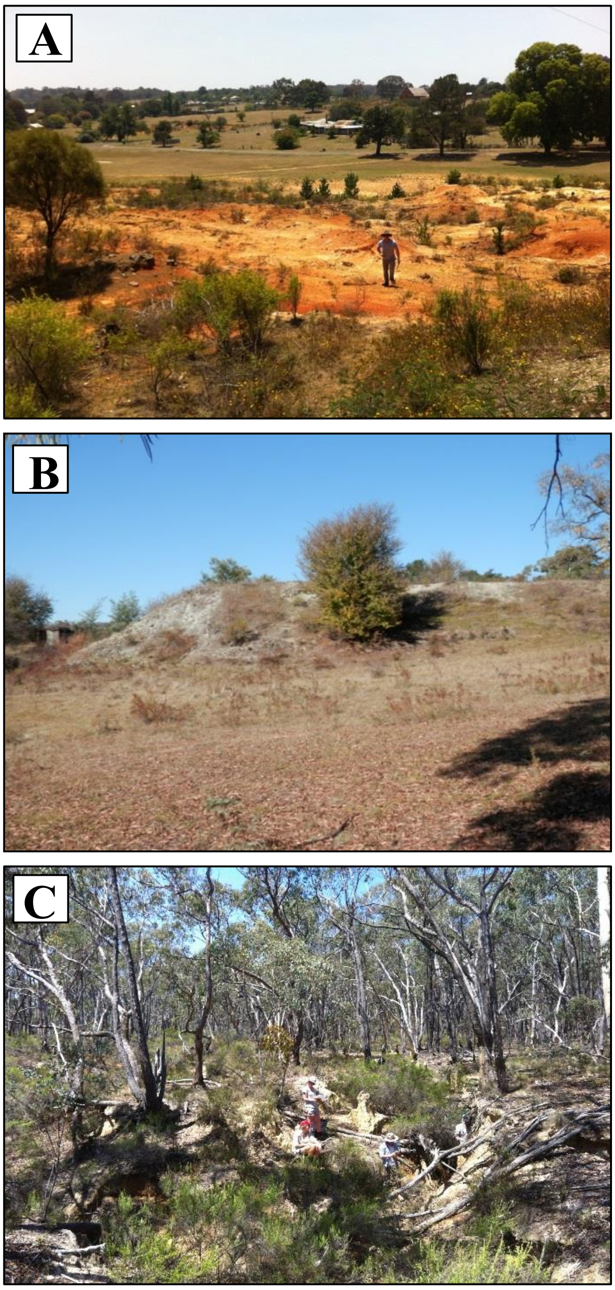

Figure 3.4: (A) Erosion on hillslope near Pullen and Rawsthorne's infilled tailings dam, (B) mullock pile near the Scandinavian Mine in Hill End, (C) gullying west of the village of Hill End near Chappell’s stamper battery with re-established native vegetation consisting of a monoculture of eucalypts.

Large volumes of mine tailings were also created from ore-processing during the gold rush at Hill End, however the current location of these tailings is largely unknown. There is little mention of the fate of tailings in historical mining records or from contemporary accounts of Hill End, but it is known that tailings generated from ore-processing were sometimes trapped in tailings dams. These dams have since been infilled with sediment and finely laminated deposits that may contain tailings can be identified in the basal layers of exposed sediment profiles within some of these dams.

There is also evidence that tailings have been dispersed throughout the catchment, since many stamper batteries in the goldfields of NSW did not use tailings dams, instead they released tailings directly into adjacent watercourses (Gojak and Allen, 2000). There are also accounts of tailings being removed from dams in Hill End once the dams began to silt up (Sydney Morning Herald, 1872). Due to relatively poor gold processing technology during the gold rush period, tailings could sometimes contain valuable quantities of gold and there were many instances of tailings being reworked by prospectors after the peak of gold mining in the region (Hodge, 1980). In Australia, tailings were also used for road surfacing and as landfill in residential areas, creeks and gullies (Bycroft et al., 1982; Pearce et al., 2010). Consequently, the current location and dispersal pathways of mine tailings at Hill End is unknown: tailings may remain in dams, they may have been abandoned and left to erode and leach in the environment, they may have used for landfill, or they may have been discharged downstream.

3.1.1 Alluvial gold mining

In 1851 alluvial gold was discovered at Ophir and at Hill End sparking the NSW gold rush. By 1852 Hill End was officially designated as a primary goldfield. The discovery of gold saw an influx of new settlers in Hill End and the surrounding goldfields, whilst the indigenous population of the region quickly declined (Figure 3.3). The drainage lines around Hill End were extensively worked during this period as large volumes of sediment were removed from channel beds and banks in search for gold and this sediment was then discharged downstream. Vegetation was also removed throughout the landscape to make room for alluvial mining operations and to provide timber for the village and mining operations increasing rates of erosion in the region.

During alluvial mining operations in the historical gold rushes, large volumes of Hg were released into fluvial systems throughout the world (Alpers et al., 2005), and, based on contemporary accounts, this also occurred in Hill End (Drinkwater, 1982). Using techniques developed on the Californian goldfields, Hg was placed in the riffles of sluices to help catch fine gold particles through the formation of amalgams, however turbulent flows of water over sluices sometimes resulted in Hg being washed through the sluice and being discharged downstream with sediment and water (Alpers et al., 2005). Hg was also lost into the environment from alluvial mining when Hg was removed from the amalgam.

As the village of Hill End began to grow, more permanent infrastructure was constructed and in 1860 the township of Hill End was officially gazetted and a town plan was created. The tents of the first settlers were replaced by huts, houses, shops and restaurants. Dams were constructed for drinking water and livestock, and villagers began to grow gardens and orchards (Hodge, 1969). By 1860 alluvial gold finds were declining in Hill End and miners began to turn to intensive reef mining (Hodge, 1964).

3.3.3 Reef mining and the peak of mining activity

The first reef mining in Hill End took place on Hawkins Hill in 1855, however it wasn't until the arrival of experienced Cornish and Californian reef miners in 1866 that reef mining replaced alluvial mining as the dominant form of gold mining (Hodge, 1980). The expansion of reef mining sparked a second and much larger gold rush in Hill End. Reef mine leases were taken up throughout the region including a large number of mining leases on the western slope of Hawkins Hill which soon became known as the "Golden Quarter Mile" (Hodge, 1980). The legacy of reef mining on the Golden Quarter Mile can still be seen today as the hillslope is covered with mullock piles from decades of mining activity which has now formed scree slopes on the hill (Figure 3.5A and B).

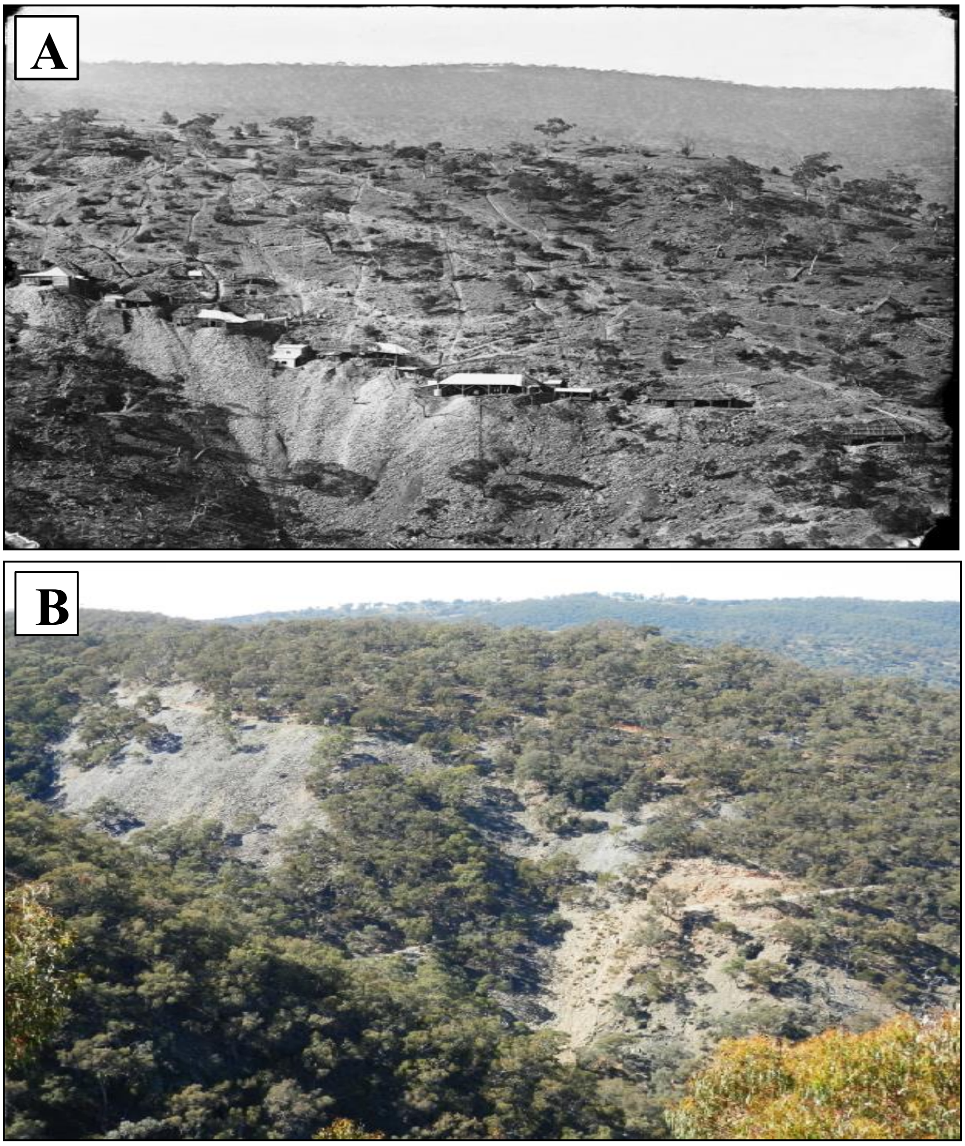

Figure 3.5: Hawkins Hill, Hill End, NSW in 1872 (A) and 2014 (B). These two photographs were taken from the same lookout and demonstrate the long-term impacts of historical gold mining on landscapes. There is evidence of past land clearing and the mullock heaps created during the gold rush by reef mines can still be seen on the hillslope. Vegetation on hillslope now consists of a monoculture of eucalypts. American & Australasian Photographic Company, State Library of NSW, (photograph identification number: a2825324).

The increase of reef mining at Hill End meant that numerous stamper batteries had to be constructed to meet the demand for crushing and processing gold bearing ore. Stamper batteries were located throughout Hill End and were generally in close proximity to mining operations to minimise the distance required for the transport of ore from the mines. Stamper batteries required an accompanying dam to supply water for the gold extraction process and also served as a place to store tailings (Figure 3.6).

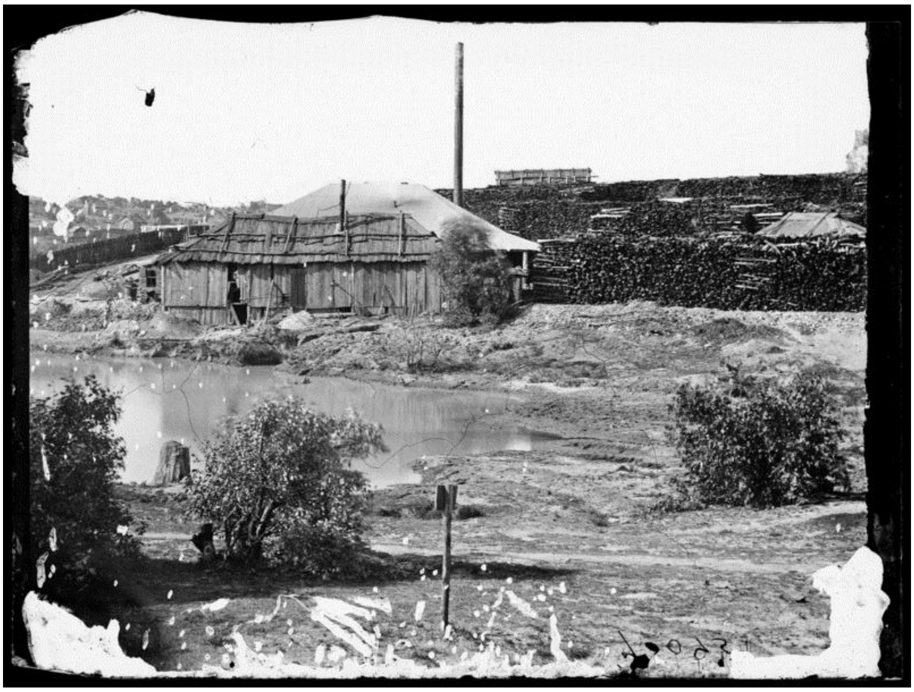

Figure 3.6: Pullen and Rawsthorne's gold stamper batteries and dam. Hill End, 1872 NSW American and Australasian Photographic Company, State Library of NSW (photograph identification number: a2822809)

The peak of mining activity at Hill End occurred during the second gold rush between 1870 and 1874. By this stage the village was well established and its population peaked at approximately 8,000 people. Hill End became one of the largest inland towns in NSW and the Borough Council of Hill End was established in 1873 which saw improvements to infrastructure within the town and the construction of a school, church and hospital. In 1872 a series of photographs were taken by Charles Bayliss and Beaufoy Merlin as part of an initiative by the American and Australasian Photographic Company to document life on the goldfields at Hill End. These photographs reveal the location of mining activities and types of mining practices used during gold rush. These photographs also provide evidence for the landscape disturbance created by mining in the region and can be compared to modern day photographs to reveal how the landscape has changed over time since mining in the region ceased.

3.3.4 Decline of gold mining in Hill End

The peak in mining activity was short lived and by 1875 mining activity had begun to decline, as had the population in Hill End (Hodge, 1980). Small mining operations continued to work in the region, however mining activity never returned to the scale seen between 1870 and

1874. Shortly after 1900 the Borough Council of Hill End was dissolved and the village was incorporated into the Turon Shire. Stamper batteries began to shut down throughout the goldfields as demand for ore processing declined. Old tailings from stamper batteries were often processed by stamper battery owners or prospectors during this period to obtain gold lost during the original gold extraction process (Hodge, 1980). Abandoned buildings and stamper batteries were often dismantled and used for other purposes throughout the village and a bushfire in the 1960s burnt down most of the shacks and mine heads on the goldfields (Mayne, 2003). Abandoned mine shafts, drives, mullock piles and the unwanted remains of stamper batteries remain scattered throughout the region. The Hill End goldfield is similar to other historic goldfields throughout Australia where widespread land clearing and the disturbance of sediment and soil meant that erosion continued in the area long after mining ceased. Abandoned dams have silted up and one of the larger dams in operation during the gold rush is now a sports field (Figure 3.7).

It is difficult to determine the total amount of gold discovered in Hill End between 1851 and present, but it is estimated that between 1865 and 1918 over 56 tonnes of gold was removed from Hill End (Western Mining Corporation Staff, 1980). However mining at Hill End began prior to 1865 and continued after 1918, so it is reasonable to assume that over 56 tonnes of gold has been discovered in the region.

Figure 3.7: Pullen and Rawsthorne's Dam in 2014, looking south toward the Scandinavian mine. The dam was used by the Pullen and Rawsthorne stamper battery and the dam has silted up since abandonment after the gold rush and now serves as the village sports field. The mine head seen in the foreground was placed there after 1967.

3.3.5 Historic site

As mining continued to decline in the 20th century, the population of Hill End decreased to approximately 166 people (Australian Buerau of Statistics, 2006). In 1967 Hill End was proclaimed a historic site for its cultural heritage values and is now managed by the NSW National Parks and Wildlife Service (NPWS). Much of the village and landscape of Hill End has been preserved, making it a popular tourist destination despite the fact that land degradation caused by historical gold mining can still be seen throughout the landscape. Although the majority of mining operations having ceased in Hill End, fossickers are commonly seen in Hill End Creek and the Turon River. There have also been recent attempts to restart mining at Hill End, with the establishment of Hill End Gold Ltd. in 1994 who have explored areas beneath historic gold workings at Hawkins Hill.

3.4 Study sites

The key study sites within Hill End were selected based on the basis of an analysis of the history of catchment land-use in Hill End. Despite nearly the entire Hill End region being impacted by mining activities, some areas were more significantly impacted than others. The following section will identify these key sites and briefly discuss their importance for this research.

3.4.1 Hawkins Hill and Nuggetty Gully

Hawkins Hill contained a series of gold bearing quartz reefs on its western slope which were mined by excavating shafts or drives into the hill. The western slope of Hawkins Hill was the most extensively mined area in Hill End. There were several attempts at mining the eastern slope of Hawkins Hill, however there is little evidence of any gold being recovered from these workings (Hodge, 1980). Figure 3.8 illustrates the large number mining leases on the western slope compared to the eastern slope. Mining on Hawkins Hill saw vegetation cleared and large volumes of mullock piled on the hillslope from the numerous mining operations (Figures 3.9 and 3.10)

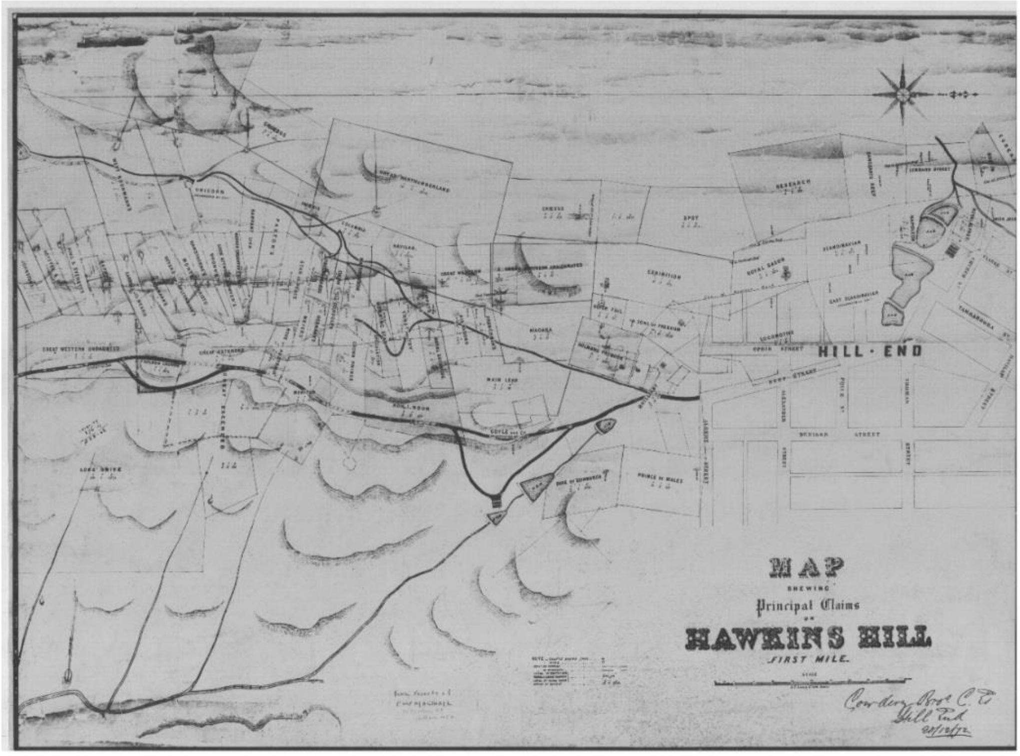

Figure 3.8: Mining leases along Hawkins Hill in 1872. Map by Coates (1872).

Nuggetty Gully drains the western slope of Hawkins Hill and the eastern slope of Prince Alfred Hill. There is evidence of some mining activity occurring on Prince Alfred Hill, however not to the same extent as that on Hawkins Hill. There were several stamper batteries and dams located along Nuggetty Gully including Peterson's battery, the Amalgamated Hill End Company's battery, the Starr of Peace battery, and the Rose of England battery (Hodge, 1969). Mining continued along Nuggetty Gully past the main workings of Hawkins Hill to its junction with Hill End Creek.

Today the huts, mine heads, stamper batteries and dams constructed during the gold rush no longer remain on Hawkins Hill or along Nuggetty Gully. Stamper batteries have mostly been dismantled or stripped of valuable parts and dams have silted up (Figures 3.9 and 3.10). The abandoned mine shafts, drives and mullock on the hillslope serve as a legacy of the past mining operations (Figure 3.11).

Figure 3.9: Remains of the Amalgamated Hill End stamper battery next to Nuggetty Gully, 2014. The building hosting the battery has been removed and most of the battery has been stripped of valuable parts. The battery has been partially been buried from hillslope erosion.

Figure 3.10: Site of the Patriach tailings dam, 2014. Dam wall has been partially removed since abandonment

Figure 3.11: Western slope of Hawkins Hill, 2014. Excessive dumping of mullock has formed scree slopes on Hawkins Hill inhibiting vegetation regrowth

Hawkins Hill and Nuggetty Gully are a key study site for this research project as it was the most heavily mined area in the region. Mullock from the hillslope and sediment enriched in heavy metals from mining and ore-processing may have been transported downhill and into Nuggetty Gully and through to Hill End Creek. The removal of vegetation combined with the steep slope of Hawkins Hill increased slope-channel connectivity with Hawkins Hill and Nuggetty Gully increasing sediment delivery to and gully. A lack of accommodation space for sediment in Nuggetty Gully may mean that mullock and metal-enriched sediment may have been transported further downstream into Hill End Creek/Oakey Creek and the Turon River.

3.4.2 Chappell's stamper battery and dams

Chappell's stamper battery (Figure 3.15) was the largest stamper battery in Hill End and was located approximately 1 km away from the main workings on Hawkins Hill next to Hill End Creek. It was constructed in 1871 along with a series of three earth dams along Hill End Creek next to Bald Hill (Figure 3.16) (Hodge, 1980). The main dam was the furthest downstream, known as Chappell's Dam, and there is little mention of the use of the other two upstream dams in historical mining records.

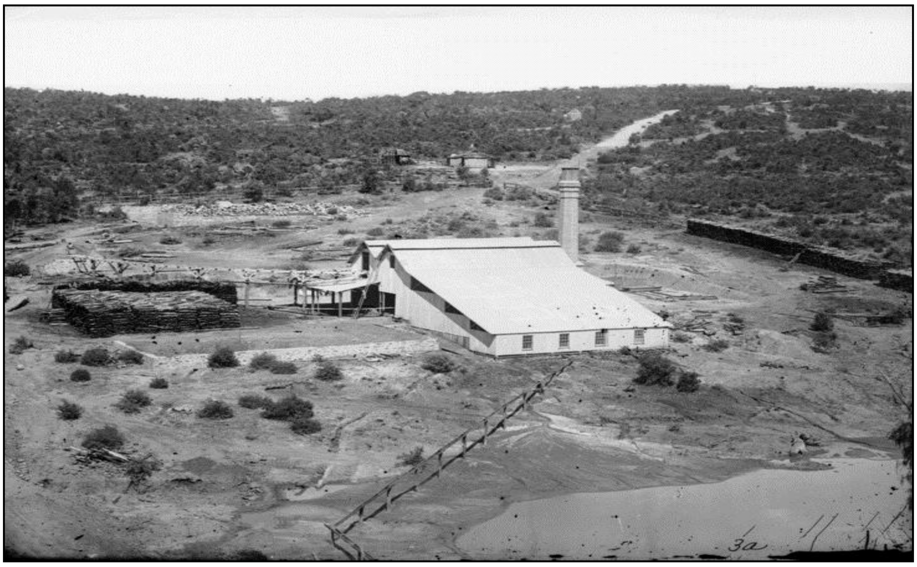

Figure 3.15: Chappell's stamper battery and the main dam (Chappell's Dam in foreground) at Hill End, NSW, 1872. Chappell's stamper battery was the largest in Hill End and the building can be seen in the centre of the picture. Timber used as fuel is stacked to the left of the battery. American and Australasian Photographic Company, State Library of NSW (photograph identification number a2824737)

During the ore extraction process at Chappell's stamper battery, ore was crushed into a fine powder. Crushed ore was placed on dressing tables made from Cu and water and liquid Hg was washed over the crushed ore forming a slurry. The Hg and gold particles would form an amalgam and the Hg was later removed from the gold by heating it using a retort. The tailings of this process were transported to a settling tank where any missed amalgam would be recovered and the remainder of the tailings were either discharged downstream or put into the largest of the dams. The liberal use of metals at stamper batteries in Hill End made them possible point sources for downstream contamination.

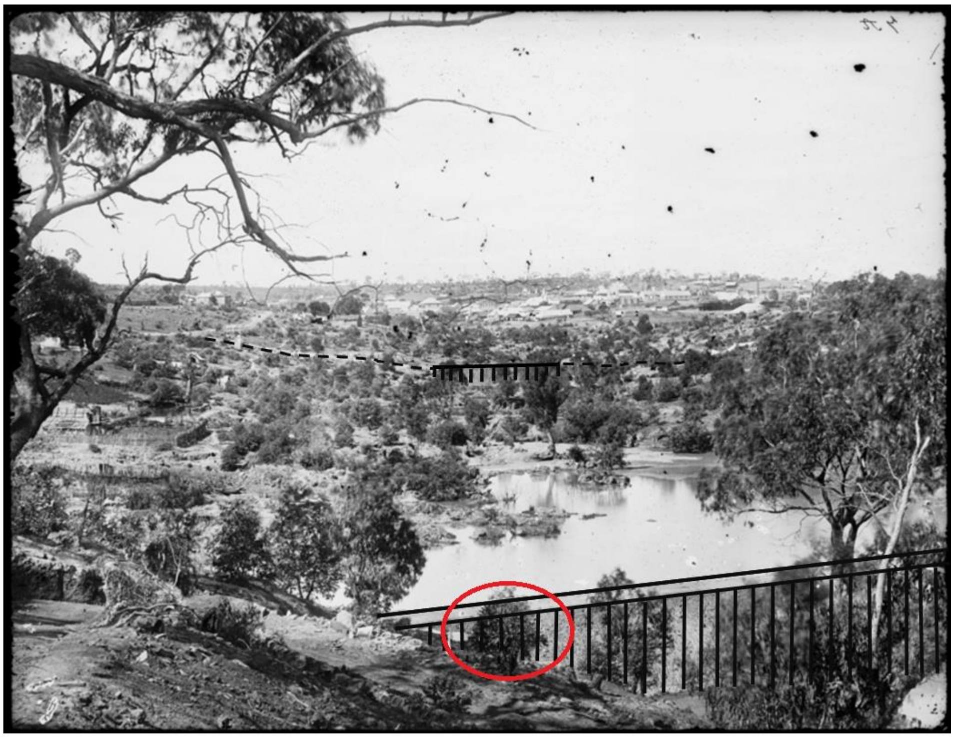

Figure 3.16: Annotated photograph of Chappell's Dam looking north east from Bald Hill. The main dam used by Chappell's stamper battery is in the foreground and was breached in the 1890s at the site of the red circle. One of the other dams used by Chappell's stamper battery can be seen in the background of the picture. The dotted line represents an old road that once crossed the dam wall of the upstream dam. American and Australasian Photographic Company, State Library of NSW (photograph identification number a2824735).

The stamper battery and dams were operational between 1871 and 1874 and were sold shortly after 1874 as demand for crushing gold bearing ore decreased. The battery was dismantled while the largest dam was likely used as a water supply for surrounding livestock until the 1890s when the dam wall was breached (Hodge, 1964). There is limited information regarding the fate of the other two upstream dams. All that remains of Chappell's stamper battery now is a stone wall while the three dams have since silted up with sediment.

