Soil bound lead (Pb) surrounding Snailbeach Lead Mine, Shropshire.

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Abstract

The toxicity of lead (Pb) is widely acknowledged and is now considered a non-threshold toxin. Given Pb's widespread usage throughout history, an extensive industry developed, mining and refining (smelting) Pb ore to form a workable product. Whilst there are no longer operational lead-zinc mines in the UK, there is an extensive contaminative legacy from historic operations, often generating regional-scale elevated background concentrations as well as acutely contaminated hotspots. Many sites have been subject to 'remedial' work to reduce active dispersal from mine tailings (spoil heaps) and to secure and stabilise old workings, though much work was done prior to the introduction of the Environmental Protection Act 1990 (EPA 1990). The EPA 1990 introduced requirements for local authorities to assess and address historic contamination where there is significant harm, or a significant possibility of harm, being caused. Later statutory guidance was issued stating that widespread geogenic contaminants should not constitute 'contaminated land' without significant evidence to suggest otherwise. This has required further study to explore the nature and availability of Pb in mining areas. The former Snailbeach Lead Mine, near Shrewsbury, Shropshire is an example of such a site. Whilst closed and derelict since last operations on the site in 1950's, local safety concerns meant the site was subject to investigation and subsequent remedial work to reduce and cap the largest spoil heap, the 'White Tip'. Subsequent studies were commissioned following the death of livestock on an adjacent field in 2002, which found bioaccessible Pb material, likely derived from the 'White Tip'. However, no subsequent significant indicators of Pb uptake in livestock or humans have been confirmed. Whilst the original aim of this project was to further characterise and determine the extent to which soil bound Pb in the Snailbeach area is bioaccessible, the study and available analyses were impacted by the 2020/21 Coronavirus pandemic. Total x-ray fluorescence spectrometry (XRF) and extractable Inductively coupled mass spectrometry (aqua regia ICP-MS) Pb concentrations were undertaken across 56 sample locations, with the data interrogated to inform future characterisations of the Snailbeach area. The study found elevated total and extractable Pb concentrations surrounding the central mine area, as well as localised elevated concentrations on varied current landuse types surrounding the 'White Tip'. A local background concentration of 3563 mg kg^{-1} was derived and is considered in the context of relevant guidance, the recent understanding of the impact of Pb, previous studies and remedial work undertaken at Snailbeach. Recommendations are made for further work that will better characterise soil Pb at Snailbeach.

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1 Introduction

In recent decades, research has found potential toxicological impacts to human health from exposure to lead (Pb). Studies have found causal links to neurological, teratogenical (Public Health England, 2017b) and potentially carcinogenic (E.F.S.A. Panel on Contaminants in the Food Chain, 2010) impacts to humans from exposure, with numerous other conditions noted e.g. renal system damage and failure (World Health Organisation, 1995). In 2010, the European Food Standards Agency (E.F.S.A. Panel on Contaminants in the Food Chain, 2010) lowered the standard accepted ‘tolerable intake’ of Pb on the basis of research by Canfield et al. (2003) who identified neurological and development impacts to children with no demonstrable threshold. Critically, Pb is now considered a ‘non-threshold’ toxin (Public Health England, 2017b) meaning there is no dose, below which, there is deemed to be no-measurable effect.

The usage of Pb has been altered and constrained in recent decades to limit mobilisation in the environment and subsequent human exposure. Examples include the phasing out of lead-based anti-knocking additives within motor vehicle fuel (Thomas et al., 1999) and phased removal/replacement of Pb piping and plumbing in domestic properties and water-supply systems (Thornton et al., 2001).

The United Kingdom (UK) has an extensive history of metal mining since the Roman Period. During the Industrial Revolution and after, this accelerated, particularly with metalwork, industrial-scale processing and manufacture, all of which fostered and demanded a significant domestic supply of metal ore extraction and refining. Whilst minimal metal mining continues within the UK today, estimates place the numbers of closed or abandoned mine and quarrying sites within the 100,000’s (Palumbo-Roe and Colman, 2010). Consequently, there is a significant and complex legacy to these sites, each with a potentially contaminative repercussions which must be assessed and managed accordingly within the bounds of relevant legislation and guidance.

UK legislation and guidance requires the investigation of both historic, potentially contaminated sites (Parliament, 1990, Defra, 2012a) and land subject to development to ensure it suitability for its proposed use (Ministry of Housing, 2021).

Former mine sites bring additional complexities for risk assessment due to the nature of their historic operations and their typically rural and or upland locations. During peak operation, financial insecurities from high-risk short-term investment often led to the subsequent bankruptcy and abandonment of many sites (Brook and Allbutt, 1973). Furthermore, many sites flooded. Financially instability triggered pumping to cease, consequently many mine sites fell into disrepair, and then remained closed.