Since the dam wall was breached in the main Chappell's Dam in the 1890s, Hill End Creek has cut away at sections of the in-filled dam exposing well defined laminations of sediment (Figure 3.17). These laminations suggest the sediment was deposited in a lacustrine environment when the dam was operational or shortly after it was abandoned and are likely to contain elevated concentrations of heavy metals as they were probably deposited during or just after the peak of mining in Hill End. The fate of the tailings produced from Chappell's stamper battery is not fully known. It is likely that some tailings still remain in the infilled dam, however it is also possible that the majority of tailings were removed prior to abandonment of the dam by prospectors searching for gold lost during the historical ore-processing process. As such, Chappell's stamper batteries and Chappell's Dam is a key study site that warrants a detailed investigation. Analysis of the geochemical properties of sediment in the dam could provide information on the timing of peak metal contamination in the catchment.

3.4.3 Drainage lines of Hill End

Hill End Creek and its tributaries were significantly impacted by gold mining activities. Large volumes of sediment were removed from channel beds and banks and were discharged downstream in conjunction with the release of Hg and other pollutants from alluvial gold mining. Reef mining and ore processing also occurred along these fluvial systems which may have resulted in the discharge of sediment and heavy metals into Hill End's rivers and creeks. There is little accommodation space for sediment along Hill End Creek and sediment may have been transported downstream to the larger Turon River or the Macquarie River which have much more accommodation space for sediment (Figure 3.18). The drainage lines of Hill End are key study sites for this research project because they may contain legacy sediment deposits and elevated concentrations of heavy metals.

3.5 Summary

This chapter has summarised the environmental setting and described how anthropogenic land use has impacted the landscape at Hill End. This chapter has also introduced and justified the selection of the key study sites of this research.

4.0 Methods

4.1 Introduction

The analysis of maps, aerial photographs, historical records, historical photographs and primary and secondary accounts of mining summarised in Chapter 3 was used to investigate the history of Hill End and to reveal the location of mining activities, the types of mining practices used, and the landscape disturbance created by mining in the region. This background investigation informed the soil and sediment sampling strategy for this research project, which was designed to identify the properties of legacy sediment and to determine the spatial and temporal patterns of metal contamination at Hill End.

This chapter explains the methods and analytical techniques used in this study to investigate the impact of historical gold mining and describe how the landscape has changed over time in Hill End. Geochemistry of soil and sediment was analysed by X-ray fluorescence (XRF) and a direct mercury analyser (DMA-80). The geochronology of a sediment core from a historical tailings dam was assessed using portable optical stimulated luminescence (pOSL), optically simulated luminescence (OSL) and excess ^{210}Pb, while XRF, DMA-80, X-ray diffraction (XRD), grain size analysis and loss of ignition (LOI) were also used throughout the cores. These sedimentological, geochemical and geochronological analyses yielded information regarding temporal changes in contamination associated with legacy sediment at hotspots within the catchment and were used to determine changes in depositional environment and sedimentation rates in the tailings dam for the historical period at Hill End, including the time of peak mining.

4.2 Sampling strategy

A spatially explicit, strategic geomorphic sampling regime was used in this study, with a focus on the key study areas. These areas included Hawkins Hill and Nuggetty Gully (the 'Golden Quarter Mile' at the centre of reef mining), Chappell's battery and other mining operations around Hill End Creek and Bald Hill, and a range of hillslopes and drainage lines in the catchment. Natural and anthropogenic landscape units were defined by their geomorphic character (Table 4.1 and Figure 4.1) and soil and sediment sampling at these landscape units aimed to determine the following:

1. spatial patterns of metal contamination, including the location of local 'hotspots' of contamination;
2. trends in metal contamination between different landscape units; and
3. temporal changes in sediment deposition and contamination at local hotspots.

In total, 175 soil/sediment samples were collected from hillslopes, gullies, creeks and streams, mine sites, tailings dams, mullock heaps, background soil sites and from bedrock. A range of sites were sampled on hillslopes, from ridges to lower slopes, and a series of depositional units (bed, banks, bars and floodplain) were sampled within drainage lines to investigate geomorphic and downstream trends in metal concentration. At the time of sampling there was no flow in the gullies, creeks and streams except for the Turon River which was in a low flow stage.

Table 4.1: Landscape units sampled throughout the Hill End catchment.

Landscape unit	**Type of samples collected**	**Number of samples**
Hillslope	Soil collected on the slope of a hill.	21
Gully	Sediment collected within gullies – does not include major watercourses.	14
Fluvial	Sediment collected within major watercourses including Hill End Creek, Nuggetty Gully and the Turon River. Samples collected includes channel bed, bank, bars and floodplains. Does not include gullies.	42
Spoil	Soil/sediment collected amongst the remains of abandoned boilers, stamper batteries, mine huts, settling tanks and urban areas.	17
Tailings dams	Sediment collected from abandoned tailings dams – includes surface (0-2 cm) samples and samples collected at depth (> 2 cm) at Chappell's main tailings dam.	52
Mullock	Piles of soil and rock excavated from mine shafts/drives during mining activities and dumped throughout the landscape.	11
Background soil	Soil samples collected on hillslopes not directly impacted by anthropogenic activities and a considerable distance away from historic mining activities.	10
Bedrock	Bedrock samples collected randomly throughout the catchment.	8
Total		**175**

Anthropogenic landscape units related to mining included tailings dams, mullock and spoil. A sediment profile at Chappell's Dam was sampled in detail for geochemical and geochronological analysis. Discrete sediment samples and continuous sediment core samples were collected from the exposed vertical profile, while a second sediment profile was sampled at a smaller tailings dam, Bald Hill Dam, immediately upstream of Chappell's Dam. Both sediment profiles were analysed by ITRAX XRF core scanning to yield high-resolution information on geochemistry and possible chemostratigraphy of sediment in the tailings dams.

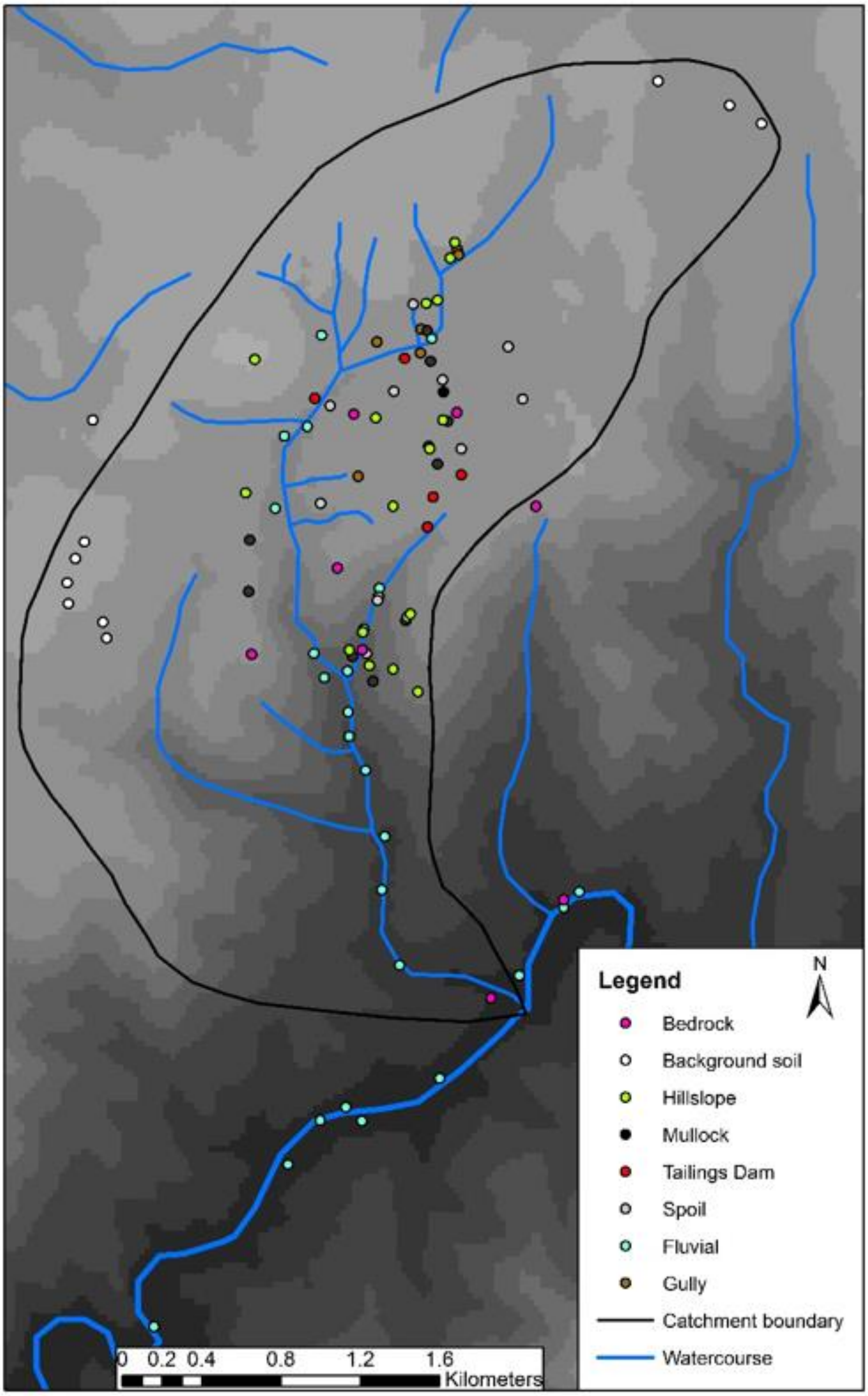

Figure 4.1: Map of the sampling sites with colour coding for landscape units

4.2.1 Soil and sediment sampling procedure

Soil and sediment samples were collected in accordance with Australian standard 4482.1–2005 (Standards Australia, 2005). Samples from hillslopes, gullies and fluvial units, spoil and mine sites in the catchment were collected from the top 2 cm of the soil/sediment surface using a plastic trowel and double bagged in polyethylene bags. In between sampling the trowel was cleaned with 5 % Decon-90 solution, then ethanol, then rinsed with deionised water and wiped dry with clean wipes to avoid cross contamination between samples. The trowel was also neutralised before each sample was collected by passing it through adjacent sediment/soil. Samples were also collected from shallow pits (up to 45 cm deep) excavated along the hyporheic zone of the Turon River upstream and downstream of the Hill End Creek confluence. The locations of all samples were recorded using a handheld GPS with a typical accuracy of 1±4 m. Soil and sediment samples were then air dried in an oven at a low temperature (30 °C) for 120 hours to avoid volatilisation of Hg and As. Samples were then mixed thoroughly and split using standard methods to obtain representative sub-samples for analysis by XRF, XRD, DMA-80, grain size and LOI.

Sediment samples were collected in 10 cm intervals from the top (0 cm) to the base (460 cm) of the exposed sediment profile at Chappell’s Dam. Before sampling, ~3 cm of sediment was removed from the face of the profile to clean it and to prevent cross contamination from elsewhere in the profile. The profile was then described for sedimentology. Portable OSL samples were also collected at 10 cm intervals down the entire profile and an OSL sample was collected at 350 cm using a similar method to Muñoz-Salinas et al. (2014). Portable OSL samples were collected by inserting aluminium tubes (~1.5 cm diameter and ~4 cm long) horizontally into the sediment profile, thereby filling them with sediment. The tubes were then removed from the sediment profile and the ends of the tubes were covered with tape to reduce sunlight exposure to a minimum. Sediment likely to be exposed to sunlight during sampling (approx. depth 2 mm) from the ends of the pOSL tubes were discarded in the laboratory before luminescence analysis. Portable OSL samples were collected first, as the results from this process were used to assist in the selection of depths to sample for OSL dating. Samples for OSL dating were collected by the same process using larger tubes (~7 cm in diameter and ~15 cm long).

Three sided steel trays (narrow catena trays, akin to open sided cores) 50 cm in length and 3 cm in diameter were used to collect continuous sediment samples from the exposed sediment profiles of tailings at Chappell’s Dam Bald Hill Dam (Figure 4.2). These U-channels were collected from the bottom of the sediment profile upwards to avoid contamination caused by sediment falling from the upper layers. The location of the two sediment profiles was recorded using a handheld GPS.

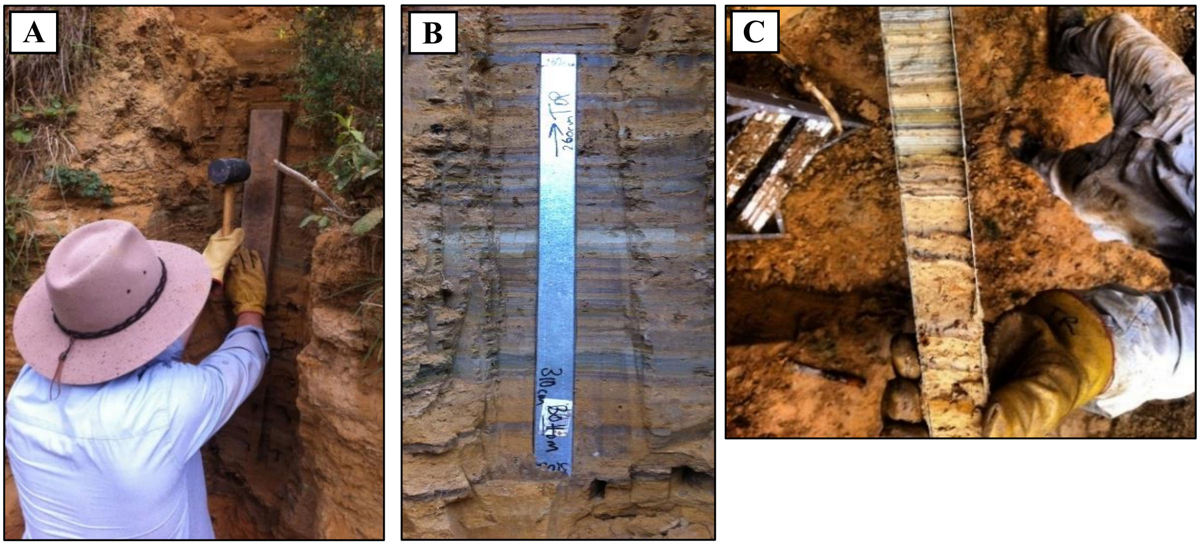

Figure 4.2: U-channels used to collect continuous sediment samples of sediment profiles of in-filled tailings dams. (A) U-channels were hammered in using a rubber mallet and a plank of wood to preserve the shape of the core. (B) When the catena was fully inserted into the sediment profile it was labelled before being peeled back with care to preserve sediment within. (C) U-channels with intact sediment profiles were wrapped tightly in plastic wrap and stored before ITRAX analysis.

4.2.2 Establishing background concentrations for Hg, Pb, As, Zn and Cu

To constrain the extent of anthropogenic contamination in soil and sediment samples at Hill End, background concentrations for Hg, Pb, As, Cu and Zn were calculated for the region. These elements were chosen as the focus for the anthropogenic contamination in this study because contamination of these metals is associated at historical goldfields in Australia (Bycroft et al., 1982; Sultan, 2007). There was no previous data for background concentrations for these key metals in Hill End. Background concentrations were determined by taking 10 soil samples at sites more than 1 km away from mining or ore-processing activity and analysing them with a hand held XRF (hhXRF) and DMA-80. A similar method was used by Dhindsa et al. (2003) to determine background concentrations for soils and sediments at the historic Gympie goldfield in Queensland, Australia. Dhindsa et al. (2003) argued that soil and sediment 1 to 2 km away from gold mining or ore-processing activity could reflect background concentrations as it was less likely to have experienced anthropogenic contamination compared to soil and sediment in close proximity to these activities. The limitation of this method is that despite their distance away from mining and ore-processing activities, soil and sediment may be anthropogenically enriched due to atmospheric deposition of metals. The impact of the atmospheric deposition of metals was not directly assessed and for this study it was assumed that atmospheric deposition of metals had a negligible effect on overall metal enrichment.

4.3 Sediment geochemistry

4.3.1 XRF

XRF was the primary method of geochemical analysis used in this research because it has the capacity to detect key elements that are likely to be enriched due to anthropogenic practices at Hill End, including Pb, As, Cu and Zn, at relatively low concentrations without wet chemistry or other forms of laborious sample preparation. XRF is a non-destructive technique used for the analysis of elements in soil and sediment (El-Taher, 2012). During XRF analysis, a primary beam of X-rays irradiates the sample material and if the energy from the X-ray is sufficient it will dislodge inner shell electrons from atoms in the sample. The atoms then become unstable and outer shell electrons will fall into the vacancy created by the dislodged inner shell electrons to make the atoms stable again, while emitting fluorescent, secondary X-rays (Brouwer, 2010; Shackley, 2011). Each element has a known characteristic fluorescent X-ray which is used to identify its presence in a sample (El-Taher, 2012). The intensity of the X-ray released by each element is used to determine the concentration of each element in the sample (Brouwer, 2010; El-Taher, 2012).

Broadly there are two types of XRF spectrometry: energy dispersive XRF spectrometry (EDXRF) and wavelength dispersive XRF spectrometry (WDXRF). Both types of XRF spectrometry have advantages and disadvantages in terms of detection limits, sensitivity, resolution and cost (Brouwer, 2010). EDXRF was used in this study as it has excellent detection limits and appropriate resolution for the metals of interest in this study, with the exception of Hg (Benyaïch et al., 1997; Brouwer, 2010; Al-Eshaikh and Kadachi, 2011; El-Taher, 2012). The XRF instruments used in this study included: an Olympus DELTA handheld 40 kV EDXRF (or handheld XRF: hhXRF), and a COX Analytical ITRAX core scanner. Every sample in this study (n=175) was analysed by hhXRF, and two sediment cores totalling 6.8 m were analysed by ITRAX.

4.3.2 hhXRF

The hhXRF is a small, portable EDXRF instrument that can measure the elemental composition of an *in situ* or *ex situ* soil or sediment sample by directly irradiating the material through a small window on the instrument. The hhXRF was the primary instrument used to analyse soil and sediment geochemistry in this study because of its portability, reliability and relative accuracy. The use of hhXRFs first emerged in the literature in 2005 and they are increasingly being used as they are easily transportable in the field, the cost of sample analysis is relatively low and they provide instantaneous results which can inform the sampling strategy during fieldwork (Aaron, 2013). The hhXRF instrument is generally considered less accurate compared with more established XRF instruments (e.g. benchtop EDXRF or WDXRF instruments) or other elemental analytical techniques such as inductively-coupled plasma mass spectrometry (Rowe et al., 2012; Dahl et al., 2013). However in their review of advances in XRF, West et al. (2014) found that hhXRFs are capable of providing reliable results, especially if satisfactory quality assurance and quality control (QAQC) measures are employed. For example, Dahl et al. (2013) were able to validate the results of the hhXRF by constraining the accuracy and precision of the hhXRF through analysis of a set of standard reference materials. QAQC measures for this study are described in section 4.3.6.

For this study, an Olympus DELTA hhXRF was taken to the field sites to analyse samples *in in situ* and *ex situ*. Samples analysed from Chappell's profile were the only samples analysed *in situ* to ensure analysis of intact sediment was equivalent to that sampled for ITRAX analysis. *Ex situ* samples were collected with a clean trowel, placed in polyethylene bags and mixed thoroughly for representativeness. When analysing all samples the hhXRF was set to the standard 'soil' mode and all three beams were set to analyse the sample for 30 seconds. A software calibration test was performed each day prior to use and two standards (NIST 2710a and NIST2711a) and a blank material (SiO_2) were also measured each day. For every sample, a thin X-ray film was placed on top of the soil/sediment to separate it from the hhXRF to avoid cross-contamination between sampling. While the hhXRF is capable of detecting Hg in samples, the use of a DMA-80 is preferred due to the low limits of detection for Hg compared to the DMA-80, and so Hg detected by hhXRF was not relied upon in this study.

4.3.3 ITRAX

ITRAX is a high resolution EDXRF (or μXRF) core scanning system that can record a radiographic and optical image of a sediment core and can provide elemental XRF scans at sub-millimetre intervals (Croudace et al., 2006). ITRAX is ideal for analysing sediment cores or U-channels with very finely laminated sediments, such as those found in the tailings dams at Hill End. ITRAX was used in this study to detect fine-scale changes in geochemistry in the sediment profiles (actual concentrations of elements in the sediment were not determined by ITRAX) at Chappell's Dam and Bald Hill Dam that could not be achieved by analysing sediment sampled manually within the sediment profile for hhXRF.

ITRAX analysis was conducted at the Australian Nuclear Science and Technology Organisation (ANSTO) with a Cox Analytical ITRAX instrument in accordance with methods used by (Croudace et al., 2006). The surface of each U-channel was cleaned to ensure a smooth surface for analysis before the sediment was placed into the core scanner which was programmed to scan each section at 1 mm intervals. Although the ITRAX can scan sediment at intervals as fine as 200 μm, 1 mm intervals were chosen for this study to reduce analysis costs and time required to scan the sediment profiles from Hill End. This approach was necessary due to the very fine laminations present in the sediment profiles from Hill End, which precluded individual layers being sampled for separate analysis.

4.3.4 DMA-80

The Milestone DMA-80 was used in this study because it has the ability to assess total Hg content at high and low concentrations and, as a result, it can overcome the limitations of XRF for Hg analysis. The DMA-80 heats the sample material in an oxygenated decomposition furnace to liberate Hg from the sample (Environmental Protection Agency, 2007). The sample is then dried and chemically and thermally decomposed within the decomposition furnace (Environmental Protection Agency, 2007). The Hg is trapped by an amalgamator which is heated and Hg vapour is released and carried through absorbance cells where Hg concentration is measured. The DMA-80 was used in this study as it has a detection limit of 0.01 ng of total Hg, making it suitable for detecting small changes in Hg concentration between samples.

DMA-80 analysis was conducted at Macquarie University and performed in accordance with the EPA method 743 (Environmental Protection Agency, 2007). Only 158 samples of the total 175 samples in this study were analysed for total Hg due to cost constraints. Bedrock samples were the only landscape group not analysed, sample selection was based on ensuring a representative spread of samples from the sub-catchment across a variety of the remaining landscape units. Samples that recorded high concentrations for Hg, As, Zn, Pb or Cu from the hhXRF instrument were favourably selected for DMA-80 analysis. Samples were sieved to <2 mm using a stainless steel sieve to remove large organic material and gravel. The <2 mm fraction was then mixed thoroughly and a representative sub-sample taken for analysis. 0.005 g of each sub-sample was placed in a clean nickel boat and analysed by the DMA-80.

4.3.5 Quality assurance and quality control (QAQC)

QAQC measures were employed to constrain the quality of data produced by the various analytical instruments in this study. Precision of data was determined through calculating relative standard deviation (RSD) and accuracy of data was determined through calculating relative percent difference (RPD).

4.3.5.1 Precision and accuracy of hhXRF

Two standards (NIST 2710a and NIST2711a) were each analysed 10 times with the hhXRF before analysis of the 175 samples in this study commenced to constrain precision (calculated through RSD) and accuracy (calculated through RPD) of the instrument (Appendix 1). A blank material (SiO_2) was also analysed to investigate if the instrument was picking up background elemental concentrations (Tables 4.2 - 4.4). RSD for NIST 2710a was 0.90, 0.91, 0.73 and 0.67 for Cu, Zn, As and Pb respectively. RSD for NIST 2711a was 3.71, 1.16, 6.92 and 0.83 for Cu, Zn, As and Pb respectively. RPD for NIST 2710a was 1.77, 2.18, 0.21 and 1.81 for Cu, Zn, As and Pb respectively. RPD for NIST 2711a was 16.22, 15.06, 22.80 and 1.43 for Cu, Zn, As and Pb respectively. This QAQC exercise demonstrated that the hhXRF is more accurate at analysing elements in high concentrations than low concentrations and it recorded negligible background concentrations of elements when compared to the blank standard. Despite waning precision and accuracy when analysing sample material in very low concentrations this instrument was deemed appropriate for the purposes of this study.

4.3.5.2 Comparison of ex situ *and pressed pellet hhXRF analysis*

Minimal sample preparation is required for hhXRF analysis, but this can lead to issues with the sample matrix, moisture content, density and the possibility of not analysing a representative portion of the sample (Vanhoof et al., 2004; Frahm, 2013). Soil and sediment samples can be pressed into pellets when being analysed for benchtop EDXRF or WDXRF instruments to resolve the above mentioned issues, however hhXRF analysis is often performed *in situ* or *ex situ* without any sample preparation. To investigate the appropriateness of analysing samples *ex situ*, 29 samples collected from the study area were analysed *ex situ* and then as pressed pellets and the analytical differences were measured. *Ex situ* samples were analysed after being placed in polyethylene bags and mixed vigorously. After this analysis the samples were pressed into pellets and analysed by hhXRF again. Preparation of pellets followed a similar procedure to Rouillon et al., (2013). For each sample, a 15.0 g representative sub-sample was milled to ~20-30 μm in a Retsch MM 301 Mixer Mill for 6 minutes at 25 Hz. In between samples, the mill components were cleaned by grinding acid-washed quartz for 2 minutes at 20 Hz followed by rinses with ethanol. Exactly 8.0 g of milled sub-sample was mixed uniformly with 1.0 g of Licowax binder in a clean plastic vial. This mixture was placed in a 432 mm pellet die which was pressed using a Herzog hydraulic ram for 90 seconds at 13 tonnes to form coherent pellets of consistent matrix. In between sample pressing, the pellet die was cleaned with ethanol and clean wipes according to standard procedures. This exercise revealed minimal minor elemental variance (mean RSD Cu = 19 %, Zn = 15 %, As = 29 %, Pb = 15 %) between the two methods of sample analysis. Minor variances may be explained by improved representativeness of the sample material and improved sample flatness in pressed pellet form, compared to *ex situ* samples. Due to the relatively low RSD for each element this exercise justified the use of *ex situ* hhXRF analysis.

4.3.5.3 Precision and accuracy of DMA-80

QAQC measures were also employed for analysis with the DMA-80. The accuracy and precision of the instrument was determined through analysing four prepared standard solutions of equal Hg concentration five times (Appendix 1). Blank samples were run between samples to measure background Hg within the instrument and background Hg within the instrument was subtracted from the measured total Hg content for each sample.

4.3.6 Quantifying anthropogenic contamination

Samples elevated above background may not necessarily be anthropogenically enriched but may be elevated above background due to natural variability (Alloway, 2013). Comparing metal concentrations in samples to background concentrations was therefore not used as the primary method to quantify anthropogenic contamination. The enrichment factor (EF) is a more robust method used to quantify anthropogenic contamination in soil and sediment by determining if high or low concentrations of metals in soil or sediment samples are due to anthropogenic sources or natural processes. Despite criticisms of the EF method (e.g. Reimann and Caritat, 2000), it is widely used throughout the literature and can be used effectively if background concentrations of key elements are known (Blaser et al., 2000; Sutherland, 2000; Loska et al., 2005; Parelho et al., 2014; Zhang et al., 2014).

The EF method assumes that in undisturbed soil or sediment there is a linear relationship between a reference element and the element being investigated for metal contamination (Parelho et al., 2014). Reference elements in a soil or sediment particle are assumed to have uniform flux from the time the particle was eroded from parent material to the time that it was deposited in the study area, while concentrations of the element being investigated for metal contamination may have increased over time due to anthropogenic sources (Sutherland, 2000). Common reference elements include Aluminium (Al), Chromium (Cr), Iron (Fe), Lithium (Li), Manganese (Mn), Scandium (Sc) and Titanium (Ti) (Sutherland, 2000; Zhang et al., 2014). Fe is frequently used (e.g. Ergin et al., 1991; Akoto et al., 2008; Karbassi et al., 2011; Okedeyi et al., 2014) and was selected for this study due to its low variability in samples from the landscape at Hill End.

Methods used to derive an EF vary throughout the literature. Background concentrations for Fe and other key metals were assessed during this study, and so they were used rather than using crustal averages for each metal. The EF equation used by Ergin et al. (1991), Parelho et al. (2014) and Okedeyi et al. (2014) was used for this study:

$$EF = \left(\frac{X\ sample}{Y\ sample}\right) \div \left(\frac{X\ background}{Y\ background}\right)$$

where EF is the enrichment factor, X sample is the concentration of the investigated element in the sample, Y sample is the concentration of the reference element in the sample, X background is the background concentration of the investigated element and Y background is the background concentration of the reference element.

The scale used to interpret to degree of anthropogenic enrichment developed by Sutherland (2000) is commonly used throughout the literature (Loska et al., 2005; Okedeyi et al., 2014) and was used for this study (Table 4.2).

Table 4.2: Scale of enrichment based on the enrichment factor. Adapted from Sutherland (2000).

Enrichment factor	**Extent of anthropogenic enrichment**
< 2	No to minimal enrichment
2 – 5	Minimal to moderate enrichment
5 – 20	Moderate to high enrichment
20 – 40	Significant enrichment
> 40	Extremely enriched

4.4 Sediment mineralogy

4.4.1 XRD

Mineralogy was analysed using XRD of sediments in Chappell's Dam at 10 cm intervals in order to provide information on possible changes to the source of sediment in the dam over time and on the history of contamination in the catchment. XRD is a non-destructive analytical technique that is widely used for assessing the mineral composition of soil, sediment and rocks (Stanjek and Häusler, 2004; Harris and White, 2008). In XRD, a sample is irradiated with X-rays which interact with the sample material causing diffraction of the X-rays (Harris and White, 2008). The location and intensities of the diffraction peaks provide data for mineral identification (Stanjek and Häusler, 2004).

Sample preparation and analysis was carried out at Macquarie University using the PANalytical X'Pert Pro MPD diffractometer. Samples were sieved to <63 µm and ~8 g sub-samples were rinsed with acetone and crushed in a mortar and pestle. Sub-samples were then placed onto Si crystal low background holder discs. Samples were scanned at 0.05° (2θ) steps from 10° to 40° (2θ) at 45 kV, 40 mA, using Cu-Ka radiation and an X'Celerator detector.

4.5 Sediment geochronology

4.5.1 pOSL

Portable OSL is a technique used to investigate luminescence intensities (represented as total photon counts) in bulk sediment samples (Sanderson and Murphy, 2010; Muñoz-Salinas et al., 2011; Stang et al., 2012). Luminescence properties assessed by pOSL can assist identification of depositional boundaries in sediment profiles, which can provide an insight into sediment character and depositional processes (Muñoz-Salinas et al., 2014). Furthermore, pOSL can be used as a diagnostic tool to identify locations in a sediment sequence that would be suitable for further sampling and analysis to determine the burial age of materials using OSL dating (Sanderson and Murphy, 2010).

pOSL analysis was conducted at Macquarie University using a pOSL reader from the Scottish Universities Environmental Research Centre (SUREC). Bulk sediment samples were removed from their canister onto a petri dish in a completely dark room (except for subdued red light) to avoid unwanted light stimulation. The samples were individually loaded into a small compartment in the pOSL reader and stimulated by infrared (IRSL) and blue (BLSL) wavelengths. Each sample was stimulated under IRSL for 30 seconds, followed by 10 seconds under dark counts and then another 30 seconds under IRSL. The same processes was then repeated for BLSL. The luminescence intensity given off by the minerals is recorded by the pOSL reader.

4.5.2 OSL dating

OSL dating has become an important chronological tool in fluvial environments where radiocarbon dating is often problematic (Rittenour, 2008). It is a numerical dating technique used to estimate the time since mineral grains (quartz or feldspar) were last exposed to sunlight, which usually corresponds to the time when grains were last deposited (Huntley et al., 1985; Jacobs and Roberts, 2007). When minerals are exposed to sunlight during sediment transport their trapped electron population is reset to zero. Sometimes a mineral's electron population is not reset to zero due to complexities involved in sediment transport, this phenomenon is known as 'partial bleaching'. Upon deposition and cessation of sunlight exposure, the trapped electron population within the crystal lattice of grains increases due to exposure to natural sources of ionizing radiation from the surrounding environment and from cosmic rays. The amount of trapped charged electrons within the mineral grain since burial is released in the form of a luminescence signal, upon stimulation by wavelengths of light in a laboratory using a RISØ instrument (Duller, 2004). The same mineral grains that produced the luminescence signal are then exposed to different doses of radiation to find which dose produces the same luminescence signal, known as the equivalent dose. An OSL age is determined by dividing the equivalent dose by the environmental dose rate, the rate of exposure to natural sources of radiation in the burial environment (Duller, 2004; Jacobs and Roberts, 2007).

Single-grain OSL analysis was conducted at the 'Traps' Luminescence Dating Facility at Macquarie University. The 90-212 µm fraction was treated with 10% hydrochloric acid and 10% hydrogen peroxide before undergoing mineral separations. The quartz fraction was treated with 40% hydrofluoric acid to remove the alpha contribution. The 90-125 µm fraction was used for single-aliquot and single-grain analysis respectively. For RISØ analysis, all sample emissions were detected by an Electron Tubes Ltd 9235QA photomultiplier tube fitted with 7.5 mm of Hoya U-340 filter fitted onto a RISØ TL/OSL-DA-20 reader. High resolution gamma spectrometry was conducted with a high purity germanium detector by the Environmental Research Institute of the Supervising Scientist (ERISS) office in Darwin, Australia, to provide data for dose rate determination. . Due to complexities often involved with OSL for fluvial sediments (e.g. partial bleaching and mixing of populations of grains with different ages), the minimum age model (MAM) was used. The MAM is a statistical model which reduces the influence of grains with higher palaeodoses, as these grains may have been partially bleached prior to burial and will therefore provide an inaccurate age estimate (usually an overestimate) (Galbraith et al., 1999). The MAM calculation requires the dose rate to be divided by the palaeodose estimate of the lowest population of grains.

4.5.3 Excess ^{210}Pb

Excess ^{210}Pb is a geochronological technique that uses disequilibrium between two fractions of the natural radioisotope ^{210}Pb to assess changes in sedimentation rates and to develop age-depth models for sediment profiles. The principles of excess ^{210}Pb and its use as a chronostratigraphic and accretion rate technique for recent sediments (less than 150 years old) have been outlined by Appleby (2001), amongst others. Essentially, ^{210}Pb (half-life 22.26 years) is the granddaughter isotope of radium-226 (^{226}Ra; half-life 1.602 ka) within the uranium-238 (^{238}U) decay series. Disequilibrium between ^{210}Pb and ^{226}Ra occurs through diffusion of the gaseous isotope radon-222 (^{222}Rn), the daughter of ^{226}Ra and parent of ^{210}Pb, a portion of which escapes into the atmosphere where it is distributed globally. ^{210}Pb produced by the decay of ^{222}Rn in the atmosphere attaches to aerosol particles that are deposited on the Earth's surface by dry fallout or precipitation. ^{210}Pb has a short atmospheric residence time before it is incorporated into fine sediments on the land surface or in the water column, and is transported and deposited with those sediments into floodplains, lakes, estuaries and other repositories. ^{210}Pb is also produced by the *in situ* decay of ^{226}Ra and ^{222}Rn in the lithosphere, and so total ^{210}Pb activity in sediment has two components: i) supported ^{210}Pb, which derives from the *in situ* decay of ^{226}Ra is assumed to be in secular equilibrium with the ^{238}U decay series, and ii) excess ^{210}Pb, which derives from atmospheric fallout and is in disequilibrium with ^{226}Ra (Appleby, 2001).

Excess ^{210}Pb cannot be measured directly, so it is determined by subtracting supported ^{210}Pb activity (determined by measuring ^{226}Ra) from total ^{210}Pb activity (determined by measuring ^{210}Pb or its daughter isotope polonium-210; ^{210}Po). For this study, analysis for excess ^{210}Pb was undertaken using standard acid digestion and alpha spectrometry source preparation following standard wet chemistry preparation methods in the Environmental Radioactivity Laboratory of the Australian nuclear Science and Technology Organisation (ANSTO).

In sediment profiles, high excess ^{210}Pb activities in surface materials usually reflect recent atmospheric inputs, while deeper sediments that have been buried by recent deposits and isolated from further inputs and/or removal of excess ^{210}Pb will have a reduced activity. Because ^{210}Pb decays at a known the rate, the proportion of excess ^{210}Pb in a sediment profile relative to the excess ^{210}Pb at the surface can be used to infer the time since atmospheric deposition ceased (i.e. the timeframe of sediment accumulation). Simple regression models can be applied to the data and age-depth models can be derived based on the radioactive decay law, that usually assume conservative behaviour of ^{210}Pb in the environment, constant atmospheric flux of ^{210}Pb and constant sedimentation rate (Appleby, 2001). Age-depth models are used to determine sedimentation rates and to establish excess ^{210}Pb chronologies. One of the most common models was applied in this study, the Constant Initial Concentration (CIC) model, which assumes that the initial concentration of excess ^{210}Pb in deposited sediment is constant despite any changes in the sediment accretion rate and therefore, that the supply of excess ^{210}Pb varies in proportion to the mean sedimentation rate (Appleby, 2001). The CIC model is appropriate for sites where the excess ^{210}Pb input is dominated by allochthonous contributions; that is, where excess ^{210}Pb is thought to be primarily supplied in sediment-bound form from the catchment (Oldfield and Appleby, 1984). An alternative model, the Constant Rate of Supply (CRS) model, assumes constant atmospheric fallout of ^{210}Pb to the waterbody, and is not suitable for sites that have significant catchment contributions of sediment-bound radionuclides.

4.6 Summary

This chapter discussed the sampling strategy used in this study, as well as providing a brief overview and justifying the use of various analytical techniques. Sediment geochemistry will be determined through a variety of XRF instruments and a DMA-80. Sediment mineralogy will be determined through XRD. Sediment geochronology will be determined through pOSL, OSL and excess ^{210}Pb.

5.0 Spatial distribution of legacy sediment and metal contamination

5.1 Introduction

It has now been over 100 years since the majority of gold mining ceased in Hill End and legacy sediment released into the environment from mining activities has been exposed to various geomorphological processes. This chapter will reveal where legacy sediment has accumulated in the catchment as well as describing the current geochemistry of soil and sediment in Hill End.

5.2 Distribution and character of legacy sediment

5.2.1 Spatial distribution

Legacy sediment is found at mine sites, on hillslopes and in the drainage outlets of Hill End. Mine sites and hillslopes were the predominant sources of legacy sediment where land clearance, the mobilisation of soil and sediment and the excessive dumping of mullock took place. Large volumes of mullock were piled throughout the landscape from reef mining. On steep hillslopes such as Hawkins Hill, these piles of mullock have formed scree slopes that now cover the majority of the slope. The removal of vegetation and excessive dumping of mullock has increased slope-channel connectivity and some of this coarse material is found in the drainage outlets of Hill End including Nuggetty Gully and Hill End Creek (Figure 5.1). In flatter areas of Hill End, mullock remains in large piles adjacent to abandoned mine shafts where there is comparatively little evidence of reworking throughout the landscape. Mining activities and vegetation clearance have also contributed to sheet, rill and gully erosion and the mobilisation of soil and sediment. Small amounts of this finer material remain on hillslopes or are stored in small deposits in the uplands or lowlands of Hill End.

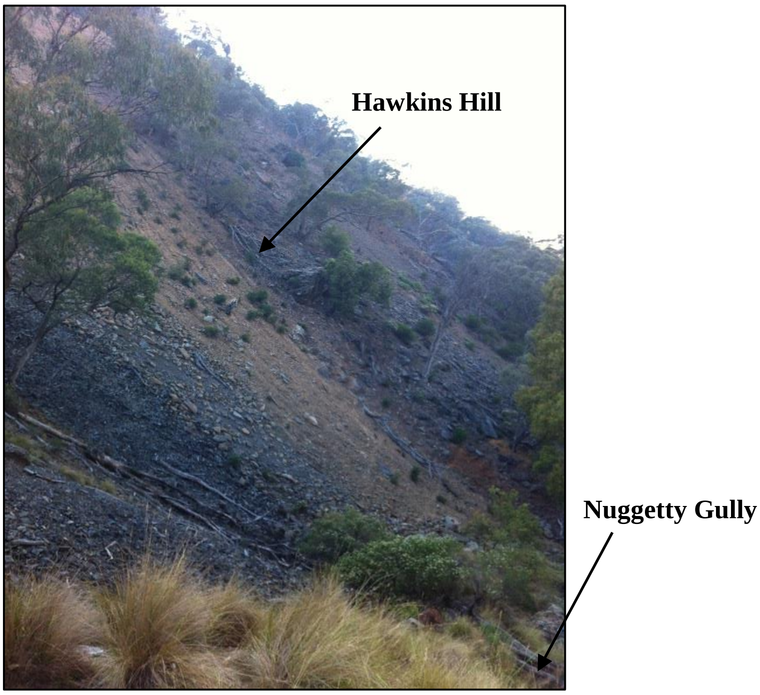

Figure 5.1: Scree slope on Hawkins Hill

There is evidence to suggest that very little of the legacy sediment sourced from mine workings and hillslopes has been retained in the Hill End catchment. For the most part, the bedrock confined creeks and streams of Hill End have very limited accommodation space and large floods combined with high stream power and high sediment transport capacity have removed the majority of fine sediment within channels leaving only large boulders. Legacy sediment storage is mostly restricted to the upstream reach of Hill End Creek in abandoned tailings dams and fluvial units such as bank-attached bars and small floodplain pockets, and in the lower reach of Hill End Creek before the confluence with the Turon River in gravel bars and occasional floodplain pockets (Figure 5.2).

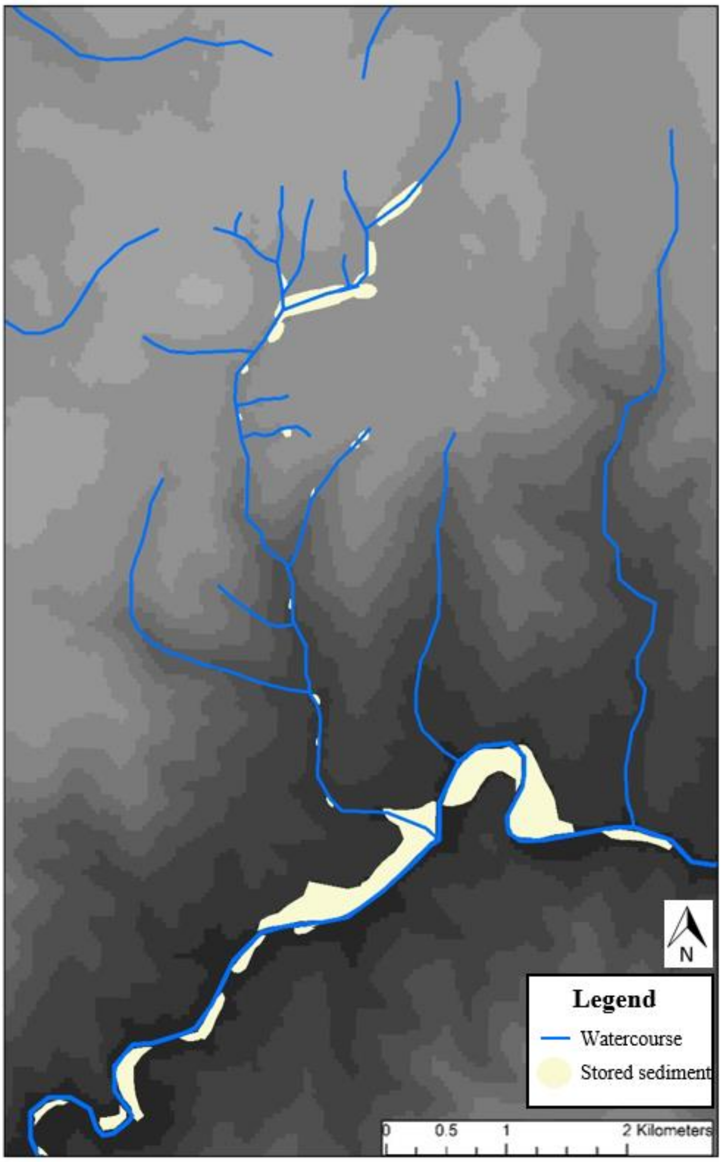

Figure 5.2: Stored sediment along Hill End Creek and the Turon River. Map derived from aerial photograph analysis and ground surveys along the length of watercourses within the catchment

The sediment/source storage zone in the upper reaches of Hill End Creek is 2.2 km long. There is no sediment stored in the narrow gorge in the middle reach of Hill End Creek. The second sediment storage zone downstream in Hill End Creek is 4 km long. Overall, the geomorphology of the catchment with limited accommodation space and a high capacity for sediment transport suggests that legacy sediment may have been exported downstream to the Turon and Macquarie Rivers. A wider valley margin, a lower longitudinal gradient and an overall increase in accommodation space has allowed the formation of larger floodplain pockets, point bars, bank attached bars and mid-channel bars in the Turon River.

There is ample evidence of sediment reworking since the cessation of mining activities. Sediment has been washed and accumulated down hillslopes and in drainage outlets of Hill End. An example of this is at the site of Chappell's stamper battery (Figure 5.3). Vegetation clearance and mine workings upslope of Chappell's stamper battery produced large volumes of legacy sediment. Sediment that wasn't delivered to Hill End Creek during the period of peak mining activities has accumulated downslope and has partly buried the ruins of Chappell's stamper battery (abandoned in 1874).

Figure 5.3 Remains of a stonework settling tank around the site of Chappell's stamper battery gradually being filled with legacy sediment, 2014.

5.2.2 Character of legacy sediment

The character of legacy sediment varies throughout Hill End. Legacy sediment at reef mining areas such as Hawkins Hill generally contains a mix of coarse and fine material as mullock consisting of rock and soil has been piled and reworked throughout the majority of the hillslope. Other mined areas with gentler gradients than Hawkins Hill generally have a separation of coarse and fine material. For example fine material is present throughout Prince Alfred Hill while coarser material is mainly restricted to mullock piles spread throughout the hillslope.

Legacy sediment stored within the upper reaches of Hill End Creek is typically fined grained. This sediment appears to be sourced mainly from sheet, rill and gully erosion on surrounding hillslopes. Sediment stored in tailings dams (Figure 5.4A) is mainly fine silts and clays deposited in laminated sequences in the lower and middle layers, and as coarser sandy layers in the upper sections. The finer laminations were deposited in a lacustrine environment when the dams were in use during the peak of mining activities c. 1871 to 1874, or shortly after their abandonment. Sediment accumulation in dams probably ceased in the late 1890s or early 1900s in the majority of tailings dams following decreased mining activity resulting and the breaching of several tailings dams (Hodge, 1964).

Legacy sediment stored in the lower reach of Hill End Creek varied in character from legacy sediment stored in the upper reaches and tailings dams. Downstream legacy sediment was stored in occasional floodplain pockets or bars. These depositional units, which contain a mix of cobbles, gravel and fine sediment were found close to the confluence of Hill End Creek and the Turon River (Figure 5.3B). Downstream legacy sediment sampled in this study was from the top 2 cm of these depositional units which did not contain any cobbles or gravel.

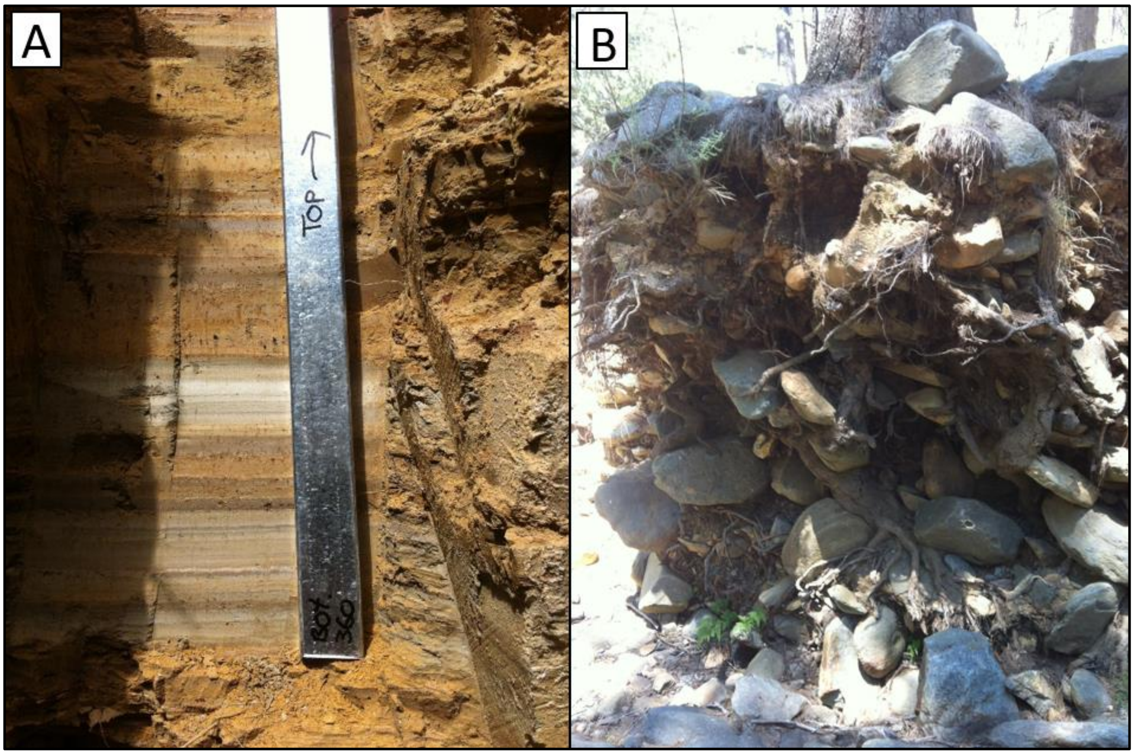

Figure 5.4: Legacy sediment at Hill End. (A) Fine laminations of legacy sediment at Chappell's Dam. (B) Legacy sediment stored in a matrix of gravel and cobbles in a mid-channel bar in the lower reach of Hill End Creek.

5.3 Soil and sediment geochemistry

5.2.3 Background concentrations of metals

The background concentrations of key elements in soils and sediments not affected by mining activities in the study area are presented in Table 5.1. Hg has a background of 0.032 mg kg^{-1}, As has a background of 2.35 mg kg^{-1}, Cu has a background of 8.63 mg kg^{-1}, Pb has a background of 12.1 mg kg^{-1} and Zn has a background of 17.2 mg kg^{-1}. Hill End is located within a global Hg belt that stretches across eastern Australia (Gustin et al., 2000), meaning that natural Hg background concentrations for soil and sediment in the region may be higher than other Australian Hg background concentrations or higher than global Hg background concentrations. Hg concentrations in soil and sediment in areas within Hg belts can range from 0.01 to 0.3 mg kg^{-1} (Jones and Jarvis, 1981), and the Hg background found in soils and sediments at Hill End is at the lower end of this range (0.032 mg kg^{-1}). The location of background samples can be seen in Figure 4.1.

Table 5.1: Background concentrations for key metals. Note that “<LOD” means less than the detectable limit.

	Hg (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	As (mg kg^{-1})	Pb (mg kg^{-1})
Mean (n=10)	0.032	8.63	17.2	2.35	12.1
SD	0.025	2.89	8.70	2.70	3.45
SE	0.008	0.91	2.75	0.85	1.08
Range	0.004 - 0.057	5.0 - 13.6	5.90 - 27.2	<LOD - 7.90	5.0 - 16.1

5.2.4 Spatial patterns of soil and sediment geochemistry

There were no obvious spatial gradients of contamination in soil and sediment samples across the catchment, however hotspots emerged that had relatively high concentrations of Hg (Figure 5.5), As (Figure 5.6), Cu (Figure 5.7), Pb (Figure 5.8) and Zn (Figure 5.9) and were in stark contrast to sites with very little or no contamination. The highest value of Hg (44.6 mg kg^{-1}) and As (221 mg kg^{-1}) were found at Chappell’s Dam. The highest value of Cu (136 mg kg^{-1}) was found in Nuggetty Gully. The highest values of Pb (540 mg kg^{-1}) and Zn (5233 mg kg^{-1}) were found in spoil in the remains of a small miner’s camp area.

Hotspots for metal contamination were generally restricted to certain landscape units. Samples from Chappell’s Dam, mullock heaps on Hawkins Hill and mine sites west of Hill End village near Prince Alfred Hill and adjacent to abandoned stamper batteries and cyanide tanks (spoil) contained high concentrations from a variety of metals. The most significant hotspot at Hill End was Chappell's Dam, where high concentrations for each metal were found in numerous samples.

There was a spatial pattern of samples with low concentrations of metal contamination, where background soil samples collected furthest away from mining historic mining activities (to the west and north east of the main study area) contained the lowest concentrations for Hg, Zn, Cu, As and Pb. Some samples within the main study area contained similar concentrations to background, however the majority of samples were elevated above background. Generally, the spatial assessment of metal contamination demonstrates that samples taken at a considerable distance away from known mining activities contained lower metal concentrations compared to samples within the known mining areas (Figures 5.5 to 5.9).

5.2.5 Geochemistry of landscape units

Differences in soil and sediment geochemistry between landscape units are presented in Figure 5.10. Landscape units including tailings dams, mullock heaps and spoil from mining activities generally contained higher concentrations of metals compared to the other landscape units. For example, mean values of Hg and As in tailings dams (Hg 3.89 mg kg^{-1} and As 22.44 mg kg^{-1}), mullock (Hg 0.62 mg kg^{-1} and As 18.30 mg kg^{-1}) and spoil landscape units (Hg 0.62 mg kg^{-1}, and As 12.63 mg kg^{-1}) were higher than the mean values of Hg and As from fluvial (Hg 0.33 mg kg^{-1} and As 9.99 mg kg^{-1}), hillslope (Hg 0.19 mg kg^{-1} and As 8.35 mg kg^{-1}), gully (Hg 0.27 mg kg^{-1} and As 7.83 mg kg^{-1}) landscape units and also higher than background (Hg 0.03 mg kg^{-1} and As 2.35 mg kg^{-1}). These findings were consistent with the spatial analysis of soil and sediment geochemistry as the majority of metal hotspots were found at Chappell's Dam, mullock heaps and spoil sites. There were few or no instances where high concentrations of metals were found in the fluvial, gully, hillslope, bedrock or background soil landscape units.