Legislation introduced to protect the human health and that of the environment, has typically placed responsibility for ‘orphan’ and abandoned sites on local authorities. The economic and resource pressures experienced by local authorities results in little investigation, assessment or monitoring of these sites, especially in recent decades. Mining sites have proved challenging to characterise under such legislation as confirmed by Palumbo-Roe and Colman (2010) who note that the type and ‘…extent of contamination, and the variety of environmental issues, between sites belonging to the same mineral deposit can vary considerably’.

Palmer et al. (2015a) concluded that ‘diffuse anthropogenic and widespread geogenic contamination could be capable of presenting health risks having risk implications for Land Management decisions in jurisdictions where guidance advises these forms of pollution should not be regarded as contaminated land’. Snailbeach Mine, Shropshire was worked extensively until final closure in 1955, for Pb and Zn (zinc) ore, and later barytes minerals. The primary spoil heap, the White Tip was identified as an active source of pollution in the 1980’s and was subject to a programme of remedial works which completed in 1995. Assessment of the Snailbeach Mine site area today must consider the variety of potential sources on the site including smelter transport from the railway transport from the reclamations scheme, the transport by local residents to gardens and in windblow from the White Tip and other related spoil heaps. Whilst the spatial variability of total concentrations on the Snailbeach site have been researched previously, they have not been considered in light of the 2010 changes (E.F.S.A. Panel on Contaminants in the Food Chain, 2010) in understanding and classification of Pb and it’s low-dose impacts to human health.

The original aim of this project was to investigate: ‘*To what extent is Snailbeach, Shropshire impacted by soil-bound Lead (Pb) contamination with specific regard to bioavailability?*’ with the key objective being identified as: *To characterise the soil-bound Pb concentrations in the Snailbeach area by undertaking site-scale bioaccessibility analysis*.

A series of topsoil samples across the 1988 study area were to be taken, as close to the 1988 sampling locations as possible to allow comparison. A limited number of samples were to be triaged by site-wide total concentration analysis by XRF. This would allow outlier values or samples representative of a particular soil-type or land-use to be identified and subject to more accurate analysis to determine the extractable concentration, by ICP-MS and then conduct in-vitro bioaccessibility analysis utilising the UBM to determine the bioaccessible element concentrations.

It was anticipated that data-collected would allow conclusions to be drawn on the viability of remedial efforts conducted on the site to date, as well as allowing more detailed characterisation of the soil-bound Pb within the locality.

The onset of the global coronavirus pandemic in March 2020 and subsequent series of local and nationwide lockdown measures proved detrimental to the planned study. Given the unforeseen and unprecedented nature of the pandemic, a number of constraints were incurred as a consequence of lockdown measures and legislative restrictions; notably; curtailed laboratory access and restricted free movement and travel. Such restrictions, and the timescale of the MSc (by Res) programme severely hampered the planned analyses of the samples.

Consequently, the scope of the project was reviewed, to account for the limited analytical options but still explore the original aims and objectives as far as possible.

In summary the new project aim was '*To assess, review and characterise the concentration and distribution of soil-bound lead (Pb) at Snailbeach, Shropshire*.'
To achieve this, several objectives were considered. Objectives and the analysis undertaken to realise each objective are listed within Table *1-1*.

Table 1-1 Revised project objectives and chosen analytical methods

	Objective	Method of Analysis
1	To identify whether any visual and/or statistically relevant spatial trends exist in the concentration and spatial distribution of heavy metals surrounding the former White Tip?	Analysis of topsoil samples by ICP-MS and XRF. Compilation of data within Geographical Information System (GIS) database to allow visualisation of data and visual identification of trends. Data Analysis by Geographical Information System (GIS) software to plot concentration data by location and visually compare with historic mapping. Visual review of data. Correlation analysis to consider influence of recorded factors (pH, soil type, land-use) on Pb concentration.
2	To compare primary data to data collected by former studies and make observations on any differences identified.	Analysis of previous and primary datasets.
3	To compare primary data to concentrations in guidance, relevant environmental standards and health criterion values and determine whether values can be considered in C4SL context.	Direct comparison of sample concentrations, calculated values and averages with relevant environmental standards and health criterion values. Derivation of a ‘background’ value for the study area and comparison to national values and relevant environmental standards and health criterion values.
4	To identify what conclusions can be drawn and the confidence that can held in them. To review current investigation and management approach by stakeholders relevant to the study area. To assess whether the site can be benchmarked against other similar sites.	Assessment of Certified Reference Material values against certificate of analysis values. Statistical analysis of any differences, correlations and trends identified. Descriptive statistics to be considered for all datasets.

2 Literature Review

Given its historical applications and uses, Pb has been significantly well-documented in the literature. This review will seek to explore literature relating to the properties of Pb and its form and mobilisation within the environment; the human health impacts of Pb exposure; and the legislative and policy context for investigating potential Pb contamination in the UK. The review will focus specifically on the extent of Pb in mining areas, and the research undertaken within this scientific field to date.

2.1 Lead and its uses

Lead has the chemical symbol ‘Pb’, derived from its Latin name ‘plumbum’, and is a naturally occurring element. Lead (Pb) is not particularly abundant and is estimated as only the 37th most commonly occurring element in the Earth’s crust (Society of Brownfield Risk Assessment, 2011). Pb is rarely found naturally as a ‘pure’ metal and is often found in combination with other elements, forming lead compounds (Steinnes, 2013). Pb has four naturally occurring isotopes (208,206, 207 and 204), and the relative concentrations of different isotopes have been found effective in identifying sources of Pb in soils and sediments (Thornton et al., 2001, Komarek et al., 2008).

Elemental Pb is silvery-white, though turns blue-grey when oxidised in the presence of air (United Nations Environment Programme, 2010c). Pb has three oxidation states: the metal Pb(0); Pb(II) and Pb(IV). Pb’s electron configuration can be written as: $[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$ (Royal Society of Chemistry, 2021)
Only two of the four electrons in lead’s outer-shell ionise readily, as such Pb’s usual oxidation state is Pb(II). Pb is renowned for its density, and comparably-low melting point, 327.5 degrees Celsius (United Nations Environment Programme, 2010c). As summarised by Thornton et al. (2001), Pb’s density is a consequence of its high atomic number and relative atomic mass, in combination with its atomic structure (face centred cubic) which by its close-packed nature forms density. It is extremely malleable; relatively soft and is low-strength compared with other metals (Thornton et al., 2001). It is, however, notably slow to corrode, with many historic lead-made articles still existing today from the Roman Era (Thornton et al., 2001).

The above-mentioned characteristics have resulted in Pb being widely utilised for anthropogenic purposes throughout human-history. Widespread usage of Pb has been established since Egyptian times as a glaze on pottery (Greenwood and Earnshaw, 1997) and extensively by the Romans, with some estimates advising that they extracted approximately 6 million tonnes across four centuries (Greenwood and Earnshaw, 1997). The Romans used Pb across a wide and varied spectrum of usages from plumbing to cookware (Thornton et al., 2001). Throughout the 17th century Pb was widely used in tableware and other domestic utensils, primarily because of its malleability and resistance to water intrusion (Thornton et al., 2001).

In modern times, the most widespread use of Pb was as an anti-knocking additive in petrol (United Nations Environment Programme, 2010a). Tetraethyl-lead and tetramethyl-lead smoothed the combustion of lower-octane petrol, increasing performance and efficacy, as well as acting as a lubricant (Thornton et al., 2001, United Nations Environment Programme, 2010c). In recent history, Pb has been utilised industrially as a metal alloy in acid-lead batteries, some paints, glass, and plastics, for example as a stabiliser in the production of polyvinylchloride (Public Health England, 2017b). Pb was also recently used in a number of applications, but due to its softness is rarely used pure (United Nations Environment Programme, 2010b). Alloying Pb with antimony was most common to produce lead-pipes, batteries, and solders (United Nations Environment Programme, 2010c).

To make a workable product from lead ore, it must be refined from its mineral state. The most abundant mineral form of Pb is as Galena (PbS). Thornton et al. (2001) summarise the extraction of metallic Pb from Galena as a two-stage process:

1. Roast the sulphide in air, to convert to the oxide
   e.g. $2PbS + 3O2 => 2PbO + 2SO2$

2. Heat the oxide in the presence of a reducing agent (such as charcoal, coal)
   e.g. $2PbO + C => 2Pb+CO2$

First sulphur is gassified in the conversion from PbS (Galena) to lead-oxide. Secondly, lead-oxide is reduced to metallic lead by the introduction of carbon, typically by coke within a blast furnace. Whilst molten at the temperatures of the blast furnace, molten Pb would be ‘tapped’ (Thornton et al., 2001) from the bottom of the furnace. This molten Pb would contain a ‘slag’ of impurities (oxides and silicates) above the molten metal which could be skimmed off and removed as waste (Thornton et al., 2001). Historically, slags were still rich in metal and, during the 19th century, it was typically re-smelted in a slagmill [Secondary Smelting] (Historic England, 1998).

Not all ‘waste products’ would be contained within the slag, with some lost in emissions or remaining within the ore (Historic England, 1998). Historical emissions from smelting works would be expected to be a mixture of lead oxides, sulphates and metallic lead within flue dusts, due to the inefficiencies and multiple handling processes within the smelter.

2.2 Lead in the environment

The stability and mobility of Pb in the environment is reliant upon its physio-chemical form and the environmental conditions of the matrix (i.e. soil, water or air) within which it is identified (Rieuwerts and Farago, 1995). Given the nature of this study, the factors influencing Pb in soil have been reviewed in greater detail.