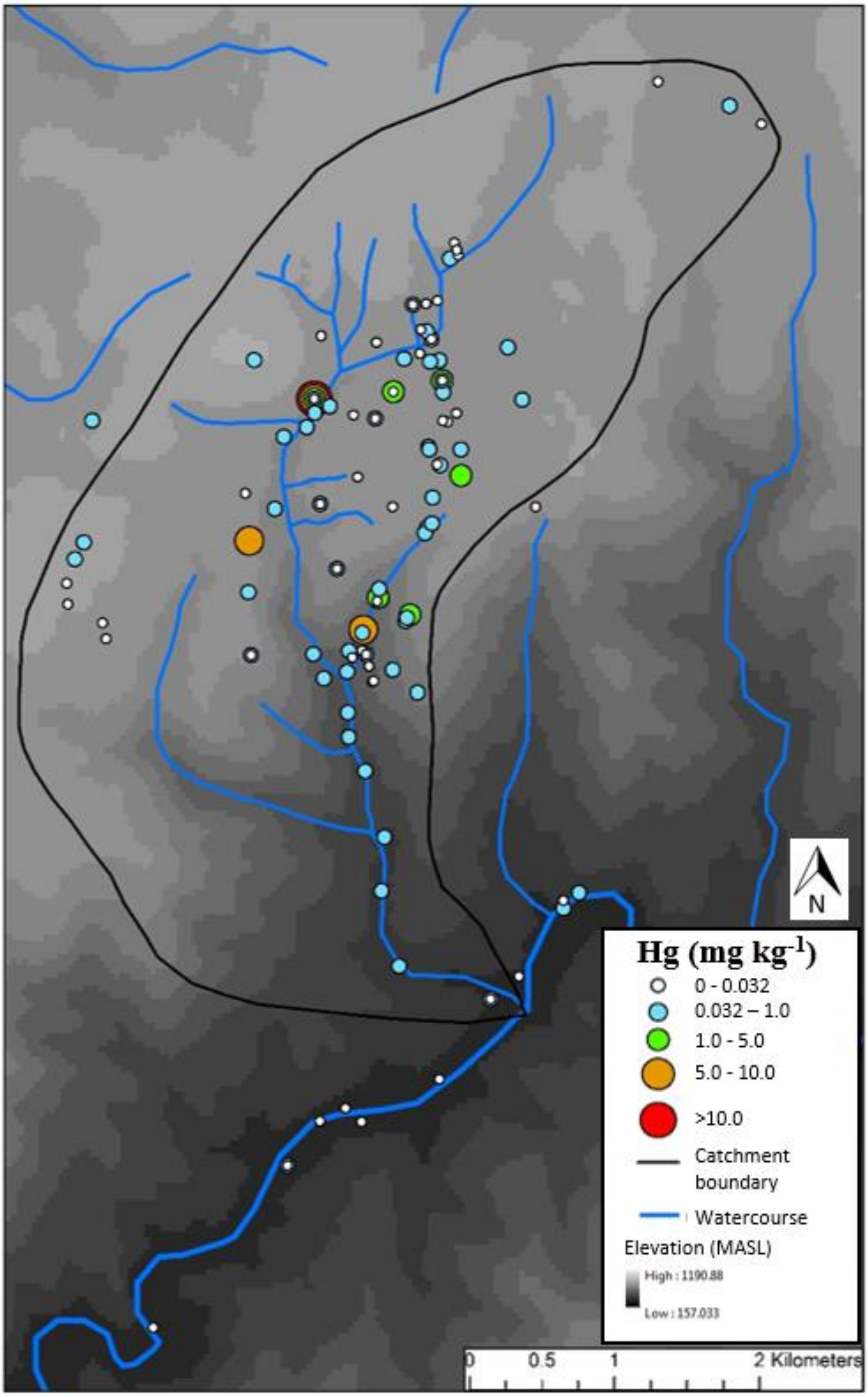

Figure 5.5: Distribution of Hg in soil and sediment in Hill End. Samples in white circles are below background

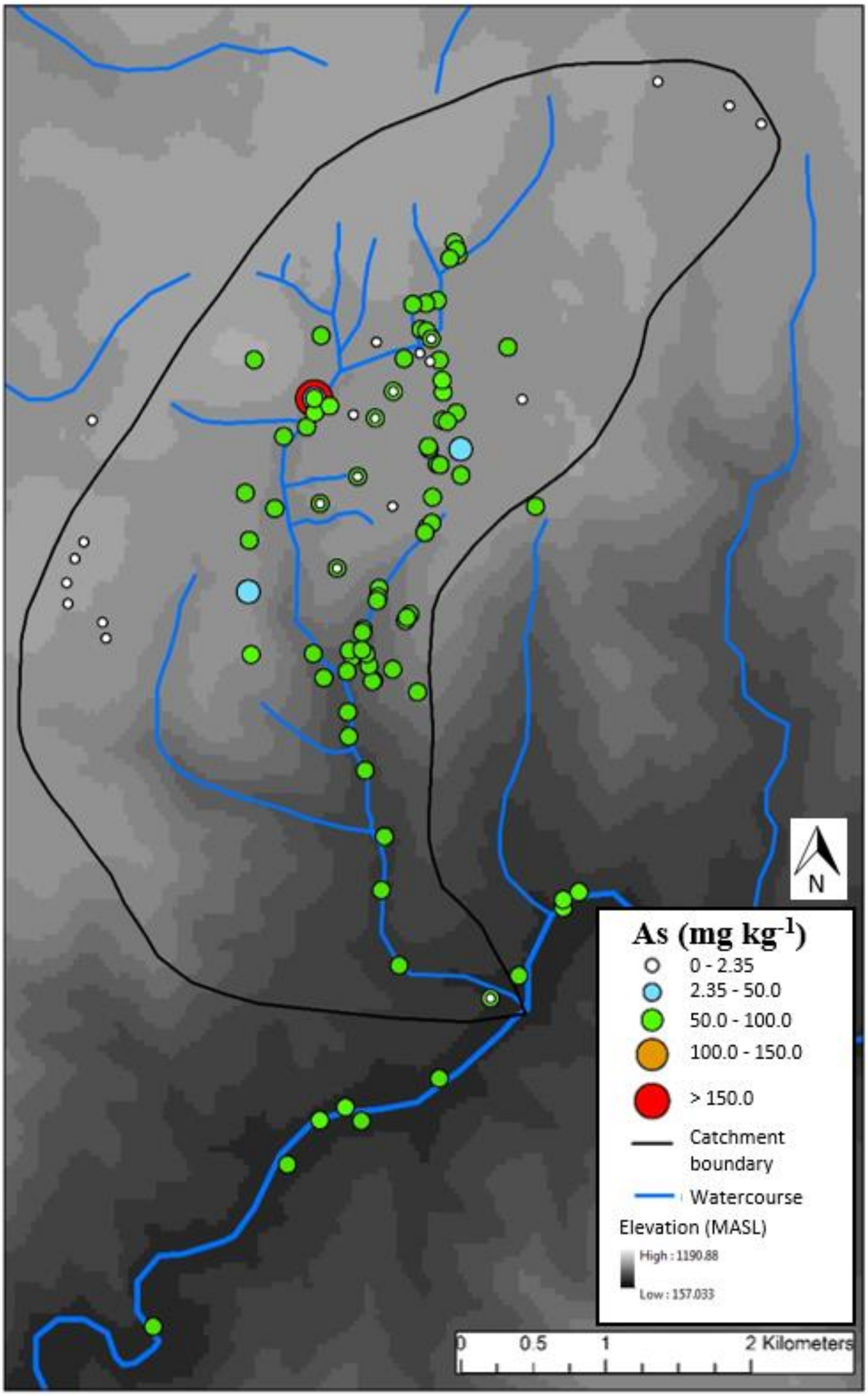

Figure 5.6: Distribution of As in soil and sediment in Hill End. Samples in white are below background.

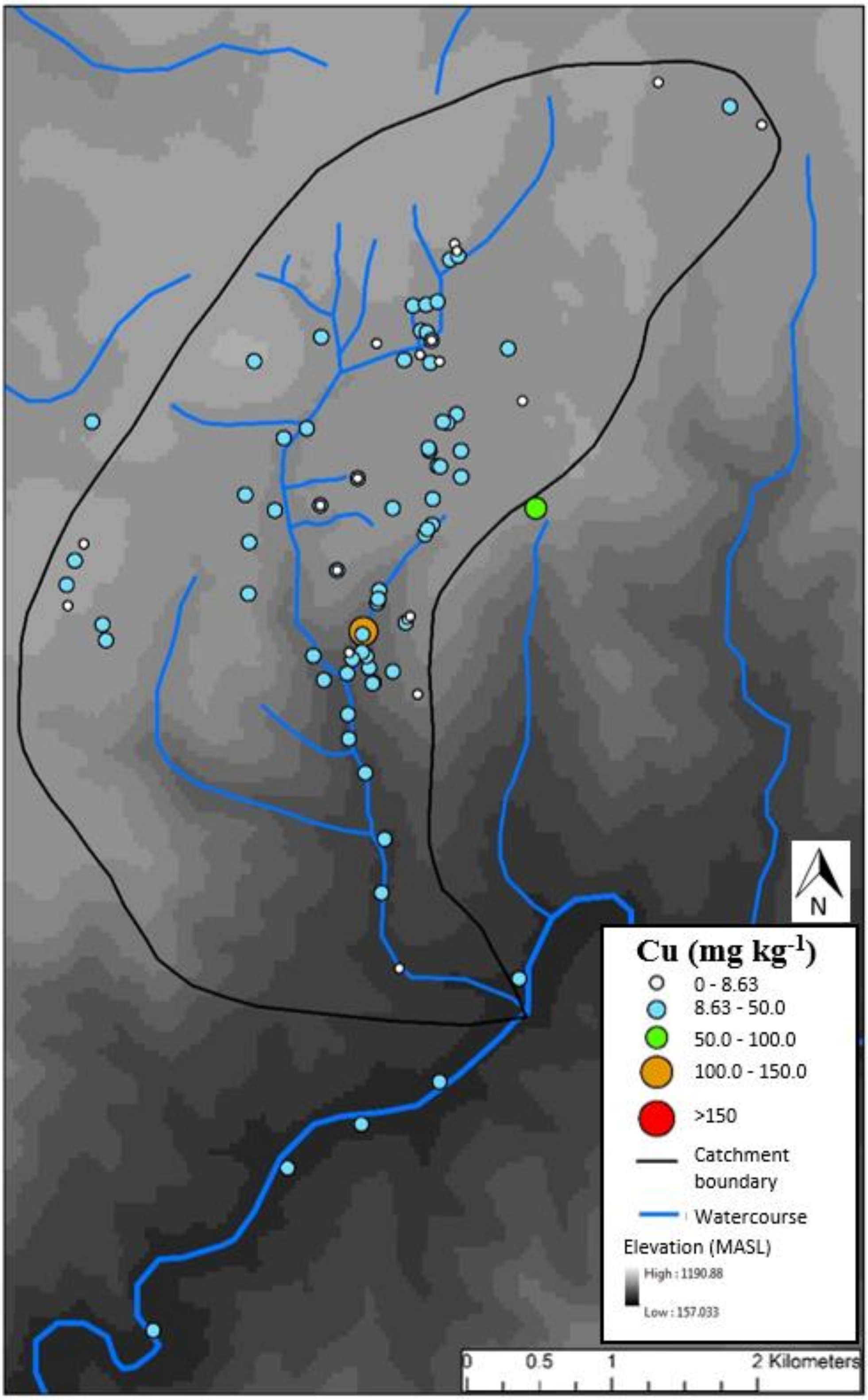

Figure 5.7: Distribution of Cu in soil and sediment in Hill End. Samples in white are below background.

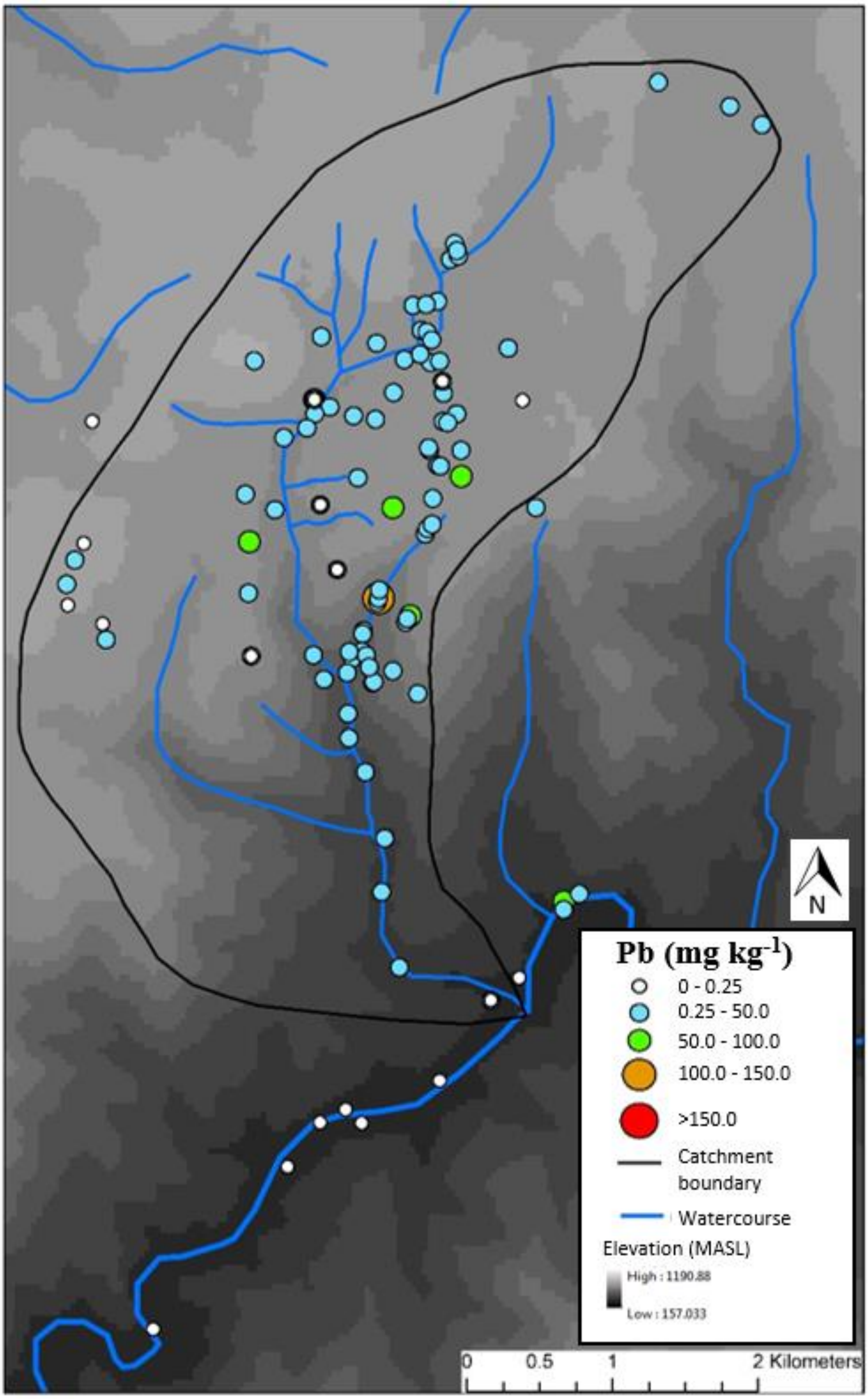

Figure 5.8: Distribution of Pb in soil and sediment in Hill End. Samples in white are below background

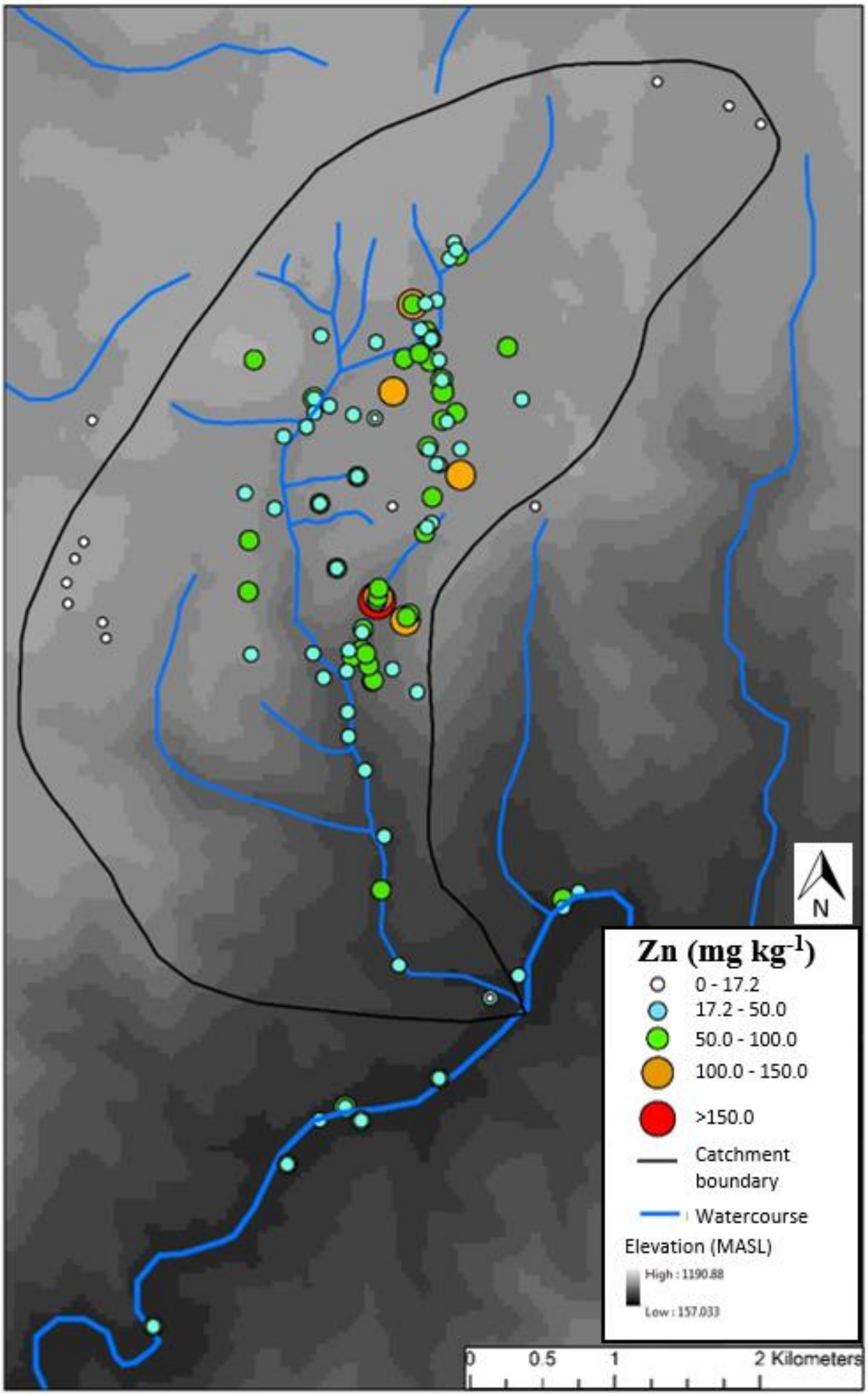

Figure 5.9: Distribution of Zn in soil and sediment in Hill End. Samples in white are below background

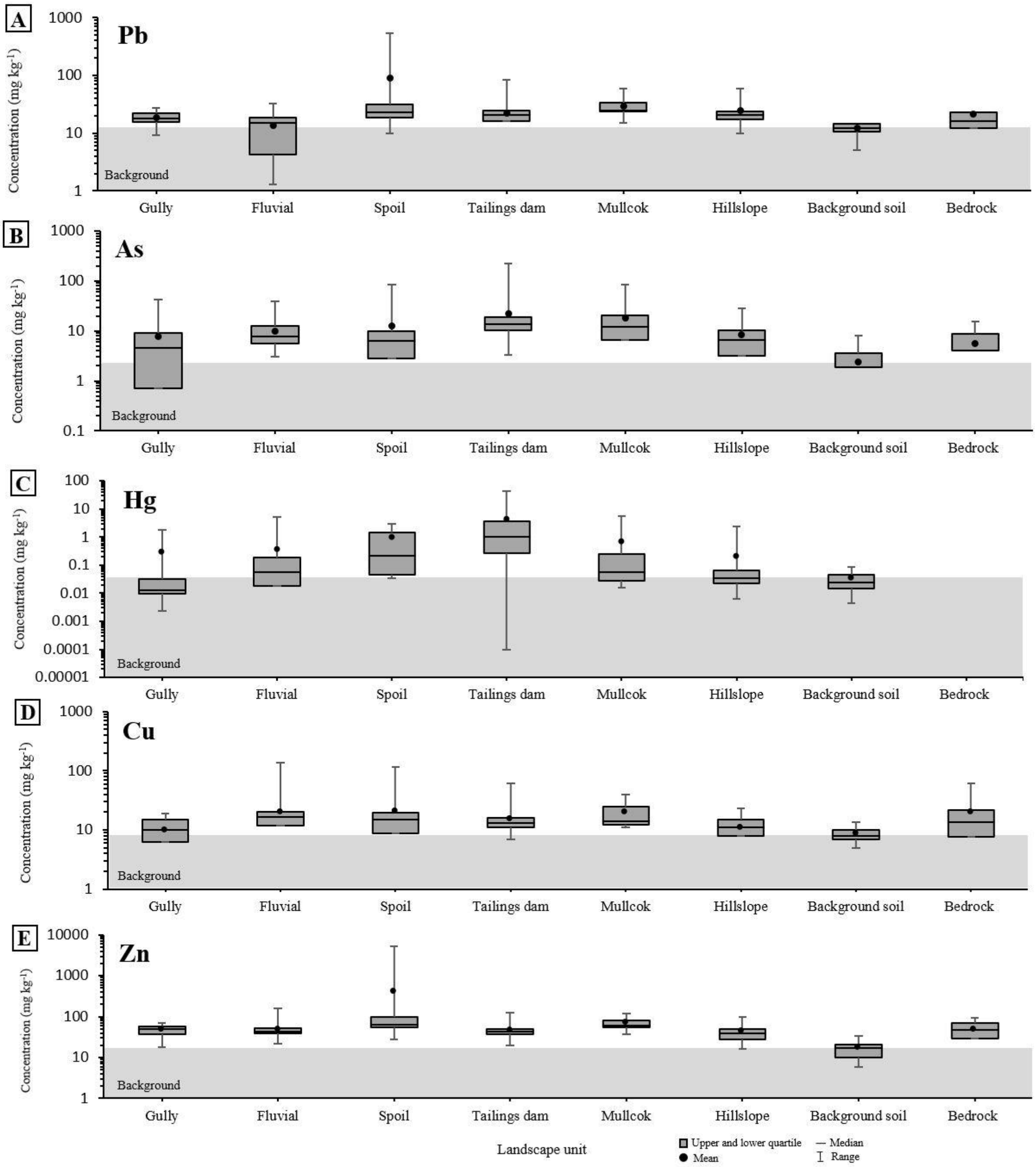

Figure 5.10: Box and whisker plots illustrating the differences in geochemistry between landscape units. Horizontal grey bars indicate the background values for each element.

The Kruskal-Wallis non-parametric statistical test was used to determine whether there were statistically significant differences between the median concentrations of each metal in the different landscape units. There were significant differences in Pb (H=45.3, p=<0.0001), As, (H=52.12, p=<0.0001), Hg, (H=56.87, p=<0.0001), Cu (H=31.21, p=<0.0001) and Zn

(H=49.19, p=<0.0001) 2.08^{-8}) between landscape units, showing that the geochemistry of these landscape units was significantly different. The non-parametric Mann-Whitney *U*-test was also used to further investigate the differences between each landscape unit (Appendix 2). This test found that most landscape units (except for the gully unit) were significantly different from background soil for each element. The hotspots of tailings dams and mine spoil were also significantly different from most other landscape units for each metal.

5.2.6 Downstream patterns of geochemistry

The downstream trends in sediment geochemistry from Hill End Creek and the Turon River are illustrated in Figure 5.11. Hg, As, Zn and Pb are all quite variable, however they show a general downstream decline in concentration, while Cu had a general increase in concentration downstream. The variability in metal concentrations in the fluvial system may be due to the selection of different fluvial units for sampling along the system, which included the channel bed, banks and bars. Fluvial units sampled were representative of the reach at the location where the sample was collected. Interestingly though, Hg and Pb concentrations were maintained above background in Hill End Creek but decreased rapidly to below background levels after the confluence with the Turon River. All metal concentrations were very low around the point where Hill End Creek descends the escarpment and, with the exception of Cu, metal concentrations appeared to decrease after the after the confluence of Hill End Creek and the Turon River. This may reflect dilution of sediment coming from Hill End Creek in the Turon River, which has an upstream catchment area of approximately 1500 km^2.

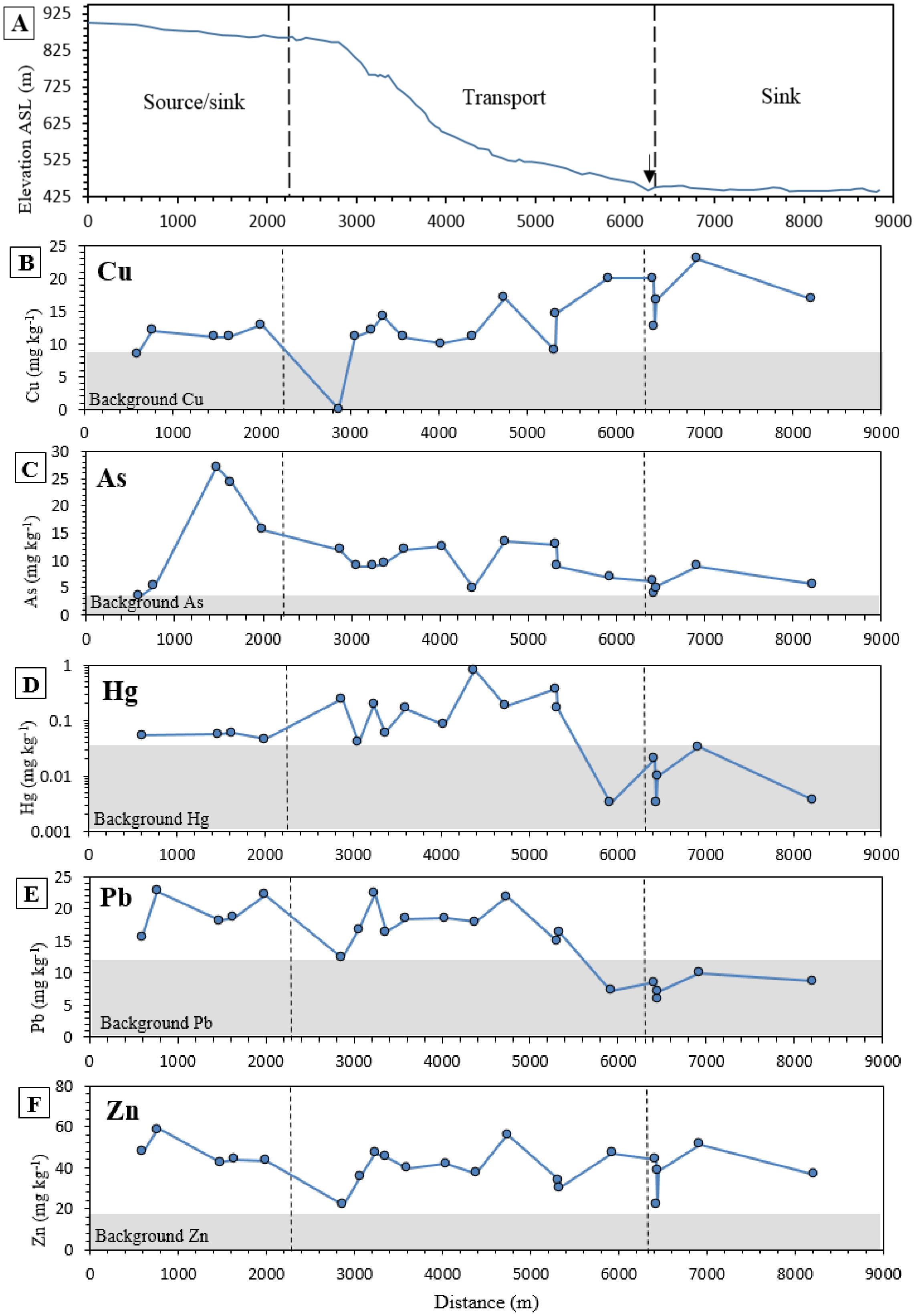

Figure 5.11: Downstream changes along Hill End Creek and the Turon River. (A) Changes in elevation and sediment storage/transport zones. Note, the arrow in (A) represents the Hill End Creek Turon River and Turon River convergence. Downstream changes in metal concentrations are presented in (B) for Cu, (C) for As, (D) for Hg, (E) for Pb and (F) for Zn. Note the Y-axis on (D) is plotted on a log scale.