Localised environmental factors (e.g., soil type, soil chemistry and moisture content) and climatic factors can influence the behaviour of Pb in the environment. These factors, in combination with the mineralogical form of the Pb and its (primary) source, will be detailed below. Additionally, the factors that influence the mobility of Pb in soil typically determine the amount of Pb that is bioavailable (Jae-Kyu et al., 2003). As such, these are also discussed.

Soil is a heterogenous matrix; the mineral form and concentration of metals within the soil can be consequential to a variety of both stable and actively competing factors. Ruby et al. (1999) list these determining factors as ‘*the presence of anionic species that form complexes with lead (e.g., organic acids, soil organic matter, phosphates, carbonates, sulphides, chlorides and hydroxides) …*’ as well as *‘iron and manganese concentrations, soil pH, cation exchange capacity and redox condition’s'* (pg3698). They elaborate that all such factors can influence the manner and extent to which chemical reactions (dissolution, precipitations, complexation and adsorption) occur (Ruby et al., 1999).

Soil organic matter content and pH have been found to influence soil Pb (Steinnes, 2013). The extent to which Pb binds or interacts with different soil components, will influence chemical interactions and lead to varying speciation potentially impacting on Pb availability. In acidic soils (pH 4 or less), Pb is absorbed to soil humus. In the absence of soil humus, lead may bind to clay minerals or other clay-sized particles and therefore precipitate in varying and more readily available species (Thornton et al., 2001). In alkaline soil, Pb can become more soluble as it forms organic and hydroxy complexes (Steinnes, 2013).

The most common mineral form of Pb is galena (PbS). Other significant ore minerals include, cerussite ($PbCO_3$) and anglesite ($PbSO_4$) both of which may be derived by the weathering of galena (Agency for Toxic Substances and Disease Registry, 2007). Typically, Pb is particle-bound within the environment, thus restricting its mobility and subsequent bioavailability (United Nations Environment Programme, 2010c). Acknowledging this, Pb can exist in soluble ionic forms and is often cause for concern to risk assessors when identified.

2.2.1 Bioavailability of soil bound lead

There are several exposure pathways by which Pb and other metals can enter the human body (Pan et al., 2016 in Gonzalez-Grijalva et al., 2019). The most relevant pathway to exposure from soils in the UK is via ingestion. Exposure via inhalation under typical circumstances is limited due to temperate climatic conditions (i.e., frequent rainfall).
For contaminants to become bioavailable, they must first become bioaccessible - mobilised from the soil during digestion (Oomen et al., 2003). Ruby et al. (1999) define absolute bioavailability as the fraction of the contaminant that ‘enters into system circulation’. Ruby et al. (1999) further identify relative bioavailability which they define as ‘the bioavailability of Pb and arsenic (As) in mine waste or soil [or contaminant and matrix of concern] relative to that of Pb and As [that contaminant] dissolved in water’. Bioaccessibility is the ‘proportion of total intake of contaminant that is extracted in the human digestive system and is available for absorption’ (Natural Environment Research Council and DTZ, 2009).

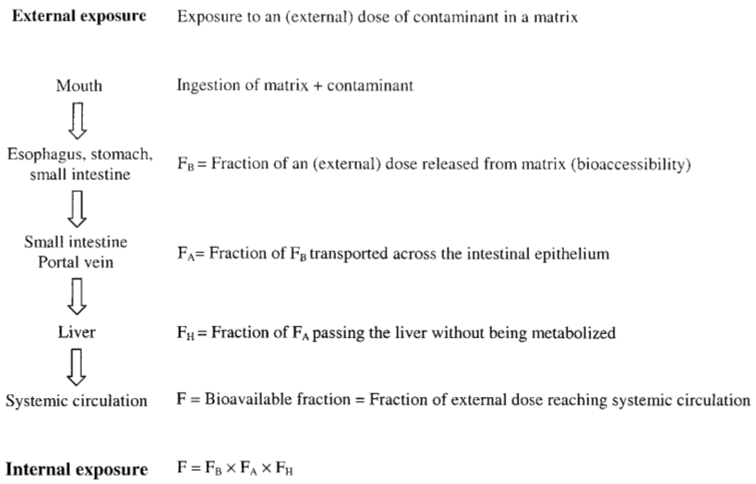

Figure 2-1 Schematic showing external to internal exposure - taken from Oomen et al.,(2003)

Oomen et al. (2003), define oral bioavailability as '*the fraction of an orally administered dose that reaches the systemic circulation*' and they sub-define oral-bioavailability into three components: bioaccessibility, transport across the intestinal epithelium, and the first pass effect (the resultant fraction of contaminant that has transported across the intestinal epithelium, then passing [through] the liver into systemic circulation without being metabolised).This classification is illustrated in Figure 2-1.

The form, stability and bioavailability of Pb in soil is dependent on a number of characteristics including, but not limited to: anthropogenic or naturally occurring source, soil type, particle size, soil pH, speciation of the metal, soil water, and local topography and hydrogeology (Liu et al., 2017). To understand how the bioavailability of lead in the soil links to bioaccessibility, studies have shown that speciation, the source of the mineral, organic matter and clay content and soil chemistry are significant (Cave, 2011 in Appleton et al., 2013).

Jae-Kyu et al. (2003) note that typically '*low Pb bioavailability is a consequence of Pb speciation and the corresponding solubility constraints…*' they elaborate further theorising that '*in mining-impacted areas, low soil metal bioavailability might be due to the presence of residual low solubility metal sulfides from the ore body*'. They concluded that Pb(II) bioaccessibility was dependant on the pH of the soil and that of the ingesting organisms gastrointestinal (GI) fluid (Jae-Kyu et al., 2003).

In terms of speciation, studies have focused on the presence of cerussite – lead carbonate ($PbCO_3$) – because of its high level of bioaccessibility (Denys et al., 2007). However, more recent studies have shown that other mineral forms are significant for bioaccessibility. Denys et al. (2007) found that, in a sample taken from mining waste material, 40% of the Pb was in the form of cerussite ($PbCO_3$) in carbonate-based soil. However, the majority of the Pb in the sample was found in a sulphur-based mineral. They suggest that in this mineral-form, it is still likely to be highly bioaccessible and this is corroborated below in Figure 2-2 – which shows Pb phosphates can vary in bioaccessibility. This highlights the need to consider both the mineral form of the Pb and the mineral content of the surrounding soil, and that the characteristics of each do not negate the need to consider them individually.

As can be seen from Figure 2-2, the smaller the particle size, the more highly bioavailable the Pb is. As Chaney et al (1988) in Thornton et al. (2001) established, smaller particles were more bioavailable since, when inhaled they were more easily dissolved or reached the alveoli and subsequently were dissolved in the blood stream.

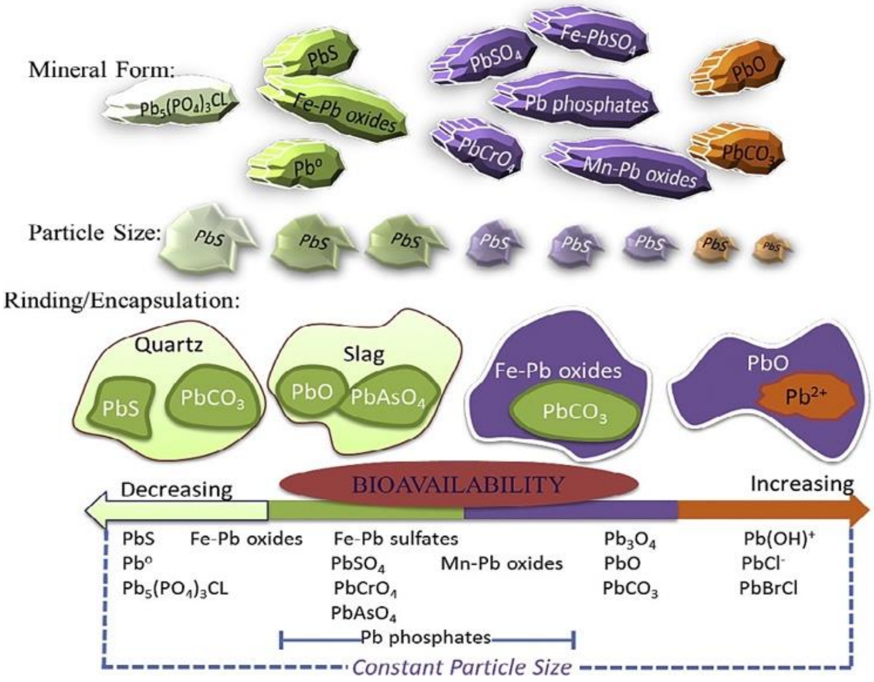

Figure 2-2 Diagram of factors affecting Pb on a scale of bioavailability taken from Ruby et al., 1999 as amended in Yan et al. (2017).

Yan et al. (2017) reviewed the effect of soil properties (pH, clay content, cation exchange capacity (CEC) and total organic carbon (TOC) and organic matter (OM)) on Pb bioavailability expressed as relative bioavailability (RBA) specifically within mining soils. Correlating the data of numerous studies, they found that soil properties do influence Pb RBA, though no single relationship was significant. They noted decreases in Pb RBA with increases of clay and CEC, and a weak positive trend for TOC and OM. They identified a larger range of Pb RBA in alkaline soils than for acidic, though most soils were neutral or alkaline.