Five shallow pits were excavated at varying distances within the hyporheic zone of the Turon River to further investigate the downstream trend in contamination and to examine possible vertical patterns of contamination. These pits were limited to depths ranging from 25-45 cm due to water depth. One pit was upstream of the Turon River's junction with Hill End Creek and five pits were downstream of this junction. There were no linear changes with depth in metal concentration; in some pits the highest metal concentrations were found at the surface sample, while in others the highest concentrations were found at depth (e.g. Figure 5.12).

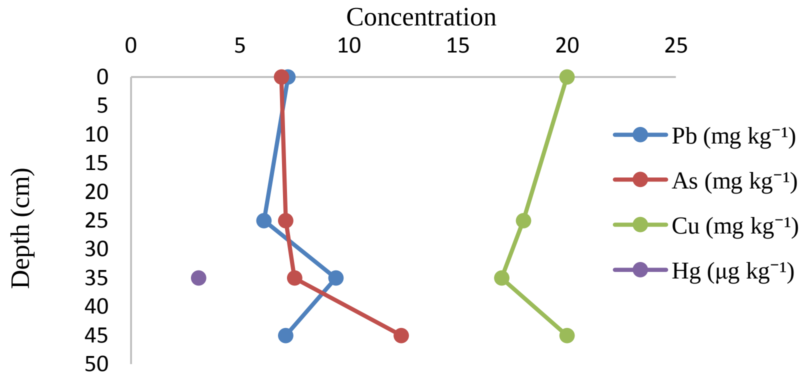

Figure 5.12: Pit excavated 500 m downstream of the junction of Hill End Creek and the Turon River on a point bar. *Note that only 1 sample from each pit was analysed for Hg content and that Hg concentration is given in µg kg^{-1}.

The samples that comprise the broader fluvial landscape unit were broken down into two sub-groups of geomorphic units: (i) depositional units (Figure 5.13) and (ii) fluvial systems (Figure 5.13). The depositional units were divided into bed, bank and bar samples and the fluvial systems were divided into samples from Hill End Creek, Nuggetty Gully and the Turon River.

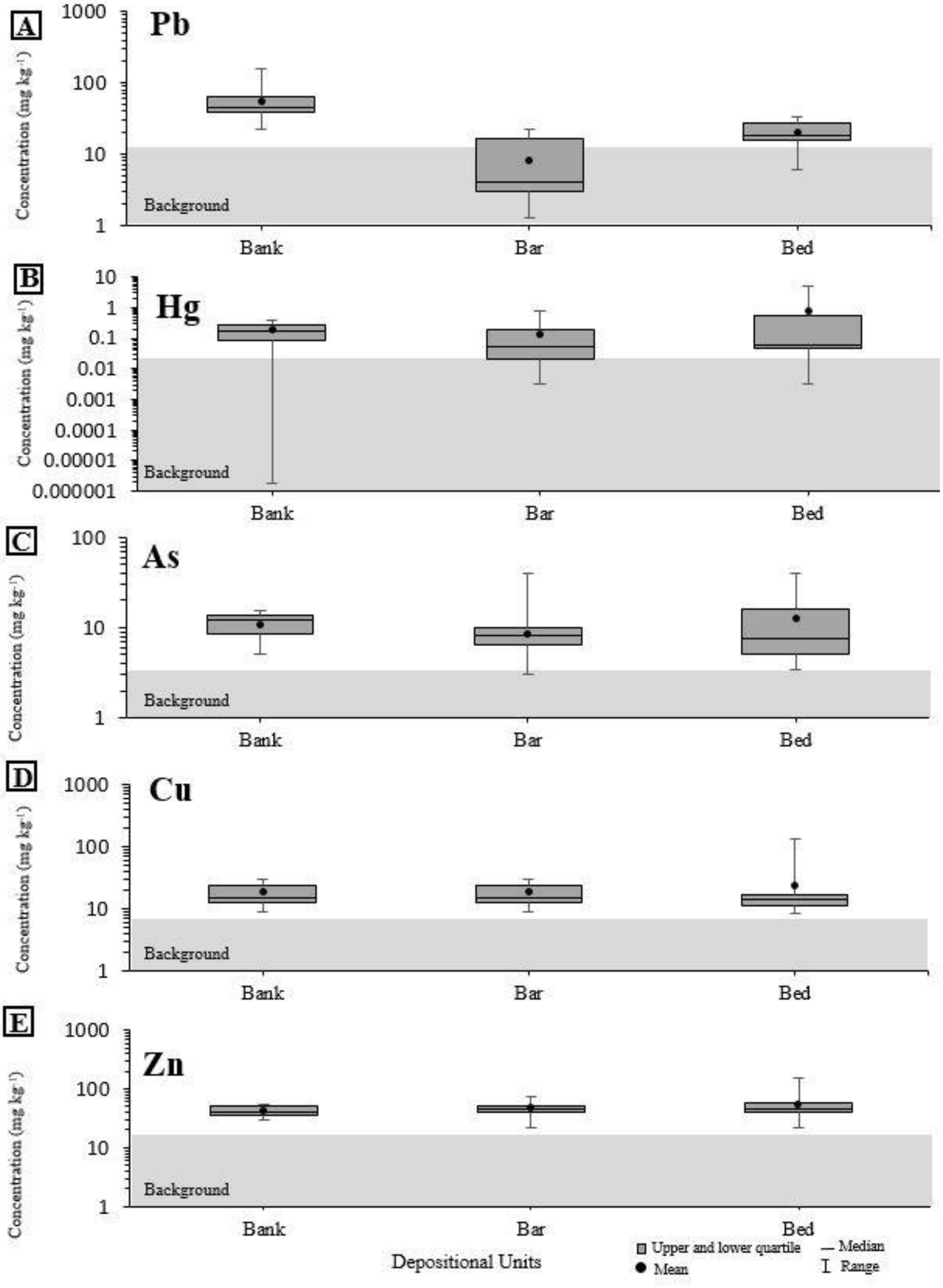

Figure 5.13: Box and whisker plots of the concentration of Pb (A), Hg (B), AS (C), Cu (D) and Zn (E) for the different depositional units within the fluvial systems of Hill End. Number of samples: bank (n=7), bar (n=20), bed (n=14).

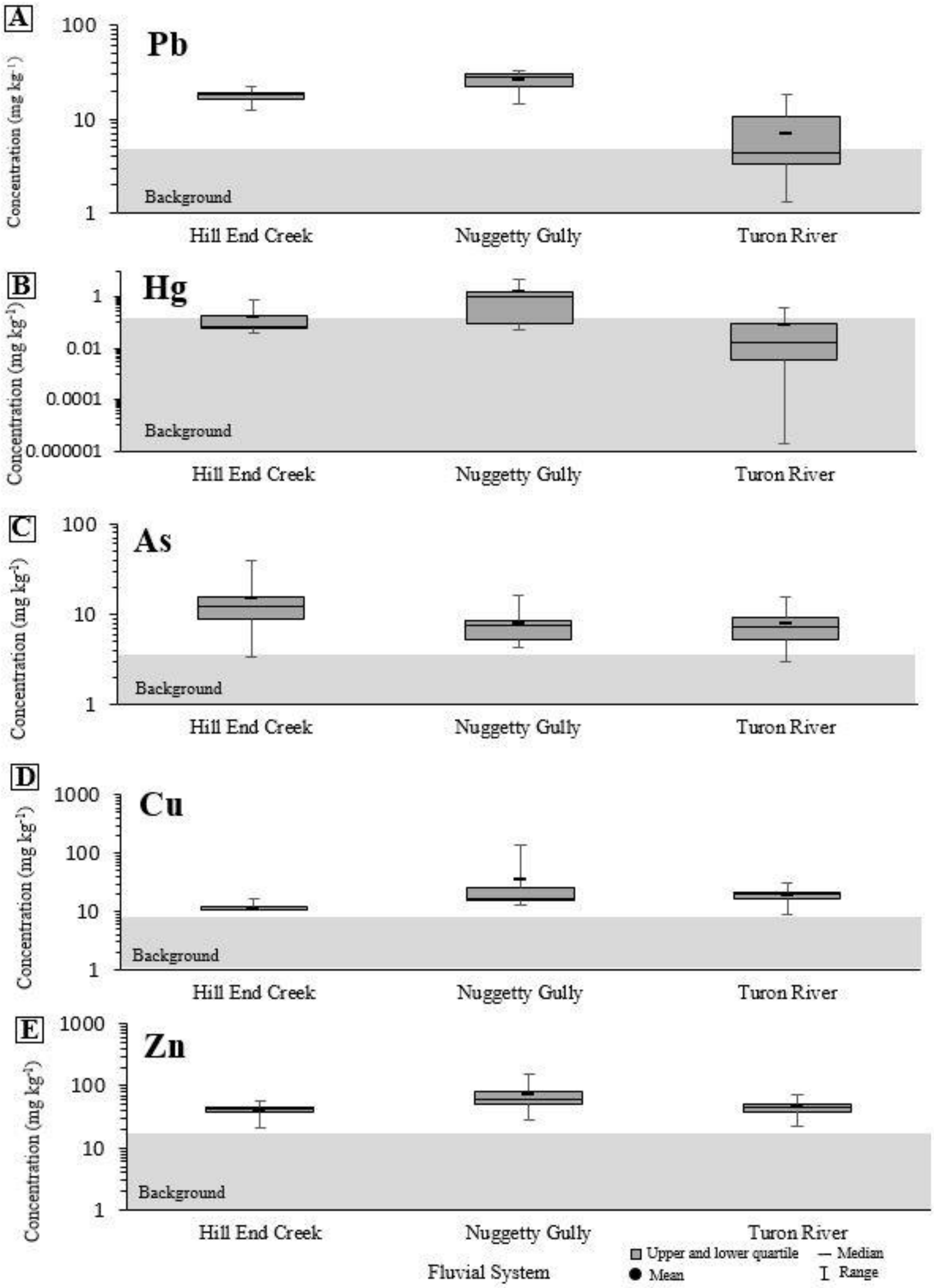

Figure 5.14: Box and whisker plots of the concentrations of Pb (A), Hg (B), As (C), Cu (D) and Zn (E) for the different fluvial systems in the study area. Number of samples: Hill End Creek (n=13), Nuggetty Gully (n=7), Turon (n=23).

The results show that channel bed samples generally contained the highest metal concentrations, while bank samples contained higher concentrations of Pb than bar or bed samples and also had the biggest range of Hg concentrations (Figure 5.13). There was a larger number of bar and bed samples compared to bank samples as samples were collected from the most representative depositional unit within the channel at the time of sampling. Despite the slight differences observed in metal concentrations in Figure 5.13, the Kruskal-Wallis test determined that there were not statistically significant differences between the median metal concentrations of the depositional units.

Nuggetty Gully was generally more enriched in Pb, Hg, Cu and Zn compared to Hill End Creek and the Turon River. This is likely because that Nuggetty Gully drains the most heavily mined area in Hill End. Large volumes of excavated rock and soil as well as the numerous stamper batteries operating on Hawkins Hill and within Nuggetty Gully are likely to have contributed to the high concentrations of metals found here. The Kruskal-Wallis test determined that there were statistically significant differences between median concentrations of Pb ($H=27.99$, $p<0.0001$), As ($H=6.052$, $p=0.048$), Cu ($H=19.9$, $p<0.0001$) and Zn ($H=6.331$, $p=0.042$) but not for Hg ($H=4.147$, $p=0.13$) in the different fluvial systems.

The very low concentrations of Hg found within the Turon River (Figure 5.14) may be due to dilution and increased accommodation space of sediment. Low concentrations of Hg within the Turon is notable due to its history of alluvial and reef mining upstream of Hill End. The Turon has more accommodation space for sediment than Hill End Creek and Nuggetty Gully and the deposition of ‘clean’ sediment not directly impacted by mining activities in the Turon River may have buried or diluted contaminated sediment.

5.2.7 Levels of anthropogenic contamination

The levels of anthropogenic contamination were investigated by comparing the concentration of soil and sediment samples to background and calculating the enrichment factor for each sample. Although the majority of samples exceeded background concentrations for each metal (Table 5.2), less than 50 % of the samples (except for As) were elevated two times (2x) above background. It is difficult to determine if samples that exceeded the 2x background have experienced anthropogenic contamination or if the high percentage of samples in this range reflect relatively low concentrations in the original background concentrations. Samples that were 5x, 10x, 20x and 50x background show clearer evidence for anthropogenic contamination.

Table 5.2: Percentage of samples below and above background concentrations

	% of samples n=175 for As, Cu, Pb, Zn and n= 158 for Hg						
Metal	**Below background**	**Above background**	**2 x background**	**5 x background**	**10 x background**	**20 x background**	**50 x background**
Hg	21.14	78.86	48	39.4	28	24	14.9
As	13.14	86.86	80.5	41.7	13.1	4	1.7
Cu	20	80	11.4	3.4	1.1	0	0
Pb	20	80	24.6	2.9	1.7	1.1	0
Zn	9.71	90.83	11.4	9.7	0.5	0.5	0.5

The majority of samples for each element (except As) had an enrichment factor <2 which implies the sample has minimal to no enrichment (Table 5.3). A large percentage of samples had an enrichment factor ranging from 2-5 (minimal to moderate enrichment) compared to samples with an enrichment factor of 5-20 (moderate to high enrichment), 20-40 (significant enrichment) and >40 (extremely enriched). Interestingly Hg and As both contain a relatively high percentage of samples with an enrichment factor >5 (44.85 and 71.42 %, respectively) compared to Cu, Pb and Zn (4.57, 4.0 and 7.43 %, respectively). Hg also had the highest percentage of samples with an enrichment factor >40 (18.99%).

Table 5.3: Range of enrichment factors for samples. Note number of Pb, Cu, As, Zn samples = 175, number of Hg samples = 158

	% of samples				
Metal	**< 2**	**2 - 5**	**5 - 20**	**20 - 40**	**> 40**
Hg	36.71	13.29	17.72	8.23	18.99
As	21.14	46.86	33.14	3.43	1.71
Cu	67.43	34.29	4.0	0	0.57
Pb	78.29	24.0	2.86	0.57	0.57
Zn	18.86	24.0	6.86	0	0.57

The levels of anthropogenic contamination were investigated for each landscape unit (Figure 5.14). Tailings dams and spoil contained the highest percentage of samples with an enrichment factor >40. Background soil, fluvial, hillslopes, gullies and to a lesser extent mullock showed less anthropogenic enrichment compared to tailings dams and spoil. Bedrock samples were included in Figure 5.13 despite not experiencing any anthropogenic contamination to compare the different range of concentrations in bedrock samples relative to the other landscape units. Figure 5.13 clearly demonstrates that extreme anthropogenic enrichment was mostly restricted to Hg and As.

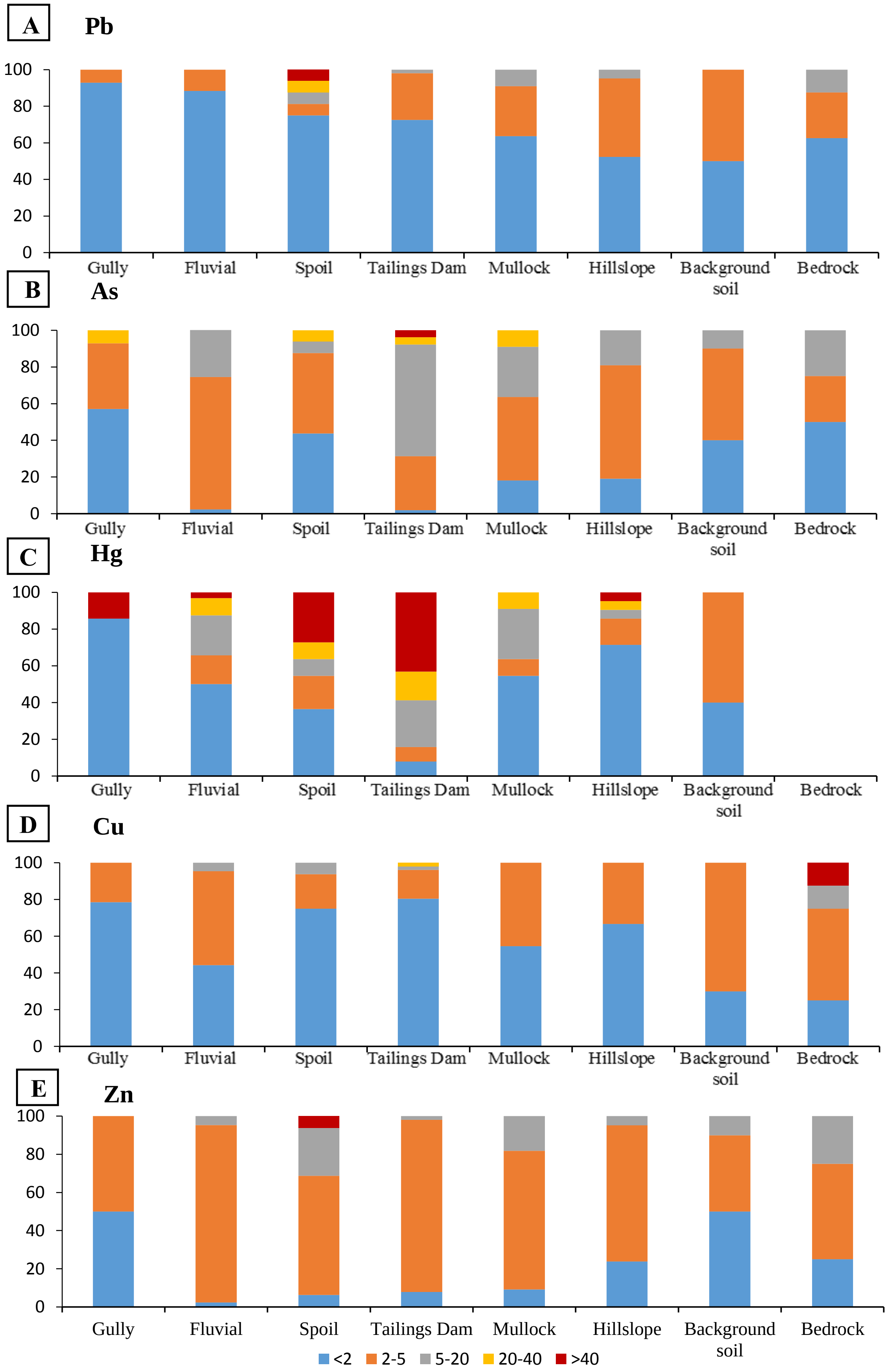

Figure 5.14: Distribution of enrichment values for Pb (A), As (B), Hg (C), Cu (D) and Zn (E) for each landscape unit.

5.2.8 Comparison of results to national and international soil and sediment guidelines

The concentrations of metals in soil and sediment samples were compared to Australian and Canadian contamination guidelines (Table 5.5 and Table 5.6). When comparing the sediment contamination guidelines, the high and low interim sediment quality guidelines (ISQG) for Australia and the ISQG and probable effect levels for Canada were used. The Canadian guidelines provide a more conservative value for each metal than the Australian guidelines. The guidelines for each metal are dependent on land-use type. Although the study area was previously an industrial landscape, the area is now a historical site and as such does not fit into any of the designated categories. Therefore, the "recreational area" category was deemed the most appropriate for this study site.

Table 5.5: Australian and Canadian soil guidelines for recreational areas Australian standards are based on the National Environment Protection Measures (NEPM) (National Environment Protection Council, 2013). Canadian values are based on Canadian Council of Ministers of the Environment (2007). * Based on inorganic samples.

Element	Australian standard (mg kg^{-1})	Samples exceeding Australian standard (n=58)	Canadian standard (mg kg^{-1})	Samples exceeding Canadian standard (n=58)
As	300	0	12*	13
Cu	20000	0	63	1
Pb	600	0	140	2
Hg	10	0	6.6*	0
Zn	30000	0	200	1

Table 5.6: Australian and Canadian sediment guidelines. Australian values are based on Australian and New Zealand Environment Conservation Council (ANZECC) guidelines ANZECC (2000). Canadian values are based on Canadian Council of Ministers of the Environment (2002).

Element	Australian standard (mg kg^{-1})		No. of samples above Australian guidelines (n=108)		Canadian standard (mg kg^{-1})		No. of samples above Canadian guidelines (n=108)	
	Low ISQG (mg kg^{-1})	High ISQG (mg kg^{-1})	Low ISQG	High ISQG	ISQG (mg kg^{-1})	Probable effect level (mg kg^{-1})	ISQG	Probable effect level
As	20	70	16	2	5.9/	17.0	86	18
Cu	65	270	1	0	35.7	197	3	0
Pb	50	220	2	0	35.0	91.3	3	0
Hg	0.1	1	56	29	0.17	0.486	53	37
Zn	200/410	410	0	0	123/	315	2	0

No samples exceeded the Australian soil guidelines for any metal and only a small number of samples exceeded the Canadian guidelines. Based on soil guideline values, the soil at Hill End poses little risk to the public today. Conversely a large number of samples exceeded both Australian and Canadian sediment guidelines, mainly for As and Hg. Two samples for As and 29 samples for Hg exceeded the Australian high ISQG and 18 samples for As and 37 samples for Hg exceeded the Canadian probable effect levels. These results suggest that concentrations of As and Hg in sediments could pose a risk to the aquatic ecosystems in Hill End.

5.4 Summary

This chapter presented results identifying the distribution and character of legacy sediment and the geochemistry of soil and sediment in Hill End. Legacy sediment has mainly been stored in a few discrete sediment sink zones within the upper and lower parts of the catchment, suggesting that large volumes of legacy sediment have been exported out of the Hill End catchment. High concentrations of metals in soil and sediment is mainly restricted to hotspots at tailings dams, in spoil and in mullock heaps. The major hotspot at Hill End was Chappell's Dam which contained very high concentrations of Hg and As and high concentrations of Pb, Cu and Zn. The majority of samples exceeded background concentrations for each metal in the study area, however they did not exhibit significant anthropogenic enrichment based on an assessment of the enrichment factor. There was, however, a large percentage of samples that showed significant enrichment for Hg and As. Few soil samples exceed Australian contamination guidelines, however there were numerous sediment samples that exceeded high Australian trigger values for ISQGs and could pose a risk to aquatic ecosystems in Hill End. The high concentrations of contamination at Chappell's Dam warrant further inquiry, and so this dam was the focus of the detailed geochemical and geochronological research presented in the next chapter.

6.0 Changes in legacy sediment and contamination at Chappell's Dam

6.1 Introduction

This chapter will present results from a detailed investigation into the sedimentology, geochemistry and changes in contamination over time recorded in legacy sediment in Chappell's Dam. This tailings dam was the major metal hotspot in the study area and, as such, warrants further investigation. The geochemistry of this dam will also be compared to the geochemistry of Bald Hill Dam, upstream.

6.2 Sedimentology and mineralogy

Chappell's Dam was in use between 1871 and 1874 and was breached sometime in the 1890s. Since being breached, Hill End Creek has cut through sections of the dam revealing finely laminated sediment (Figure 6.1 and Figure 6.2). The exposed sediment profile at Chappell's Dam that was analysed in detail was 460 cm deep and was characterised by finely laminated layers in the lower 240 cm of the profile and more massive layers in upper 220 cm of the profile (Figure 6.2). The uppermost part of the profile contained evidence of minor soil formation, some mottling and coarse laminations, and the sediment was generally orange to yellow in colour. The laminations fined from a depth of 145 cm and were very fine by 175 cm below the surface. In the lower section of the profile, the laminations were darker in colour and included orange, brown, light grey and dark grey layers. Fine laminations were interspersed with thicker clay units ranging from 5-10 cm in depth. There was little variability in the LOI in the profile until 160 cm. There was also little variability in sand content except for the top 40 cm of the profile and at 140 cm and 360 cm where there were small peaks in sand content.

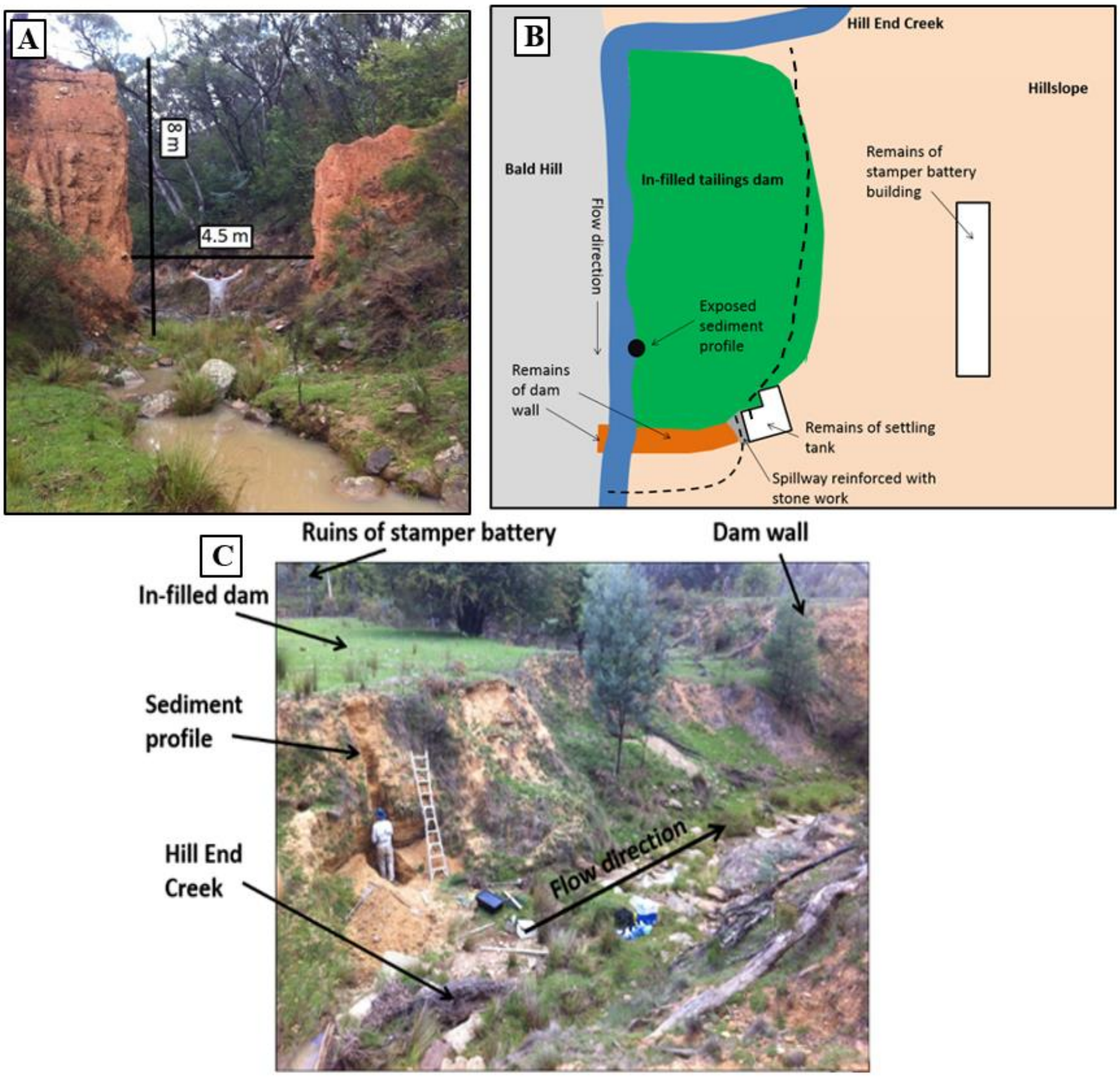

Figure 6.1: Chappell’s Dam (A) looking downstream of Hill End Creek at the breached dam wall, (B) a planform map of Chappell’s Dam showing the location of the exposed sediment profile studied in detail and the site of the abandoned stamper battery, and (C) the view of the exposed sediment profile and Chappell’s Dam from Bald Hill. When Hill End Creek was dammed, water was diverted to flow over the spillway, as represented by the dotted line seen in (B). After the dam wall was breached Hill End Creek has gradually eroded the dam wall and cut through sections of the infilled dam revealing finely laminated sediment.