Figure 2-2 shows the influence of encapsulating matrix on Pb bioavailability, this is particularly evident with cerussite (PbCO3) that when encapsulated with quartz is less bioavailable, but when within an iron-lead (Fe-Pb) oxide mineral matrix, becomes increasingly bioavailable. Palmer et al. (2015a) summarises the solubility of the surrounding matrix as influential stating ‘Pb encapsulated by insoluble minerals generally displays decreased bioavailability and bioaccessibility’.

2.2.2 Measuring bioaccessibility through Blood Lead Levels

Different mining sites have differing levels of bioaccessible fractions. Some studies, have found high total concentrations of lead in the soil leading to elevated concentrations in human Blood Lead Levels (BLL) (Garavan et al., 2008). Whereas other studies have found consistently high concentrations of lead in the soil but low BLL (Cotter-Howells and Thornton, 1991). Rieuwerts and Farago (1995) reviewed contamination in smelting and mining environments and compared variations in the chemical form of lead and its bioavailability in each area. Reviewing UK studies, they note the inconsistencies between Pb topsoil concentration (exposure) and BLL in mining areas. They referenced examples from Gallacher (1984) as cited in Rieuwerts and Farago (1995) who found that with a topsoil concentration of 1,159ug g^{-1} (n=62) 61 children had a mean elevated capillary BLL of 21.8ug dL^{-1}, compared to 31 children in a control area with a mean of 17ug dL^{-1}. In contrast, Strehlow and Barltrop (1988) as cited in Rieuwerts and Farago (1995) found values of 8.9ug dL^{-1} (n=99) and 8.8ug dL^{-1}between a mining area and a control area respectively, with a topsoil concentration average in the mining area of 1,850ug g^{-1}. Similar results were found by Garavan et al. (2008) whilst assessing children in a mining community, following the deaths of nearby livestock. Total concentration in the soil ranged from 12.3mg kg^{-1} to 7500 mg kg^{-1}, however BLL were less than 4ug dL^{-1} over a three-year period. This data indicates that the form of lead that enters the human body is critical to the level of Pb in the blood and the consequent health effects that may arise.

2.2.3 Characterisation of mine sites

Research has indicated that Pb bioavailability is typically lower in mining regions than in areas in the locality of smelters (Rieuwerts et al., 2000). Pb varies in physical and chemical properties dependent on the source mineral and local environmental conditions (Davies et al, 1994 in Rieuwerts and Farago, 1995). These factors influence bioavailability and subsequent exposure to human health.

2.3 Lead in Mining Areas

2.3.1 Mobilisation of (and exposure to) lead in the mine waste environment

There are many means by which heavy metals are mobilised and can be identified within mining and historic-mining regions. These range from the natural minerals contained within formative material in local soils, to minerals exposed by mining and successive treatment. These processes are discussed in the context of the study mine site, Snailbeach in Section 3.

Extraction typically involved blasting, drilling, and other means of breaking rock, and can consequently mobilise minerals within dust, and water – where used as a means of dust suppression. Records from historic mining, highlight chronic illnesses amongst miners – including silicosis of the lungs, indicating high levels of dust within many metalliferous mines, as well as the limited use of clean water suppression (Mills and Adderley, 2016).

Following extraction, the ore required processing by size reduction and separation. Size reduction typically involved crushing, grinding, and screening (Balasubramanian, 2015) and various separation techniques were employed dependant on the mineral of interest.

It is recognised, that early material handling processes on such mines, could cause inadvertent releases of metal-bearing fines and dusts (Brook and Allbutt, 1973). Most infrastructure, similar to that of the ‘Dressing Floors’, was open including conveyors, small-gauge railways and the handling-points between. It is reasonable to assume that such exposure to the elements facilitated substantial wind and rain dispersion within the immediate locality.

Transportation of processed ore led to treatment and refining by smelting. Typically, smelting of ore was undertaken within the local vicinity of the mine where feasible, to minimise the volume and costs of material transportation (Brook and Allbutt, 1973). Historically, inefficiencies within the smelting process resulting in significantly elevated Pb concentrations within waste products, both aerially and within slag waste (Thornton et al., 2001).

Research by Davies and White (1981) theorised and identified the risk of mobilisation of tipped material by windblow - the process by which fines and small particulates are eroded and whipped from mine waste spoil heaps by wind. They utilised a series of samples and suspended nylon mesh bags of moss, to assess concentrations within wind-borne particulates arising from tips upwind. Davies and White (1981) considered the pathway to be significantly under researched stating: ‘*Mobilisation by wind blow has received little attention probably because many tips contain sufficient large debris to mask and minimise the effects of deflation, but where they are composed dominantly of fine material they often appear to be sculpted by the wind*.’(pg.58).

Davies (1981) noted the impact of windblow across a range of mine sites and evidenced with studies investigating Welsh mines, undertaken by Griffith, 1919 (in Davies and White, 1981) and Johnson and Roberts, 1978 (in Davies and White, 1981). They report that wind transportation and wind erosion are factors leading to '*contamination close to heaps*' (Davies and White, 1981). Griffith (in Davies and White, 1981) found that '*sand, and… slime'* can be carried for over a mile from the heap source.

2.4 Studies of former mining areas

The polluting-potential of historic mine sites has been widely recognised in recent decades. The development of the current UK land contamination legislation has necessitated a process of investigation and remediation. Rieuwerts et al. (2009) highlights the many other complications associated with remediating legacy former contaminated mine sites, these include the heritage and historical importance on such sites; the ecological framework existing and developing from niche conditions; and the requirement to make previously industrial areas stable and safe for their current and future use.

Mine site studies are a specialised and niche area of study, there are many factors to consider dependent on the receptor of interest, these include source material, hydrogeology, soil chemistry, topography, and land-use. Different countries and regions have varying research approaches, local environmental characteristics to consider, and these have developed over time. A large body of research has investigated the potential impact to human health from exposure to contamination from soil-bound pollution within mining wastes (Rieuwerts and Farago, 1995). Original research and subsequent reviews have sought to define and estimate this exposure. In the UK such research had developed in concurrence with the development of the risk-based land management approach. Data collected is dependent on the exposure route of interest.

As identified by Rieuwerts and Farago (1995) a smaller body of research has focused on the chemical form of Pb at mine sites and by the bioavailability of such Pb, and sought to investigate and establish any links between the two. A more recent review undertaken by Yan et al. (2017) stressed the wide range of Pb concentrations that are found at mining and smelting sites (Mining: 200-42214 mg kg^{-1}(N=82), Smelting: 536-30155 mg kg^{-1}(N=22)). Of the mining sites the mean RBA was 33% (Median RBA: 38%)

In 1990, Steele et al, (1990) reviewed numerous relevant early research studies assessing the contribution from lead in mining wastes to human blood lead levels. Table 2-1 is adapted from Steele et al, (1990) to include relevant data from recent reviews.

Table 2-1 Summary table of mining site study data adapted from Steele et al (1990).

Study Location	**Study Date**	**Study Authors**	**Period of Operation**	**Range Soil Samples**	**Mean Soil Conc. (GM*)**	**No. of Soil samples**	**Garden Topsoil Pb Concentrations**	**House Dust Conc.**	**No. of Children**	**Blood Lead Level (ug/dL)**	**Method**	**Data source**
Winster, Derbyshire	1993	Li and Thornton		2400 - 22800	7140 ug/g	42		GM:15860	10	Mean: 9.5	Mg(Nox)2/ HCl	Danse 1995
Matlock, Derbyshire	1974	Barltrop et al,			909ppm					Spring GM Mean 20.1 Spring GM Mean 24.7		Steele et al 1989
Buxton, Derbyshire	1974	Barltrop et al,			398ppm					Spring GM Mean 22.8 Spring GM Mean 28.1		
Wales	1984	Gallacher et al.			1159 ug/g	62				GM Mean	HNO3	
Halkyn, Wales	1985	Davies	1845 to - 1938		1127 ug/g	59					HNO3	
Shipham	1988	Thornton et al, 1988	1650 to 1850		2002 ug/g	329				9.4		Danse1 995
Snailbeach, Shropshire	1988	Wardell Armstrong	up to 1955	96mg/kg to 138000 mg/kg		350		MEAN 3728 ug/g Control: MEAN 876 ug/g				(Wardell Armstro ng, 1988b)
Snailbeach, Shropshire	1975 to 1982	Becker, Shropshire Health Authority							7	Range: 25 - 40		
Silvermines, Ireland	1999 to 2001	Garavan et al.,	C19th to 1993 (Plus TMF)				RANGE 12.3mg/kg to 7500mg/kg (n=119)	MEAN 276.45 mg/Kg (N=114)	(Y1,Y2,Y3)370, 218, 188	>4		

Kossoff et al. (2016) theorised the potential remobilisation of Pb via acidity, oxidation/reduction and physical remobilisation, within their review of Pb impacted region in Derwent, Derbyshire. They concluded that due to the alkaline nature of the underlying soils, that acidity-related chemical remobilisation was unlikely, however, there was potential for physical remobilisation via flooding and physical transfer of material, and for remobilisation by the oxidation and reduction of Pb mineral compounds.