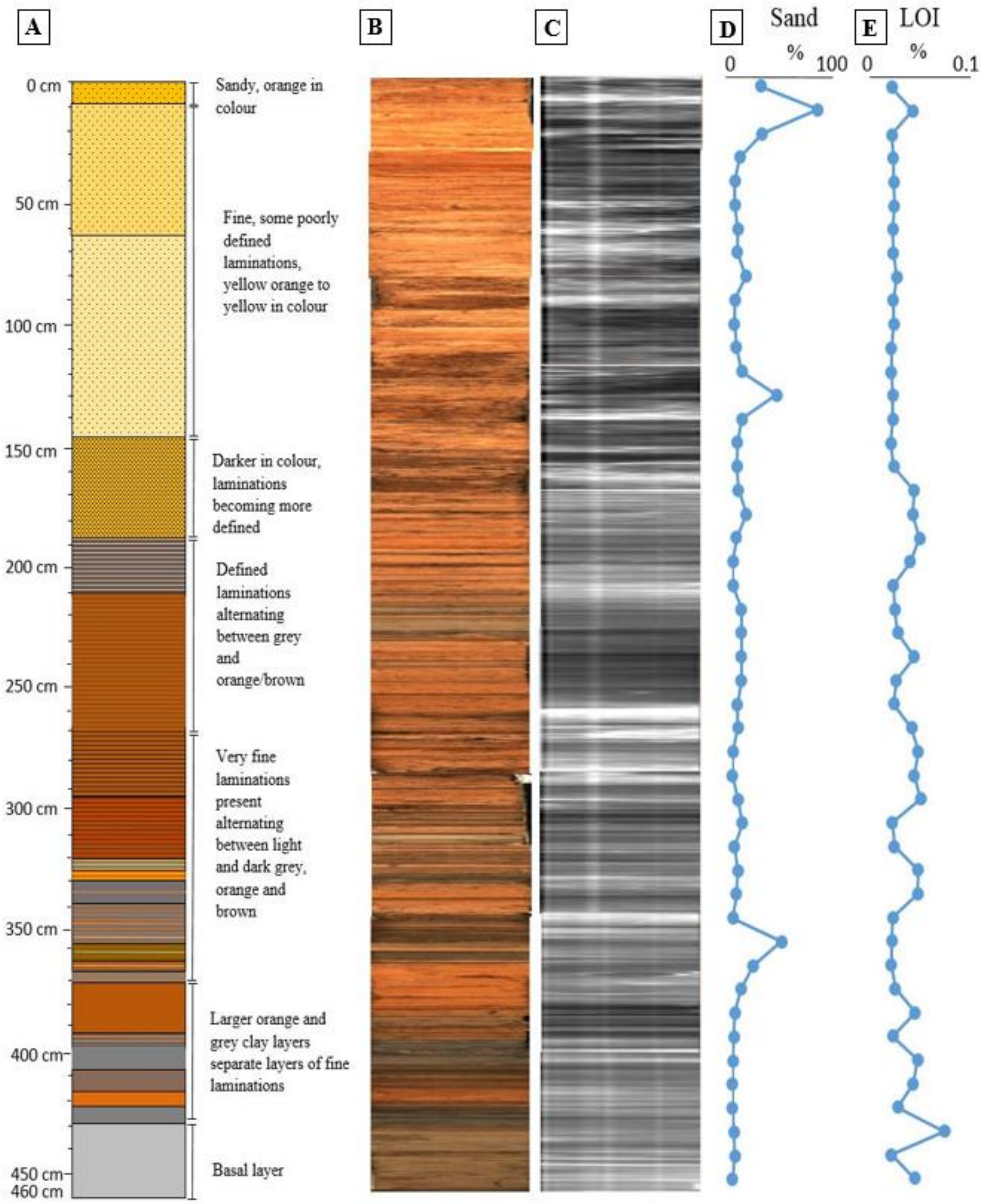

Figure 6.2: (A) Sedimentology, (B) optical image, (C) Radiograph, (D) Sand % and (E) LOI % of Chappell's Dam

XRD was conducted to determine if there were distinct changes in the mineralogy of sediments throughout the sediment profile at Chappell's Dam (Appendix 3). The mineralogy was relatively homogenous with no significant changes throughout the profile. Quartz and muscovite were present throughout the profile with inclusions of albite, birnessite and langite at varying depths.

6.3 Geochemistry

hhXRF and DMA-80 results from 10 cm intervals down the exposed sediment profile at Chappell's Dam revealed several sections where each of the key metals coincide with a peak in contamination (Figure 6.3). The largest of these peaks is between 350 and 370 cm in depth where then highest concentrations of Hg (44.6 mg kg^{-1}) and As (221 mg kg^{-1}) were found. There were relatively large fluctuations in metal concentrations throughout the profile. For example, As drops from 221 mg kg^{-1} at 370 cm to 23 mg kg^{-1} at 380 cm. ITRAX data was able to inform on fine changes in geochemistry between hhXRF samples. ITRAX, hhXRF and DMA-80 data are plotted together to observe the differences in geochemistry recorded by each instrument (Figure 6.3).

ITRAX core scanning revealed a similar pattern of metal contamination to the hhXRF and DMA-80 profiles (Figure 6.3). These methods all detected the peak in metal contamination to be from 360 to 370 cm and provided little evidence of metal contamination throughout the rest of the profile. The peak in metal contamination corresponds to a sand layer leading to the suggestion that this sediment was deposited when Chappell's Stamper Battery was operational and supplying metal contaminated tailings to the Dam as tailings often consisted of fine to coarse sand (Ritchie and Hooker, 1997). It is clear from Figure 6.2 that contamination highest towards the bottom of the sediment profile for all metals except Zn which varies greatly throughout the profile.

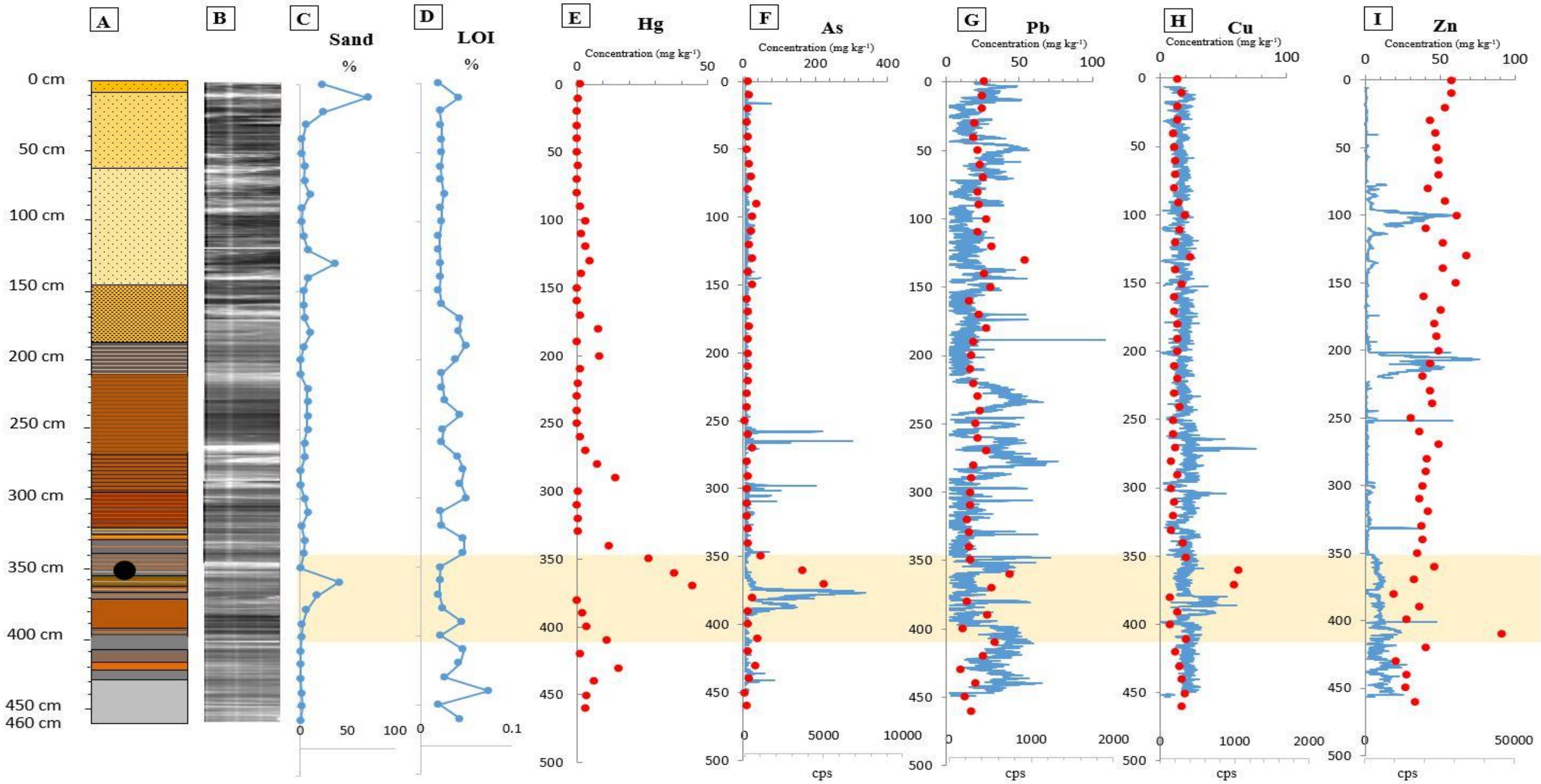

Figure 6.3: Comparison of (A) Sedimentology and location of OSL sample at 350 cm, (B) Radiograph, (C) Sand content, (D) LOI, and metal contamination profiles developed by hhXRF, DMA-80 and ITRAX for (E) Hg, (F) As, (G) Pb, (H) Cu and (I) Zn for Chappell's Dam. Red dots in (E) represent DMA-80 data and red dots in (F), (G), (H) and (I) represent hhXRF data. Blue lines in (F), (G), (H) and (I) represent ITRAX data. Yellow band represents peak contamination period in the dam. Note that ITRAX data for Hg was not included in (E) due to limitations associated with Hg analysis by XRF.

6.4 Geochronology

6.4.1 pOSL

Portable OSL data from the sediment profile at Chappell's Dam shows large fluctuations in total photon counts throughout the profile (Figure 6.4). BLSL varied consistently throughout and showed no obvious trend, however there was a peak in luminescence at 390 cm which also matched an IRSL luminescence peak. After this luminescence peak at 360 cm, both BLSL and IRSL luminescence decreased which may be indicate of a change in depositional environment. IRSL appeared to increase with depth until its peak at 390 cm, after this peak luminescence decreases and remains low until the bottom of the profile. This pOSL data was used in conjunction with the geochemical data from the Chappell's Dam profile to guide sampling for OSL dating and excess ^{210}Pb analysis.

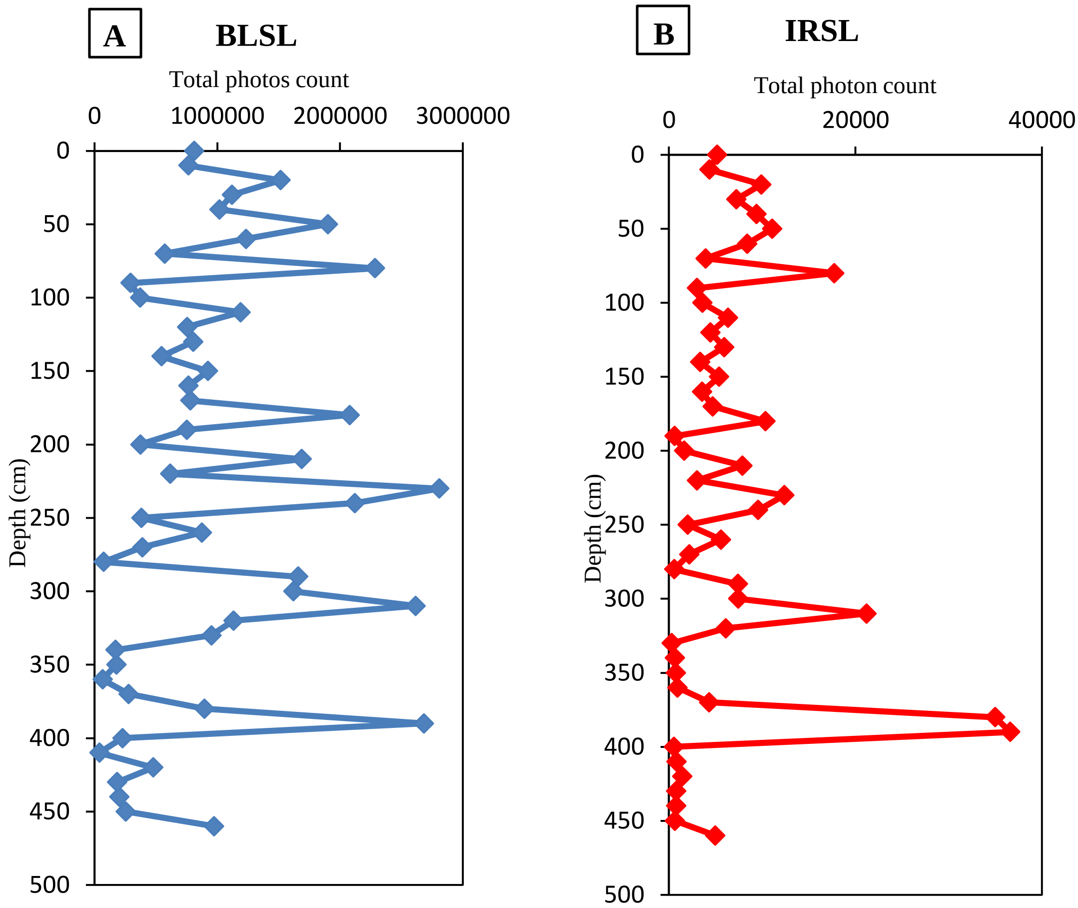

Figure 6.4 pOSL data from Chappell's main tailings dam. (A) BLSL and (B) IRSL.

6.4.2 OSL

Single grain OSL analysis and an age estimate using the minimum age model as used by Galbraith et al. (1999) found that sediment at 350 cm in Chappell's Dam was deposited 130 years before 2014 (±12 years) (Table 6.1 and Figure 6.5). This equates to a calendar age of 1884 ± 12 years, or a conservative estimate of the period 1872 to 1896. A single aliquot OSL age yielded a significantly older age estimate, but this result was deemed to be unreliable given the known averaging effect and age overestimation that single aliquot OSL dating gives for samples with a mix of well bleached and partially bleached grains. The sediment at 350 cm contained several fine laminated sections which would have been deposited at slightly different times, therefore the single grain OSL age represents a best estimate of the burial age of sediment deposited just after the peak of mining. Sediment at 350 cm was selected for OSL dating as it was just above the layer that contained the highest levels of metal contamination (360 cm to 370 cm) which were likely deposited during the peak of mining activity in Hill End when the dam was being used to store contaminated tailings. Sediment at 350 cm contained relatively little metal contamination compared to 360 cm, this significant drop in metal contamination provided evidence that this sediment was deposited towards the end of the period that Chappell's Stamper Battery was in operation or shortly after it was abandoned. From 350 cm to 360 cm there was also a change in BLSL and IRSL luminescence providing evidence for a possible change in depositional environment between these two sections. Therefore, the geochemistry and geochronology of sediment at 350 cm provides a stratigraphic marker for the end of peak mining at Hill End. Historical records show that the dam was built in 1871 and was used intensively as a tailings dam until at least 1874 when Chappell's stamper battery was abandoned. It is therefore possible that this sediment was deposited as early as 1872, but certainly through to 1874. The dam was breached sometime in the 1890s, and so there may have been a lag between some contaminated sediment entering the dam between the middle of the 1870s and the 1890s.

Table 6.1: Summary of the total dose rate, equivalent dose and optical OSL ages obtained using the MOM for single aliquot OSL (OSL_{SA}) and single grain OSL (OSL_{SG}). (a) Radionuclide concentrations were determined from high resolution gamma spectrometry measurements of dried and milled samples, (b) time-averaged cosmic does rates, after Prescott and Hutton (1994) and (c) water content given by drying sample (dry weight/wet weight). Latter values indicate the estimation of potential variation in water content over time used to calculate total dose rates

Sample Code	**Sample depth (cm)**	**Radionuclide activities (Bq kg^{-1})^a**						**Cosmic-ray dose rate (Gy ka^{-1})^b**	**Water content (%)^c**		**Total dose rate (Gy ka^{-1})**	**Equivalent dose (Gy)**	**OSL age (years)**
		^{238}U	**^{226}Ra**	**^{210}Pb**	**^{228}Ra**	**^{228}Th**	**^{40}K**						
HEOSL - 3	350	42 ± 5	39.9 ± 1.1	46 ± 5	50.7 ± 2.3	51.1 1.5	935 ± 30	0.114 ± 0.011	27.7 (25 ± 5)	OSL_{SG}	3.685 ± 0.227	0.48 ± 0.03	**130 ± 12**
										OSL_{SA}	3.781 ± 0.234	8.9 ± 0.3	2,354 ± 172

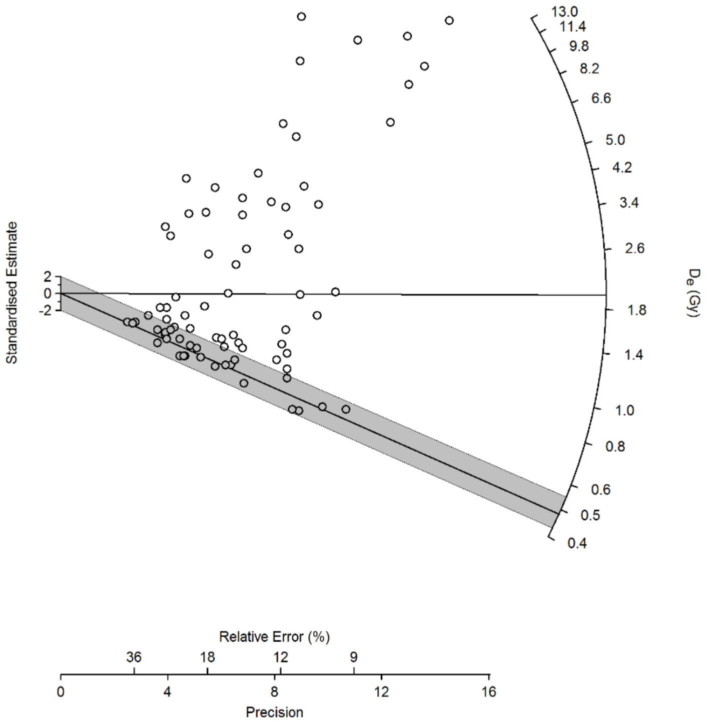

Figure 6.5: Radial plot showing the best fit of the minimum age model (black and grey line) and the central age model (black line) for the single grain OSL dating.

6.4.3 Excess ^{210}Pb

Supported and total ^{210}Pb were analysed throughout the sediment profile at Chappell's Dam Figure 6.6A and 6.6B), however excess ^{210}Pb activities in the sediment profile were extremely low except for the surface sample (Figure 6.6C). Excess ^{210}Pb data that yielded suitable results were used to develop a regression relationship that was used for sedimentation rate estimation and to develop and age-depth profile using the CIC model (Figure 6.6D). A mean sedimentation rate of ~3.5 cm yr^{-1} was derived for the profile, however this rate assumes that sedimentation was constant over the time period despite the reality that sedimentation was probably quite variable. Nevertheless, this assumption allows an age-depth correlation for the profile, which shows that sediment at the base of the profile (~450 cm) and near the peak of contamination at 360 to 370 cm was deposited sometime between ~110 and ~140 years ago (Figure 6.6E). The ^{210}Pb calculations from this sediment profile must be treated with caution, due to the lack of data and low ^{210}Pb activities. Single grain OSL analysis was used to validate the calculated ages and the sedimentation rate.

The excess ^{210}Pb age estimates are consistent with the single grain OSL age determined for the layer at 350 cm. The bottom ~50 cm of the dam are thought to be the remnants of mine tailings deposited during Chappell's Dams peak period of operation between 1871 and 1874. The two excess ^{210}Pb age estimates below the OSL sample corroborate this evidence and the mean sedimentation rate of ~3.5 cm yr^{-1} indicates rapid sedimentation in the lower section of the dam. After the dam was abandoned, it is likely that sedimentation began to decrease as fewer tailings from the nearby area were deposited in the dam, however tailings and other legacy sediment from other mining operations would have continued to wash through Hill End Creek and into Chappell's Dam for decades after the abandonment of Chappell's stamper battery. As such, the rate at which sediment accumulated in the dam is likely to have varied over the past ~130 years, despite the average sedimentation rate described here.

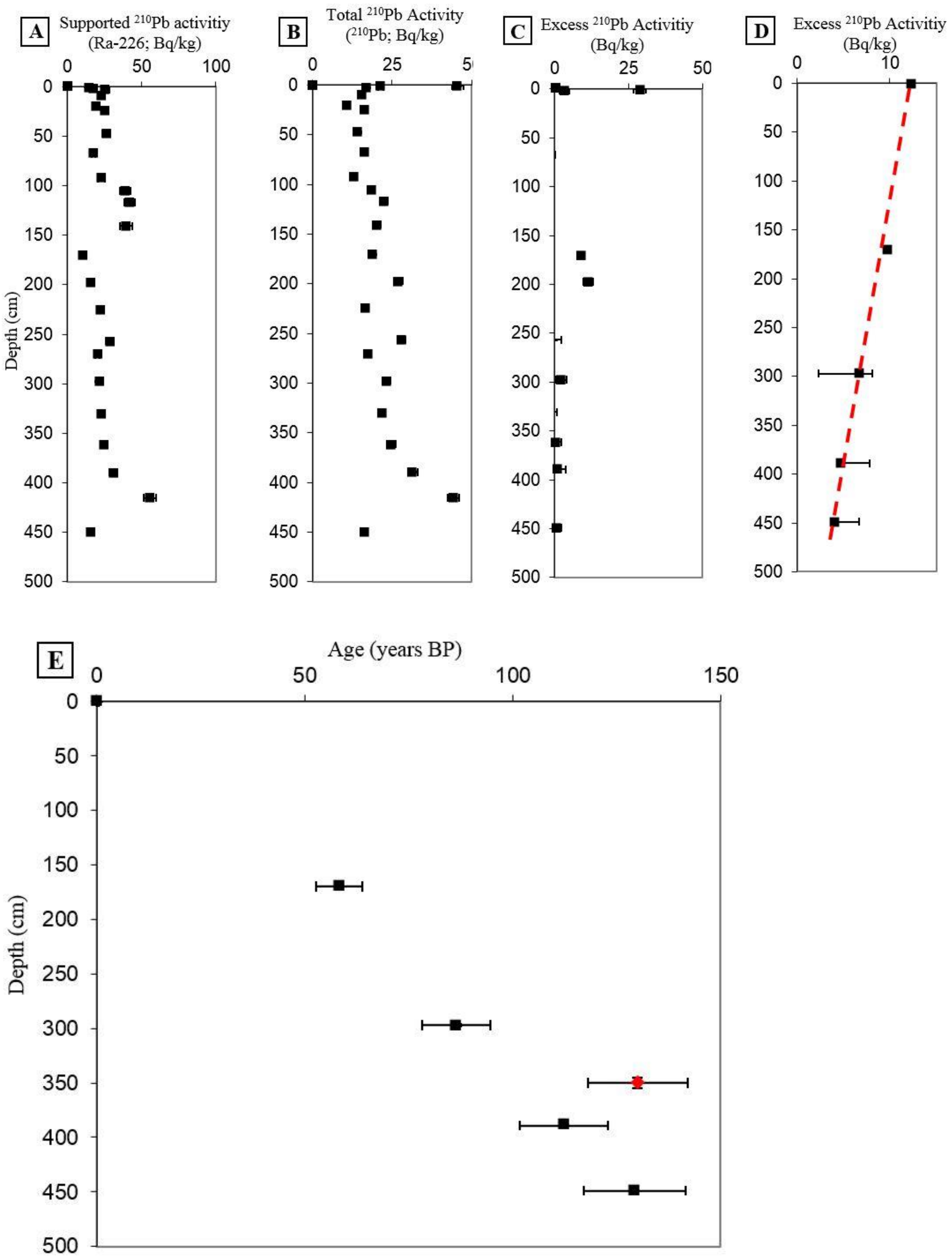

Figure 6.6: (A) Supported ^{210}Pb activity, (B) total ^{210}Pb activity, (C) excess ^{210}Pb activity, (D) excess ^{210}Pb activity with a line of best fit for age-depth estimation using the CIC model, and (E) age estimates from the CIC model (black symbols) compared with sediment dating from single grain OSL (red symbol).

6.5 Geochemistry in Bald Hill Dam

ITRAX analysis of the Bald Hill Dam (refer to Figure 3.1) is presented in Figure 6.7. There appears to be a small peak in As, Pb and Cu towards the top of the profile, a small Zn peak at 145 cm and Zn concentrations increase from 200 cm onwards. There are no sections of the dam where there are large metal peaks for multiple metals like in Chappell's Dam. The lack of metal contamination evidence may be due to the primary use of the dam. The primary use of Bald Hill Dam is not known, it may have been a tailings dam, however it may have only been used to provide water to Chappell's Stamper Battery.

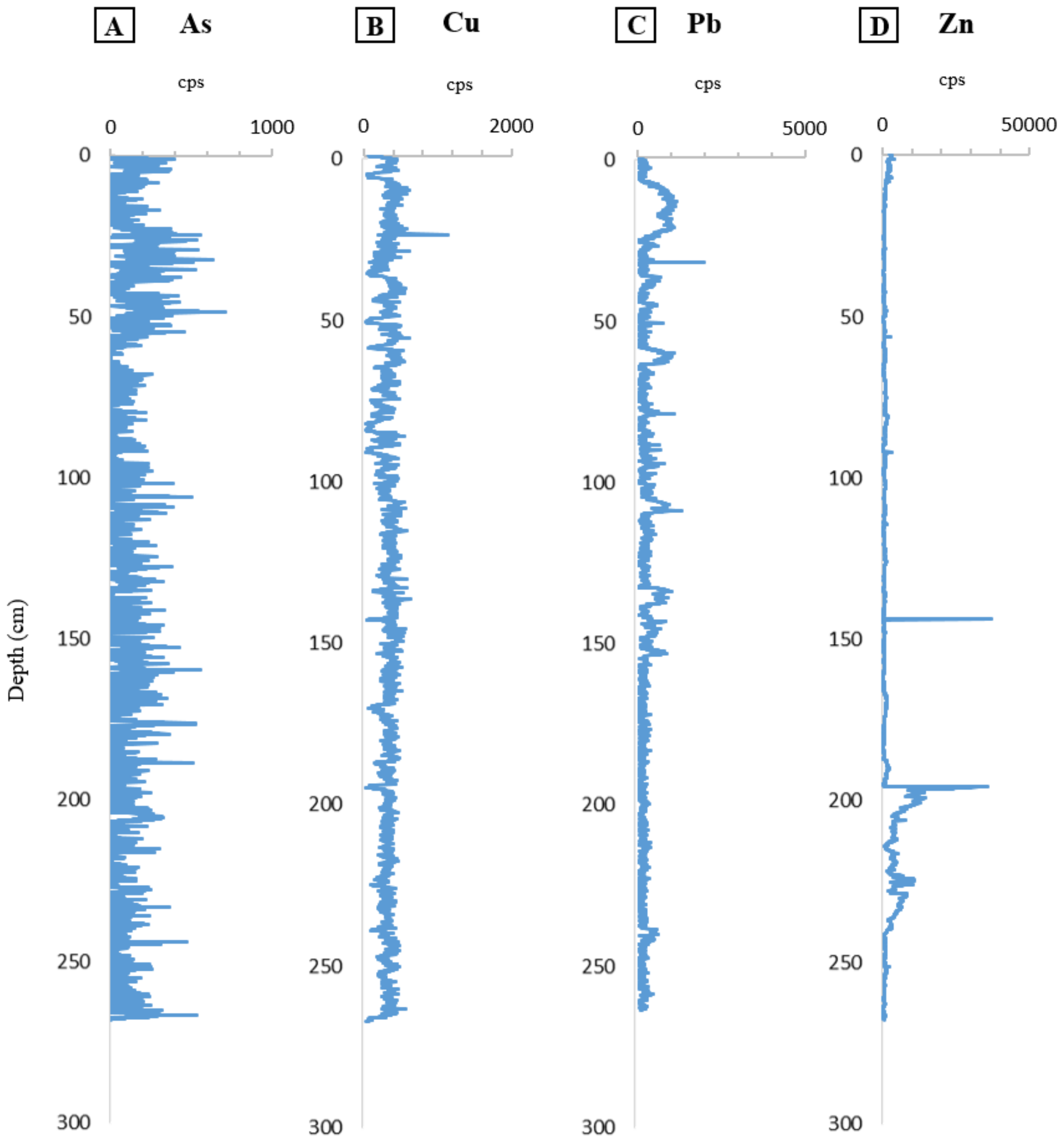

Figure 6.7: ITRAX profiles from Bald Hill Dam. (A) As, (B) Cu, (C) Pb and (D) Zn

6.6 Summary

This chapter discussed the sedimentology, geochemistry and geochronology of Chappell's Dam. The Dam contains laminations throughout the majority of its profile while metal contamination peaks between 360 and 370 cm. OSL and ^{210}Pb dating was used to determine that the peak of metal contamination in Chappell's Dam occurred concurrent with the peak period of mining in Hill End. Since the dam was abandoned it has rapidly accumulated sediment. ITRAX analysis of Bald Hill Dam was unable to identify any depths that indicated metal contamination. Although close in proximity to Chappell's Dam, Bald Hill Dam may have not stored tailings explaining the contrasting metal profiles between the two dams.

7.0 Discussion

7.1 Introduction

This chapter discusses the major research findings, including the local and wider scale environmental impacts of the production of legacy sediment and the release of metals from historical gold mining at Hill End. The chapter will also discuss the implications of this research in the context of previous studies related to legacy sediment and historical mining contamination. Finally a conceptual geomorphic model is presented that describes the main biophysical processes and the role of catchment sediment connectivity responsible for dispersal and storage of legacy sediment and historical mining pollutants in headwater catchments.

7.2 Local impacts of historical gold mining at Hill End

Historical Au mining had a significant impact on the landscape at Hill End. Widespread land clearing and mining activities across the sub-catchment have caused severe rill, sheet, gully and hillslope erosion and produced large volumes of legacy sediment. This sediment was mobilised in conjunction with the release of metals from the excavation and processing of gold-bearing ore. Geomorphological adjustments in the landscape and varying degrees of metal enrichment in soil and sediment is present throughout the catchment as a result of Au mining.

7.2.1 The production and storage of legacy sediment at Hill End

Anthropogenic activities first began to produce legacy sediment in and around Hill End in the early 1850s through the disturbance and release of sediment throughout Hill End Creek and its tributaries from alluvial mining and land clearing. Reef mining and ore processing began to produce legacy sediment in the region from the mid-1860s through the excavation and release of crushed rock and soil and sediment onto hillslopes and into tailings dams and drainage lines. The production of legacy sediment from mining activities at Hill End has had a lasting, detrimental effect on the landscape. There is evidence of previous periods of extensive sheet, rill and gully erosion along with large piles of mullock and other legacy sediment deposits throughout the region.

Evidence of previous periods of intensive legacy sediment production is especially pronounced in the uplands of Hill End. Tailings dams and small fluvial deposits on Hill End Creek store fine deposits of legacy sediment sourced from mining activities and slope wash from eroding hillsopes. It is highly likely that tailings dams interrupted the balance of hillslope-channel and also longitudinal connectivity during the gold rush period inhibiting sediment transport downstream and accumulated large volumes of sediment during the gold rush period. Since the breaching of numerous of dams in the late 1890s (Hodge, 1964), there has been increased longitudinal sediment connectivity as Hill End Creek has cut through and eroded large sections of these dams, allowing sediment transport downstream.

There is no legacy sediment storage within the steep confined gorge of Hill End Creek and there is some legacy sediment storage just before the Hill End Creek and Turon River confluence as channel slope begins to decline. Any sediment from upstream that has entered the gorge has been transported downstream together with sediment sourced from steep and heavily mined hillslopes such as Hawkins Hill along this drainage system. The lack of accommodation space for sediment and high stream power of this reach makes it highly unlikely that any sediment was able to accumulate here during the gold rush. There is some evidence of legacy sediment storage in the lower section of Hill End Creek before the convergence with the Turon River, with occasional legacy sediment deposits consisting of cobbles, gravel and fine sediment. However there are no major sediment buffers (e.g. floodplains) or barriers (e.g. bedrock sills) in this section that have enabled significant sediment storage.

Although this study did not quantify the volume of legacy sediment exported out of the Hill End catchment, it is highly likely that most of the material that entered the steep gorge of Hill End Creek has been exported to the Turon River. The Turon River has a much higher capacity for sediment storage than Hill End Creek due to its wider valley margins and decreased channel slope, and the large depositional units in the Turon River including point bars, bank attached bars, mid-channel bars and floodplain pockets provide evidence of this storage. It is also highly likely that some of the legacy sediment entering the Turon River from Hill End has been transported into the Macquarie River downstream, however the quantity, geochemical properties and current locations of storage of this exported sediment is unknown.

7.2.2 Pollution sources at Hill End

Compared to Pb, Cu and Zn, there was a relatively high percentage of samples that contained high to extreme Hg enrichment and, to a lesser extent, As enrichment at Hill End. The discrepancy between the enrichment of these metals is due to the various pollution sources in the catchment. The major source of Hg was the use of liquid Hg during ore processing, and it is unlikely that excavated ore is a major source of Hg at Hill End since bedrock samples yielded hhXRF results (no bedrock samples were analysed by DMA-80) below detection limit (< 5 mg kg^{-1}) and no major hotspots of Hg were found in mullock heaps. The contribution of liquid Hg to Hg contamination in historical gold mining areas can sometimes be less clear, for example Hg contamination throughout San Francisco has been attributed to a combination of historical gold mining activities and Hg rich ore (Donovan et al., 2013).

The total volume of Hg released into the environment can be estimated through the Hg emission factor (that is the amount of Hg released into the environment to produce 1 kg of gold from amalgamation during gold processing). Most emission factors throughout the world range from 1 (1 kg of Hg released per 1 kg of gold produced) to 2, however in some cases emission factors can exceed 4 (Lacerda, 1997). Emission factors vary geographically as they depend on climate, the grade of ore and methods used during amalgamation. Due to uncertainties regarding the grade of ore and use of Hg during amalgamation at Hill End, emission factors of 1 and 2 were calculated (Table 7.1) to provide an estimate of the volume of Hg released into the environment. This calculation was based on the assumption that 56 t of gold was recovered during the gold rushes at Hill End (this is a conservative estimate based on historical records). However it is likely that more gold was recovered from Hill End but not officially recorded, as was common with many goldfields during the gold rush period

(Dhindsa et al., 2003; Lecce and Pavlowsky, 2014). Using the most conservative estimate of the emission factor, there was approximately 56 t of Hg released into the environment at Hill End, of which between 7.28 t and 19.6 t was released onto soil and drainage systems. Table 7.1 also demonstrates that large volumes of Hg were released atmospherically in Hill End, however this component of contamination was not focused on in this study.

Table 7.1: Hg emission factors for Hill End. 65-87% of Hg released into the environment was released into the atmosphere and 13-35% was released into soil and waterways.

Emission factor	**Total Hg released into the environment (t)**	**Hg released into the atmosphere (t)**	**Hg released into soil and waterways (t)**
1	56	36.4-48.72	7.28-19.6
2	112	72.8-97.4	14.56-39.2

In Australia, As, Cu, Pb and Zn contamination in soil and sediment in historical gold mining areas is mainly due to the excavation and processing of ore naturally enriched in these metals (Sultan, 2007). Currently there are no known measures that can be used to estimate the volume of these metals released into the environment from gold mining that can be used to compare to the volume of Hg released into the environment. Due to the relatively low percentage of samples containing high As, Cu, Pb or Zn contamination compared to Hg it is inferred that there was more Hg contamination than As, Cu, Pb or Zn contamination from gold mining activities at Hill End. Enriched concentrations of Hg appears can be found at historical gold mining sites throughout the world due to the widespread use of Hg for amalgamation (Lacerda, 1997; Lacerda and Salomons, 1998; Müezzinogˇlu, 2003), however As, Cu, Pb and Zn enrichment is less common and is only found in areas where ore is naturally rich in these metals (Sultan, 2007).

As contamination was more pronounced in Hill End compared to Cu, Pb and Zn contamination. This trend is common throughout Australian goldfields due to the mineralisation of gold bearing ore (Smith et al., 2003; Wilde et al., 2004; Sultan, 2007). Ore in Hill End is likely to have contained higher concentrations of As compared to Cu, Pb and Zn explaining the different contamination levels of these metals. As contamination is less reported than Hg and to some extent Cu contamination from historical gold mining, however in select geological settings it can cause significant environmental problems (Kusiak et al., 1991; Chakraborti et al., 2013).

7.2.3 Spatial patterns of metal contamination at Hill End

Metal contamination at Hill End was assessed by comparing metal concentrations to background and by determining the enrichment factor (EF) for key contaminants. Soil and sediment with an EF>2 were considered to have some degree of anthropogenic enrichment while samples with an EF<2 were not considered to have anthropogenic enrichment. Although the majority of samples were elevated above background for each metal, only a relatively small percentage of samples were considered to have experienced moderate to extreme anthropogenic enrichment for Hg, As, Cu, Pb and Zn.

Soil and sediment metal concentrations varied greatly throughout the catchment. Samples a considerable distance away from mining activities (such as the background soil samples) showed little evidence of enrichment and, overall, there was little evidence of significant enrichment of most non-anthropogenic landscape units (including fluvial systems, gullies and hillslopes), especially when compared to anthropogenic landscape units. The major metal hotspots were found in anthropogenic landscape units in areas where metals were used or released from ore processing, including tailings dams and in spoil adjacent to stamper batteries and cyanide tanks. By comparing the relatively high EFs of samples from anthropogenic landscape units to the EFs of samples from landscape units a considerable distance away from mining activities, it is clear that historical gold mining is responsible for significant metal contamination at Hill End. Despite evidence for metal contamination in anthropogenic landscape units, the overall lack of moderate to high metal enrichment throughout the catchment implies there is generally poor metal preservation in the landscape at Hill End. Although there is limited information in the literature regarding different contamination levels of landscape units throughout goldfields, this finding reflects previous studies that have determined contamination levels of metal (especially Hg) to be highest in close proximity to pollution sources in goldfields (Bycroft et al., 1982; Lecce et al., 2011).

Higher levels of metal contamination were expected to be found in fluvial systems downstream of metal contamination hotspots. Despite there being no major metal hotspots found in fluvial systems (except for tailings dams which were assessed separately), the majority of samples were elevated above background with EFs mostly ranging from 1 to 2, and some up to 5. There was an overall downstream decrease in metal concentration in sediments in Hill End Creek and the Turon River (except for Cu). Despite the overall decrease in metal concentration downstream, there were sections of these fluvial systems where metal concentrations varied greatly (especially Hg). Declines in metal concentrations downstream from pollution sources are common (e.g. Leigh, 1997; Coulthard and Macklin, 2003; Pavlowsky et al., 2010; Bakatula et al., 2011), however alluvial mining and ore processing occurred along the length of Hill End Creek and in parts of the Turon River, meaning that there were pollution sources throughout these fluvial systems, not just in the upper catchment. Variations of metal concentrations in these fluvial systems were not uniform, which may be due to the multiple pollution sources in the catchment.

The poor preservation of metals in the landscape and fluvial systems compared to metal hotspots could be explained by high hillslope-channel sediment connectivity and high longitudinal connectivity and transport capacity of sediment within the fluvial systems of Hill End. Vegetation clearance may have increased hillslope-channel connectivity, influencing the rate at which soil and sediment could be delivered to drainage lines. Therefore metal contaminated soil and sediment may no longer remain on hillslopes as it has been delivered to fluvial systems. The high capacity for sediment transport in the fluvial systems of Hill End are likely to have flushed this sediment out of the catchment and exported it to the Turon River and the Macquarie River. Decreases in metal concentration downstream can also occur from dilution of contaminated sediments with clean uncontaminated sediments (Coulthard and Macklin, 2003; Taylor and Little, 2013; Lecce and Pavlowsky, 2014). At Hill End, clean sediment may have entered the fluvial systems and diluted contaminated sediments and metal contaminated sediment entering the Turon River would also have been diluted. Alternatively, contaminated sediment within Hill End Creek may have been buried by clean sediments over time.

7.2.4 Temporal patterns of metal contamination in Hill End

A detailed investigation into the geochronology of a deep sediment profile from Chappell's Dam on Hill End Creek in the heart of the gold field revealed a complex history of contamination and sedimentation. The sediment within the dam was predominantly fine sediment with three coarser sand layers at 360 cm, 130 cm and 0 to 40 cm. Laminations throughout the sediment profile indicate that most of the sediment was deposited in a lacustrine environment. Fine sandy laminations are not uniformly dispersed through the profile and are interspersed with thicker layers of clay. Coarser laminations towards the top of the profile indicate that the source or mode of deposition for this sediment has changed from the lower section of the profile.

Metal concentrations varied markedly throughout the profile, but there was a major peak in the concentration of Hg, As, Cu, Pb and Zn found between 350 cm and 370 cm that corresponded with a series of sand layers. Together, the high concentrations of metals and the relatively high percentage of sand in this section of the profile proves that these layers are the remnants of mine tailings. Stamper batteries would crush ore into fine sand and the waste material (tailings) were dumped into dams (Ritchie and Hooker, 1997) and high concentrations of Hg, As, Pb, Cu and Zn are often associated with mine tailings in Australia (Sultan, 2007). Despite only a small portion of the sediment profile at Chappell's Dam exhibiting peaks in sand, the major peaks in Hg, As, Pb, Cu and Zn from 360 to 370 cm provide strong evidence of anthropogenic metal contamination in mine tailings. OSL dating and an excess ^{210}Pb chronology showed that this peak of metal contamination related to gold mining occurred just prior to ~130±12 years ago (c. 1884), or during the period 1872 to 1896. A mean sedimentation rate of ~3.5 cm yr^{-1} was also derived for the profile although the rate at which sediment accumulated in the dam is likely to have varied over the past ~130 years. This means that the sediment layers below 350 cm were deposited during and just after the peak mining period when the dam was used to store tailings from Chappell's stamper battery. Sediment at the base of the profile was likely deposited just after the construction of the dam in 1871, coinciding with the peak of mining at Hill End. Rapid sedimentation in the dam is explained by the accumulation of mine tailings during the peak operation of Chappell's stamper battery (c. 1871 to 1874) and sedimentation from slopewash and upstream sediment sources.

In the upper part of Chappell's Dam sediment profile, changes in sedimentology and variations in supported ^{210}Pb activity may be indicative of changes in source materials. Since the dam was abandoned the major source of sedimentation in the dam were likely a combination of slopewash sediments and upstream sediments. The variations in supported ^{210}Pb may have occurred when one of these sources become more dominant than the other. Despite the uncertainty of the sources of this sediment it is clear that the uplands of Hill End were (and still may be) significant sources of sediment.

The metal profiles from Bald Hill Dam showed few similarities to Chappell's Dam. The height and elevation of these two dams varied considerably, meaning that the sediment profiles cannot be directly compared. Despite some small metal peaks towards the top of the profile there was little evidence of significant metal contamination in Bald Hill Dam due to the absence of sediment layers with large peaks in Hg, As, Pb, Cu and Zn. The lack of metal contamination in Bald Hill Dam could be due to the different history of use of the dam, since there is no evidence that the dam was used to store tailings and, instead, it was probably used mainly for water storage. One similarity between Chappell's Dam and Bald Hill Dam was the high variation of Zn throughout both profiles.

Despite the lack of metal contamination in Bald Hill Dam, it is highly probable that other abandoned tailings dams at Hill End contain similar geochemical sequences to Chappell's Dam, since many of these other dams were used to store tailings adjacent to mines and stamper batteries. Chappell's Dam was located adjacent to a major stamper battery providing metal contaminated tailings directly to the dam, and tailings may have been deposited from upstream sources. Further investigation of other tailings dams at Hill End is therefore warranted to determine whether they contain similar concentrations of metals to Chappell's Dam. Tailings dams (and dams in general) constructed during historical times are important sinks of contamination. For example, in the United States the construction of thousands of mill dams in historical times resulted in the storage of large volumes of sediment enriched in pollutants and mobilisation of these sediments can contribute to significant environmental degradation (Walter and Merritts, 2008; Niemitz et al., 2013). Similarly tailings dams at Hill End may be acting as pollution sinks and the continued mobilisation of sediment from these dams could lead to environmental degradation.

7.3 Wider scale impacts of historical gold mining at Hill End

Metal contamination has been one of the most extensive and most severe environment impacts of historical gold mining throughout the world. Large volumes of contaminated sediment produced by historical gold mining can cause significant problems for human health and aquatic ecosystems (Bycroft et al., 1982; Lacerda and Salomons, 1998; Hornberger et al., 1999; Churchill et al., 2004; Alpers et al., 2005; Pavlowsky et al., 2010). At Hill End there was relatively little metal contaminated sediment that remained within the catchment. Metal contaminated sediment sourced from historical mining activities does not necessarily remain at the pollution source, sediment can be transported downstream, temporarily stored and then remobilised again (Coulthard and Macklin, 2003). The extent of sediment transport is dependent on a number of geomorphological factors including connectivity, sediment delivery and transport capacity (Fryirs, 2013).

It is possible that metal contaminated sediment has been exported out of the Hill End system and into the Turon River or Macquarie River. No metal hotspots were found within the channel or near the channel along the Turon River near Hill End, but it is possible that metal contaminated sediment has been buried by clean, uncontaminated sediment. Small pits were excavated within the hyporheic zone of the Turon River to explore this possibility. These pits revealed no significant metal contamination at depth, however due to the shallow depths of the pits, it is possible that metal contaminated sediment is stored at greater depths within the Turon River. However contaminated sediment may also be stored within floodplain pockets of the Turon River or diluted by clean uncontaminated sediment.

Large volumes of legacy sediment exported to the Turon River may also have created geomorphological adjustments in the fluvial system. The amount of sediment exported from Hill End Creek since the beginning of mining in the region is not known, but Hill End is a highly connected system and the lack of sediment storage compared to the extent of mining and erosion in the region leads to the suggestion that a large volume of sediment has been exported out of the catchment outlet.

This study did not focus on the atmospheric processes involved in metal contamination, but it was estimated that large volumes of Hg were emitted into the atmosphere in Hill End. Once Hg is emitted into the atmosphere it can travel large distances before being deposited on soil or sediment (Nelson et al., 2011). The atmospheric deposition of Hg is therefore likely to have impacted landscapes some distance away from Hill End that were not directly impacted by gold mining. Gold mining at Hill End not only enriched soil and sediment in Hill End with Hg, but in combination with other goldfields during the gold rush it may have contributed to widespread atmospheric deposition of Hg in Australia.

7.4 Implications of the major findings

7.4.1 Implications for legacy sediment and historical gold field research

This study has found that historical gold mining has impacted the Hill End landscape through the production of legacy sediment and metal contamination. These environmental impacts have been reported in previous studies (Porcella et al., 1997; Hornberger et al., 1999; Scott, 2001; Alpers et al., 2005; Sultan, 2007; Lecce et al., 2011; Singer et al., 2013) and this study was able to further inform on these impacts through identifying spatial patterns of metal contamination and on pathways of legacy sediment storage. Increased sediment production and metal contamination at historical goldfields has left a lasting effect at historical goldfields as well as sites downstream of goldfields.

In Australia, the type and extent of landscape disturbance from anthropogenic land-use following European settlement have been well recorded. Poor soil conservation practices coupled with land clearing and intensive anthropogenic land-use can increase channel-slope and upstream-downstream connectivity. Most of this literature has focused on the contribution of agriculture, land clearing or anthropogenic land-use as a whole to landscape disturbance (e.g Wasson et al., 1996; Brooks and Brierley, 1997; Brierley et al., 1999; Olley and Scott, 2002; Rustomji and Pietsch, 2007; Fryirs et al., 2009; Hughes et al., 2010). There has been comparatively little research into the production of legacy sediment from historical gold mining, so this study has filled a considerable knowledge gap by determining the distribution and dispersal patterns of legacy sediment and the hotspots of metal contamination at Hill End.

Previous Australian studies investigating impacts from historical gold mining have mostly focused on Hg contamination (Bycroft et al., 1982; Dhindsa et al., 2003; Churchill et al., 2004) or As (Smith et al., 2003; Sultan and Dowling, 2006). The major findings from Hill End show that legacy sediments there contain similar concentrations of Hg and As as those reported in previous studies, providing further evidence that Hg and As contamination from historical gold mining occurred throughout eastern Australia. Although there is evidence of Cu, Pb and Zn contamination at Hill End, there have been few studies that have investigated these metals that can be compared to Hill End. Sultan (2007) investigated Cu, Pb and Zn contamination from gold mining in Victoria, however this study was spread across a range of goldfields did not focus on one particular goldfield. Sultan (2007) found similar results to this thesis and demonstrated that the highest concentrations of these metals were found in mine tailings or mullock. More research into metal contamination produced from historical gold mining in Australia is clearly needed in order to better understand the extent of Hg, As, Cu, Pb and Zn contamination from historical mining.

Legacy sediment at Hill End is not strictly associated with metal contamination. Although there were many samples that showed at least minimal metal enrichment at Hill End, there was still a relatively large number of samples that showed no enrichment and were below background concentrations. Legacy sediment showed strong associations with metal contamination in anthropogenic landscape units but there was less evidence of contamination in natural landscape units. These findings are similar to other studies at goldfields where metal concentrations can vary from very high (demonstrating a strong association with metal contamination) to very low (demonstrating no association with metal contamination) (Churchill et al., 2004; Lecce et al., 2011). These associations are often dependent on proximity to the pollution source.

Chappell's Dam provided evidence of substantial sedimentation during and prior to the peak of gold mining activities in Hill End. Rapid sedimentation of the dam has continued but sediment deposited above 350 cm (c. 1872-1896) is relatively uncontaminated. The large volume of uncontaminated sediment from slopewash and upstream sources suggests that contaminated sediment remained within the uplands of Hill End for a relatively short period of time after mining and ore processing began to wane.

The impacts of legacy sediment production vary throughout historical goldfields. These impacts are relatively unknown in Australia compared to North American goldfields. For example, goldfields in the Sierra Nevada in North America produced enormous volumes of sediment through hydraulic mining and large volumes of this sediment still remain within downstream channels (Gilbert, 1917; James, 1989). In contrast, little is known of the fate of legacy sediment produced at goldfields such as Hill End and many goldfields within NSW. A better understanding of the fate of legacy sediment produced in Australian goldfields can provide information on the history, magnitude and frequency of environmental impacts created by gold mining in Australia how these changes have impacted modern environments.

7.4.2 Implications for contemporary environmental management

Environmental management implications from this study mainly relate to the impact that contaminated sediment is having on aquatic ecosystems. Soil and sediment at Hill End poses a relatively minor risk to human health. There were very few samples that exceeded NEPM guidelines and there is limited human exposure to soil and sediment that exceeded the Australian NEPM or ANZECC guidelines. However high concentrations of Hg in sediment may pose risks for aquatic ecosystems. At Hill End, 26.85 % of sediment samples had Hg concentrations exceeding the Australian high ISQG and Chappell's Dam was the major source of this Hg contamination, with 55% of samples from the dam exceeding the Australian high ISQG for Hg.

The high percentage of sediment samples exceeding the Australian high ISQG warrants further investigation into the risk that this sediment poses to the environment. Furthermore, as per the ANZECC guidelines, if one or more samples exceed the high ISQG in a given area then it is recommended that further ecological investigation is undertaken. It has previously been demonstrated that high concentrations of Hg in sediments can cause significant impacts to aquatic ecosystems, in particular through the bioaccumulation of Hg in various fish species (Bycroft et al., 1982). The bioavailability of Hg in these samples is not known and it is recommended this is further investigated to assess the risk that this sediment poses to aquatic ecosystems. This study has demonstrated the importance of understanding the long term and broad scale impacts that historical and derelict mine sites can have to the environment. Downstream movement of mining material can impact landscapes not directly affected by mining activities.

7.5 Conceptual geomorphic model for the dispersal and storage of legacy sediment and metal contamination

The major findings of this research can be summarised through a conceptual geomorphic model (Figure 7.1). This model was developed to help explain the main biophysical processes and the role of catchment sediment connectivity responsible for dispersal and storage of legacy sediment and historical mining pollutants. Landscape configuration and catchment sediment connectivity play a major role in the delivery and storage of sediments in fluvial systems (Fryirs, 2013). In low relief landscapes, sediment can be readily stored and sediment conveyance through fluvial systems can be restricted to large flood events, in contrast steep landscapes with confined rivers that have much less capacity for sediment storage and where sediment is more easily transported downstream (Kuo and Brierley, 2013). It should be noted that Figure 7.1 is a catchment scale model and does not take into account more complex local controls that can influence sediment storage such as barriers, blankets and buffers (Fryirs, 2013).

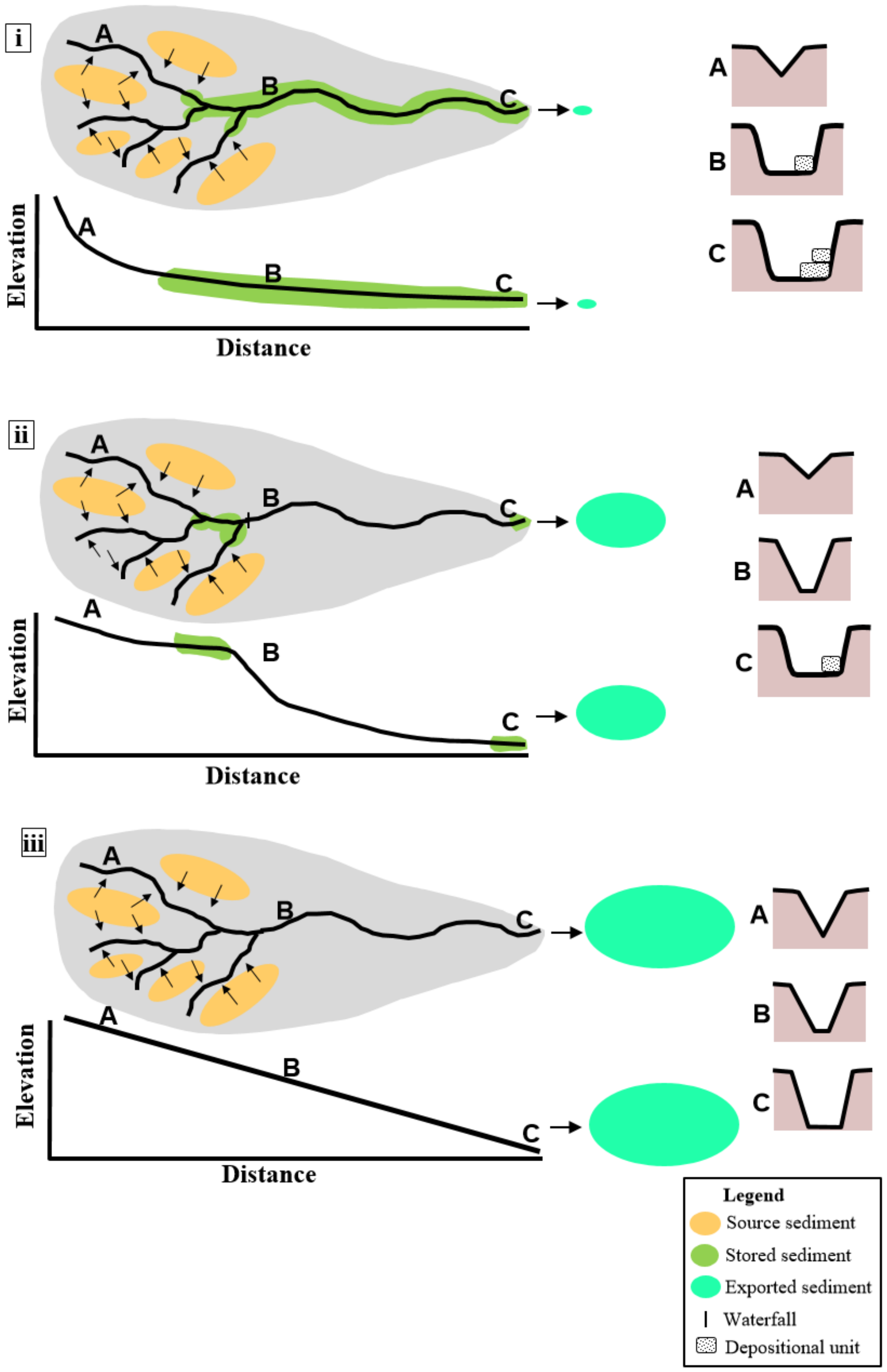

Figure 7.1: Conceptual diagram. Scenario (i) Catchment begins with a steep gradient but gradually decreases to a low gradient and sediment storage zone. Scenario (ii) Catchment begins with a relatively low gradient and sediment storage zone then the middle reach greatly steepens and continues to be steep until the sediment storage zone at C. Scenario (iii) Steep gradient throughout catchment and no sediment storage zone.

Figure 7.1 presents three different scenarios for landscape configuration and shows how this configuration can impact sediment connectivity and legacy sediment storage within channels and within a catchment as a whole. Scenario (i) begins in steep confined uplands and channel slope gradually decreases as the catchment transitions to less confined lowlands. There is little or no sediment storage in the fluvial system in the uplands, however as the channel slope begins to decline the capacity for sediment storage increases and eventually sediment deposits become continuous. There is little sediment exported out of the catchment due to the high capacity of sediment storage within the catchment. Scenario (ii), similar to Hill End, begins with moderate to steep uplands and the upper catchment has some reaches of the fluvial system with low channel slope where sediment can accumulate. This catchment then experiences a sudden change in landscape configuration as it shifts into a steep, confined reach (a gorge) before gradually transitioning to lowlands where sediment can once again accumulate. Despite some discontinuous sediment storage zones, there is relatively little sediment stored within the catchment compared to scenario (i) and there is a relatively large volume of sediment exported from the catchment. Scenario (iii) is a steep confined catchment and does not have any low lying regions or low gradient reaches. There is very little sediment storage in the fluvial systems of this catchment due the consistently steep slope resulting in greater sediment transport and eventually all of the legacy sediment being exported out of the catchment.

Controls on sediment storage are intrinsically linked to the long term storage and transport of pollutants in a catchment. If sediment is not able to accumulate then there is little capacity for a pollutant to remain within a catchment. For example, in scenario (iii) contaminated sediment that entered this catchment would have a short residence time and this contaminated sediment would be quickly transported out of the catchment. Conversely, in scenario (i) contaminated sediment would more readily be stored in the catchment and there would be relatively little export of contaminated sediment out of the catchment. This is in keeping with some of the fundamental principles of sediment dynamics, where the capacity for sediment storage in a catchment increases as channel slope and stream power decrease, while the capacity for sediment storage in a catchment decreases as channel slope and stream power increase (Church, 2002).

7.6 Summary

This Chapter has discussed the major findings of this thesis, including the dispersal of legacy sediment, levels of metal contamination in soil and sediment and temporal patterns of contamination in Hill End. Overall, these findings are significant because there is relatively litte research into the long term environmental impacts caused by historical gold mining activities. The broader implications of this study are for other historical mine sites around Australia, especially for those with similar landscape settings to Hill End. This study demonstrated that metal contamination still exists at historical gold fields, however it is mainly restricted to artificial hotspots.

8.0 Conclusions

8.1 Introduction

The broad purpose of this study was to investigate the environmental impacts of historical gold mining at Hill End. Specifically, this research investigated the character and distribution of legacy sediment as well as the type and severity of soil and sediment metal contamination throughout the Hill End catchment. Temporal patterns of sedimentation and metal contamination were also investigated in detail at the most significant metal contamination hotspot found in Hill End. The main hypothesis of this research was that while the liberation of rock, soil and sediment from hillslopes and mining activities introduced legacy sediment and associated metal contamination into the landscape at Hill End, the legacy sediment and pollutants now exist primarily in discrete depocentres within the catchment due to the operation of hydrological and geomorphic processes. It was also hypothesised that legacy sediment was likely to be stored in natural (floodplain pockets, bars, benches) as well as artificial depocentres (dams) and that the chemostratigraphy of these depocentres could reveal a detailed record of environmental impacts over time.

This hypothesis has been proven, as there was little evidence of legacy sediment storage and metal contamination except in depocentres such as tailings dams throughout the landscape. The sediment source and sink zone in the upper reach of Hill End Creek contained the largest legacy sediment deposits in the catchment, including the major metal hotspot in the study area: Chappell's Dam. Chemostratigraphy in Chappell's Dam revealed that metal contamination peaked during the height of gold mining and declined shortly after the cessation of ore processing in the adjacent stamper battery, coinciding with the decline of gold mining in the region. There was minimal legacy sediment and metal contamination found throughout the confined gorges of Hill End and minor legacy sediment deposits were found in the sediment sink zone in the lower reach of Hill End Creek. There was no evidence of significant metal contamination in this downstream reach or in the Turon River beyond Hill End Creek.

The main implications of this study are important for understanding legacy sediment character, contamination and sediment dynamics at historical mine sites and goldfields in a similar landscape setting to Hill End. Despite the high transport capacity in the Hill End catchment, this study demonstrated that metal contamination hotspots can still remain within historical goldfields in discrete depocentres. This study also found that a landscape that has experienced extensive land clearing and legacy sediment production may not necessarily store this sediment within the catchment.

Using a variety of analytical techniques, this research also demonstrated that knowledge of the distribution and timing of legacy sediment and contamination can help to explain the history of environmental impacts in a goldfield landscape. hhXRF was shown to be an effective tool at analysing soil and sediment geochemistry. The emergence of hhXRF can change the way that investigations of potentially contaminated landscapes are conducted. Rapid data collection across a wide study area can be achieved relatively quickly and easily by analysing soil and sediment *in situ* or *ex situ* and confidence in these results can be constrained through robust QAQC procedures. Results can be viewed immediately informing a more detailed sampling strategy to further investigate the hotspots of contamination.

8.1 Major findings

The major findings of this thesis are directly related to the aims of the research:

1. *Assess the character and spatial distribution of mining materials and metal contamination that reside in the landscape.*

This study has demonstrated that mining materials consisting of rock, soil, sediment and metals were released on hillslopes and into drainage lines at Hill End. Mullock still remains on hillslopes and finer sediment has accumulated within small fluvial units, tailings dams and on the lower sections of hillslopes. Overall there was minimal evidence of metal contamination throughout non-anthropogenic landscape units. The majority of samples in this study had an EF<2 (no anthropogenic enrichment) or between 2 and 5 (minimal to moderate anthropogenic enrichment). High levels of metal contamination were mostly restricted to metal hotspots in anthropogenic landscape units such as Chappell's tailings dam and in spoil adjacent to stamper batteries and cyanide tanks.

2. *Identify the primary locations of legacy sediment in the landscape and its geochemical signature.*

Legacy sediment was primarily found in the upstream sediment source and sink zone of Hill End Creek and in the downstream sediment sink zone. Legacy sediment has accumulated in small fluvial units such as floodplain pockets and bank attached bars, as well as tailings dams. There was no apparent geochemical signature of legacy sediment *per se*, as sediment geochemistry varied greatly throughout the catchment. Legacy sediment within non-anthropogenic landscape units generally contained concentrations of metals close to background, while high concentrations of Hg, As, Cu, Pb, or Zn were found in metal contamination hotspots.

3. *Determine whether metal contamination is specifically associated with legacy sediment and the timeframe of peak contamination associated with mining.*

Metal contamination was associated with legacy sediment, but not all legacy sediment contained significant levels of metal contamination. Despite the presence of legacy sediment in patches throughout the catchment, metal contaminated sediment was mainly found in anthropogenic landscape units close to where metals were used in mining operations (spoil near stamper batteries and tailings dams) or where metals were released from the excavation of ore (mullock heaps).

Geochemical and geochronological analysis of sediment in Chappell's Dam found that the peak of contamination was concurrent with the peak of mining activity in Hill End, or shortly after (c. 1872-1896). The extent of contamination prior to this period was not measured as Chappell's Dam was constructed in 1871. The input of contaminated sediment declined with the decline in mining activity in the region. In particular, the closure of stamper batteries (one of the major pollution sources) concurrent with the decline in mining activity is likely to have resulted in rapid declines in contamination at Hill End.

4. *Develop a conceptual geomorphic model that describes the main biophysical processes and the role of catchment sediment connectivity responsible for transport and deposition of legacy sediment and historical mining pollutants.*

The geomorphic model developed in this study describes the main biophysical processes and the role of catchment sediment connectivity responsible for transport and deposition of legacy sediment and historical mining pollutants. The model demonstrated that changes in landscape configuration can greatly influence sediment storage and consequently the extent of contamination that resides in modern landscapes.

8.2 Directions for future research

Future avenues for research that stem from the findings of this study include:

1. Investigate the impact that historical gold mining at Hill End and other goldfields that drain into major rivers have had to sediment flux and metal contamination within major rivers and their catchments.
2. Quantify the current volume of heavy metals stored within legacy sediment deposits at Hill End and other historical goldfields and the bioavailability of these metals to determine if they pose significant risks for aquatic ecosystems and human health.
3. Investigate different pathways and storage patterns of legacy sediment and metal contamination in catchments impacted by historical gold mining with similar and contrasting landscape configurations to Hill End.
4. Compare and contrast the environmental impacts experienced at historical goldfields with modern gold mining areas.

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10.0 Appendices

10.1 Appendix 1 – QAQC

Table 10.1: Comparison of actual value of standard material NIST2710a and measured value from hhXRF. SD = standard deviation, SE = standard error, RSD = relative standard deviation, RPD = relative percent difference.

	Cu (mg kg^{-1})	Zn (mg kg^{-1})	As (mg kg^{-1})	Pb (mg kg^{-1})
Actual value NIST2710a	3420±50	4180±150	1454±100	5520±30
Measured Mean	3360	4090	1447	5480
Measured SD	30.3	37.2	10.6	36.8
Measured SE	9.13	11.2	3.18	11.1
RSTD	0.901785714	0.909535452	0.732550104	0.671532847
RPD	1.769911504	2.176541717	0.207110804	1.818181818

Table 10.2: Comparison of actual value of standard material NIST2711a and measured value from hhXRF.

	Cu (mg kg^{-1})	Zn (mg kg^{-1})	As (mg kg^{-1})	Pb (mg kg^{-1})
Actual value NIST2711a	140±2	414±11	107±5	1400±10
Mean	119	356	85.1	1380
SD	4.41	4.13	5.89	11.4
SE	1.33	1.25	1.78	3.44
RSTD	3.705882353	1.16011236	6.921269095	0.826086957
RPD	16.21621622	15.06493506	22.80062467	1.438848921

Table 10.3: Comparison of actual value of blank $Si0_2$ and measured value from hhXRF

	Cu (mg kg^{-1})	Zn (mg kg^{-1})	As (mg kg^{-1})	Pb (mg kg^{-1})
Blank SiO2 values	0±0	0±0	0±0	0±0
Mean	4.97	<LOD	0.18	<LOD
SD	2.92	0	0.57	0
SE	0.92	0	0.18	0
RSTD	58.75251509	0	316.6666667	0
RPD	200	0	200	0

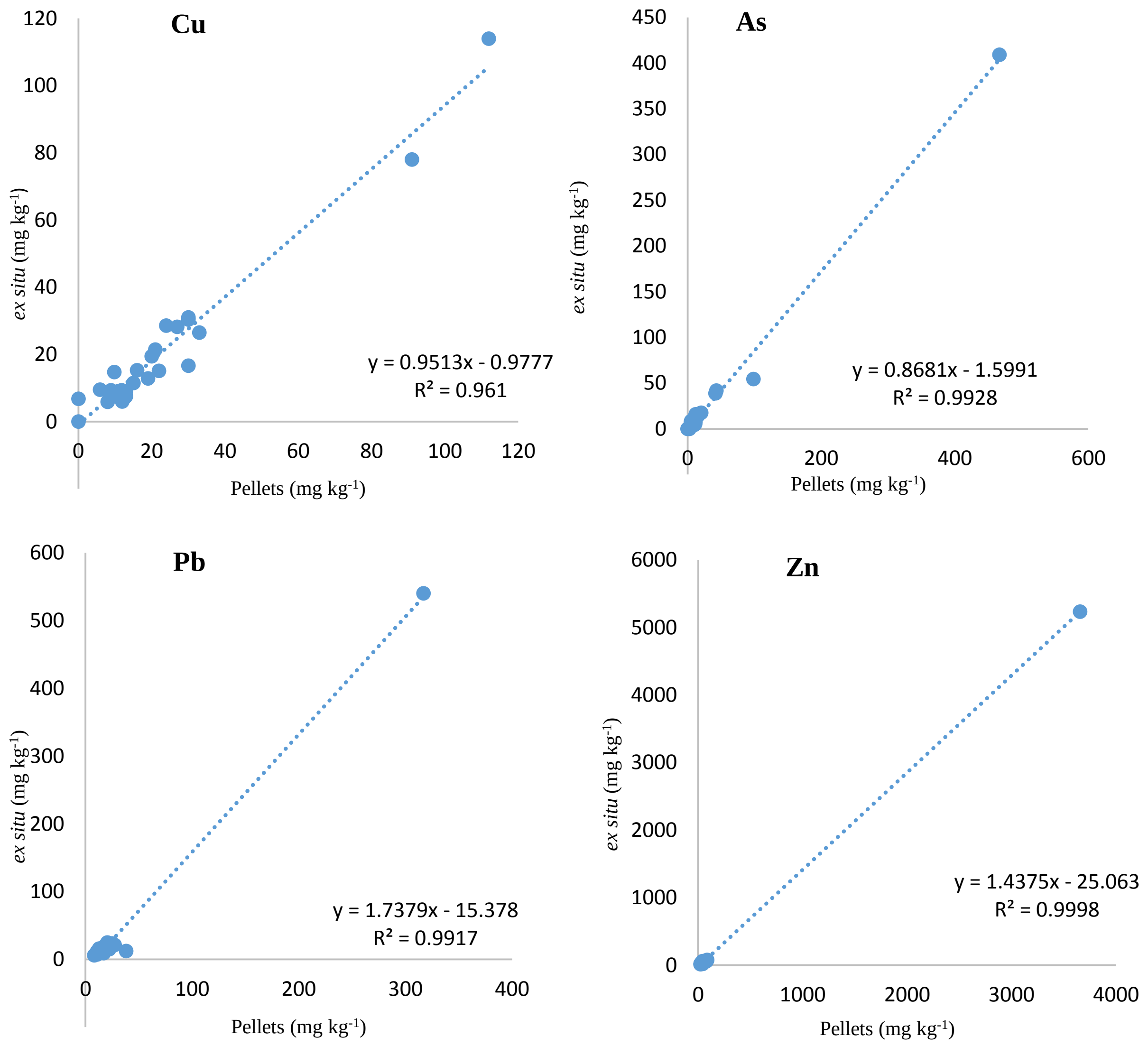

Figure: 9.1: Comparison of results from hhXRF of samples analysed *ex situ* and as pressed pellets.

Table 10.4: Comparison of actual value of standard solution and measured value from DMA-80 data.

Standard solution	102 μg kg^{-1}
Mean (n=5)	100.2914 μg kg^{-1}
SD	0.43634159
SE	0.19513789
RSTD	0.43507378
RPD	198.267244

10.2 Appendix 2 – Statistical analysis

Table 10.5: *Post hoc* pairwise Mann-Whitney *U*-test for median Hg value of each landscape unit. Values in bold are significantly different.

	Gully	Fluvial	Spoil	Tailings Dams	Mullock	Hillslope	Background soil
Gully		0.2128	**0.01447**	**0.000833**	**0.03725**	0.08955	0.4068
Fluvial	0.2128		0.09287	**3.70E-08**	0.4479	0.4724	0.1547
Spoil	**0.01447**	0.09287		**0.02577**	0.2934	**0.006976**	**0.005411**
Tailings Dams	**0.000833**	**3.70E-08**	**0.02577**		**0.000973**	**3.78E-08**	**,<0.001**
Mullock	**0.03725**	0.4479	0.2934	**0.000973**		0.2187	**0.03173**
Hillslope	0.08955	0.4724	**0.006976**	**3.78E-08**	0.2187		0.2285
Background soil	0.4068	0.1547	**0.005411**	**2.80E-06**	**0.03173**	0.2285	

Table 10.6: *Post hoc* pairwise Mann-Whitney *U*-test for median Pb value of each landscape unit. Values in bold are significantly different

	Gully	Fluvial	Spoil	Tailings Dams	Mullock	Hillslope	Background soil	Bedrock
Gully		**0.04139**	0.08824	0.3588	**0.007296**	0.2065	**0.003107**	0.5618
Fluvial	**0.04139**		**0.000354**	**9.13E-05**	**9.26E-05**	**0.000289**	0.5775	0.3927
Spoil	0.08824	**0.000354**		0.1317	0.5373	0.263	**0.00061**	0.1046
Tailings Dams	0.3588	**9.13E-05**	0.1317		**0.01285**	0.6378	**9.00E-05**	0.2682
Mullock	**0.007296**	**9.26E-05**	0.5373	**0.01285**		**0.04503**	**0.000218**	0.07585
Hillslope	0.2065	**0.000289**	0.263	0.6378	**0.04503**		**5.42E-05**	0.2132
Background soil	**0.003107**	0.5775	**0.00061**	**9.00E-05**	**0.000218**	**5.42E-05**		0.1976
Bedrock	0.5618	0.3927	0.1046	0.2682	0.07585	0.2132	0.1976	

Table 10.7: *Post hoc* pairwise Mann-Whitney *U*-test for median Cu value for each landscape unit. Values in bold are significantly different

	Gully	**Fluvial**	**Spoil**	**Tailings Dams**	**Mullock**	**Hillslope**	**Background soil**	**Bedrock**
Gully		**0.001051**	0.09971	**0.03232**	**0.01069**	0.5106	0.5775	0.2883
Fluvial	**0.001051**		0.3477	**0.01023**	0.6513	**0.001019**	**7.89E-05**	0.452
Spoil	0.09971	0.3477		0.791	0.2357	0.1768	**0.03274**	0.9024
Tailings Dams	**0.03232**	**0.01023**	0.791		0.072	**0.04454**	**0.000855**	0.868
Mullock	**0.01069**	0.6513	0.2357	0.072		**0.008257**	**0.001051**	0.3855
Hillslope	0.5106	**0.001019**	0.1768	**0.04454**	**0.008257**		0.1506	0.4788
Background soil	0.5775	**7.89E-05**	**0.03274**	**0.000855**	**0.001051**	0.1506		0.2303
Bedrock	0.2883	0.452	0.9024	0.868	0.3855	0.4788	0.2303	

Table 10.8: *Post hoc* pairwise Mann-Whitney *U*-test for median As value for each landscape unit. Values in bold are significantly different.

	Gully	**Fluvial**	**Spoil**	**Tailings Dams**	**Mullock**	**Hillslope**	**Background soil**	**Bedrock**
Gully		0.05264	0.6305	**0.000182**	0.08838	0.4784	0.1009	0.8351
Fluvial	0.05264		0.1472	**1.83E-05**	0.3501	0.1486	**4.69E-05**	**0.0475**
Spoil	0.6305	0.1472		**0.000314**	0.1255	0.8179	**0.02062**	0.459
Tailings Dams	**0.000182**	**1.83E-05**	**0.000314**		0.3426	**0.00012**	**1.81E-06**	**0.002899**
Mullock	0.08838	0.3501	0.1255	0.3426		0.1418	**0.003266**	0.08157
Hillslope	0.4784	0.1486	0.8179	**0.00012**	0.1418		**0.00547**	0.3654
Background soil	0.1009	**4.69E-05**	**0.02062**	**1.81E-06**	**0.003266**	**0.00547**		0.3845
Bedrock	0.8351	**0.0475**	0.459	**0.002899**	0.08157	0.3654	0.3845	

Table 10.9: *Post hoc* pairwise Mann-Whitney *U*-test for median Zn value for each landscape unit. Values in bold are significantly different.

	Gully	**Fluvial**	**Spoil**	**Tailings Dams**	**Mullock**	**Hillslope**	**Background soil**	**Bedrock**
Gully		0.7809	**0.01054**	0.4976	**0.02296**	0.162	**1.58E-04**	0.9184
Fluvial	0.7809		**0.000311**	0.5564	**0.003034**	0.1191	**2.26E-06**	0.9793
Spoil	**0.01054**	**0.000311**		**0.000124**	0.4739	**0.000354**	**3.51E-05**	0.0576
Tailings Dams	0.4976	0.5564	**0.000124**		**0.000745**	0.2343	**2.66E-06**	0.8594
Mullock	**0.02296**	**0.003034**	0.4739	**0.000745**		**0.002096**	**0.000123**	0.3016
Hillslope	0.162	0.1191	**0.000354**	0.2343	**0.002096**		**6.68E-04**	0.5913
Background soil	**1.58E-04**	**2.26E-06**	**3.51E-05**	**2.66E-06**	**0.000123**	**6.68E-04**		**0.04559**
Bedrock	0.9184	0.9793	0.0576	0.8594	0.3016	0.5913	**0.04559**	

10.3 Appendix 3 – Mineralogy of sediments from Chappell's Dam

Table 10.10: XRD results table. The mineralogy within sediment samples was identified using PANalytical HighScore Plus version 2.2a software. Confidence of presence of mineral:

Definite
Very highly probable
Highly probable
Probable

Mineral Name	Quartz	Muscovite	Albite	Birnessite	Kaolinite	Illite	Calcite	Portlandit	Langite	Chalcoph	Sinnerite
Formula	SiO2	KAl2(AlSi3O10)(F,OH)2	Na (AlSi3O8)	K0.296Mn0.926O2 (H2O)0.40	Al2Si2O5 (OH)4	(K , H30) Al2 (Si3Al) O10 (OH)2	CaCO3	Ca (OH)2	Cu4 (SO4 (OH)6H2O) H2O	ZnMn3O7 (H2O)3	Cu12 (As3S7) (As5S11)
Depth (cm)											
0	Definite	Very highly probable	Probable	Highly probable		Highly probable					
10	Definite	Very highly probable	Probable	Highly probable		Probable					
20	Definite	Very highly probable	Probable	Highly probable							
30	Definite	Very highly probable	Probable	Highly probable							
40	Definite	Very highly probable	Probable						Highly probable		
50	Definite	Very highly probable	Probable						Highly probable		
60	Definite	Very highly probable	Probable	Highly probable							
70	Definite	Very highly probable	Probable		Highly probable						
80	Definite	Very highly probable	Probable	Highly probable							
90	Definite	Very highly probable			Probable						
100	Definite	Very highly probable							Highly probable		
110	Definite	Very highly probable	Probable						Highly probable		
120	Definite	Very highly probable	Probable						Highly probable		
130	Definite	Very highly probable	Probable	Highly probable							
140	Definite	Very highly probable	Probable	Highly probable							
150	Definite	Very highly probable							Highly probable		
160	Definite	Very highly probable							Highly probable		
170	Definite	Very highly probable							Highly probable		
180	Definite	Very highly probable	Highly probable						Highly probable		
190	Definite	Very highly probable	Highly probable						Highly probable		
200	Definite	Very highly probable		Highly probable							
210	Definite	Very highly probable							Probable		
220	Definite	Very highly probable	Highly probable						Probable		
230	Definite	Very highly probable	Highly probable	Highly probable							
240	Definite	Very highly probable	Highly probable	Highly probable							
250	Definite	Very highly probable	Highly probable	Highly probable							
260	Definite	Very highly probable	Highly probable	Highly probable							
270	Definite	Very highly probable	Highly probable						Probable		
280	Definite	Very highly probable		Highly probable							
290	Definite	Very highly probable	Probable	Highly probable							
300	Definite	Very highly probable	Highly probable	Highly probable							
310	Definite	Very highly probable	Highly probable						Highly probable		
320	Definite	Very highly probable	Highly probable						Highly probable		
330	Definite	Very highly probable	Highly probable						Highly probable		
340	Definite	Very highly probable	Highly probable						Highly probable		
350	Definite	Very highly probable		Highly probable							Probable
360	Definite	Very highly probable							Highly probable		
370	Definite	Very highly probable	Highly probable						Highly probable		
370	Definite	Very highly probable	Highly probable						Highly probable		
380	Definite	Very highly probable	Highly probable	Highly probable							
390	Definite	Very highly probable		Highly probable			Very highly probable				
400	Definite	Very highly probable		Highly probable				Highly probable			
410	Definite	Very highly probable		Highly probable							
420	Definite	Very highly probable			Probable						
430	Definite	Very highly probable		Highly probable							Probable
440	Definite	Very highly probable		Highly probable							
450	Definite	Very highly probable								Highly probable	
460	Definite	Very highly probable		Highly probable							