Studies in Northern Ireland researching the effects of lead sources on oral bioaccessibility in soil and implications for contaminated land risk management. Palmer et al. (2015a) sampled 163 locations across the Northern Ireland and Irish border region analysed by the UBM to determine bioaccessibility. This data was correlated with regional scale total (XRF) and extractable (ICP-MS) datasets, which were used to spatially determine Pb 'domains' (Urban, Rural, Granite, Mineralisation and Peat). The study identified that higher maximum gastric bioaccessible fractions could be found in Urban (97.6mg kg^{-1}) and Mineralisation (199.8 mg kg^{-1}) domains and that areas of elevated concentrations, spatially aligned with these domains, as well as the Peat domain and areas of high Pb solubility. As Northern Ireland does not currently have a legislative framework for the assessing potential risks from existing land contamination, guidance is typically adopted from the English Environmental Protection Act 1990 (EPA) Part 2A legislation and Statutory Guidance. Palmer et al. (2015a) highlight that the EPA Part 2A guidance states that '*normal presence/levels of contaminants…should not be considered to cause land to qualify as contaminated land*' unless there is significant evidence to demonstrate possibility of significant harm. On this basis, and the implications of the data, the study concluded that '*both diffuse anthropogenic and widespread geogenic contamination could be capable of presenting health risks having risk implications for land management decisions in jurisdictions where guidance advises these forms of pollution should not be regarded as contaminated land'*. It is important to note that the data relied upon for detailing the Mineralisation domain, originated from '*prospectivity maps and not the locations of working or historic mines*'. Palmer et al. (2015a) clarify that they consider the Mineralisation domain as '*geogenic and naturally occurring for the purposes of the research*'.

2.5 Human health effects of exposure to lead

Today, Pb is listed as one of the World Health Organisations 't*en chemicals of major public health concern*' (Science Communication Unit, 2013, p. 9). Research into the health effects of exposure to Pb have identified health impacts from both acute and chronic exposure. Consequently, Pb is now widely recognised as a non-threshold toxicant (Palmer et al., 2015a). Palmer et al, (2015a) summarised current scientific consensus, arguing that no amount of *'lead exposure can [now] be regarded as safe based on the available research to date'* . Following the above classifications, the UK soil guideline value (SGV), used in human health risk assessment (Discussed in Section 2.7), was withdrawn (Defra and Environment Agency (EA), 2002a, lines. 77-78, as cited in Palmer et al., 2015a).

To understand the human health effects, it is important to note that Pb can '*accumulate in the body, primarily in the skeleton'* and that Pb '*affects virtually every system in the body*' (E.F.S.A. Panel on Contaminants in the Food Chain, 2010). In England, the most recent national and governmental review considering the potential health effects of exposure to lead was reported by Public Health England. PHE's (2017b) analysis concludes that both acute and chronic exposure can have consequences for human health, ranging from gastrointestinal (GI) disturbances to increased risk of various adverse birth outcomes.

2.5.1 Neurological effects

Chronic exposure to Pb via the oral pathway has been evidenced to impact upon neurological systems. Whilst assessing exposure to lead within human dietary food chains within the EU, the E.F.S.A. Panel on Contaminants in the Food Chain (2010) identified that the provisional tolerable intake (PTWI) of 25ug kg^{-1}b.w. was '*no longer appropriate*' (p. 5) as there is no demonstrable threshold at which there is no risk of neurotoxicological impacts. Noting food and water as the primary exposure (at European level) to Pb, EFSA acknowledged the air, dust, and soil as potentially significant contributors to exposure also (E.F.S.A. Panel on Contaminants in the Food Chain, 2010). Pb has more recently been associated with the reduction of Intelligence Quotient (IQ) in children, with an estimated reduction of 1 to 3 IQ points per 10µg dL^{-1} of Pb (Science Communication Unit, 2013, Canfield et al., 2003).

2.5.2 Teratogenic effects

Public Health England (PHE) (2017b) particularly highlight the reproductive and developmental toxicological risks from Pb exposure, especially to babies and young children, stating; '*the most critical effects of Pb toxicity occur in children exposed during foetal and/or post-natal development'* (p. 12). This is due to exposure, even low exposure, to the mother: '*Low levels of environmental Pb exposure are also of concern in adults, particularly pregnant and lactating mothers...*' (Gomaa et al., 2002, as cited in Entwistle et al., 2019, p.131) and the EFSA (2010) also acknowledge that the impact on cognitive development in children can be seen even at low exposure levels (E.F.S.A. Panel on Contaminants in the Food Chain, 2010, p. 11). However, the influence of elevated concentrations and acute exposure is widely acknowledged. In their review PHE (2017b) conclude, '*numerous studies suggest [that] the higher the maternal concentration [of Pb], the greater the [risk] of adverse neurodevelopmental effects in the child'*(p.12).

2.5.3 Other documented effects

There is a growing body of evidence implicating impacts to humans from exposure to Pb to numerous other conditions. One such example was the classification in 2006, by the International Agency for Research on Cancer. They determined that inorganic Pb to was '*probably carcinogenic to humans (Group 2A)*' (E.F.S.A. Panel on Contaminants in the Food Chain, 2010, p.14).

Pb has been identified as toxic to the nervous system with other known effects to the liver, kidneys, heart and bone marrow (Appleton, 1995) . Studies suggests that Pb exposure might lead to anaemia and Pb can have a significant effect on haemoglobin synthesis (Public Health England, 2017b).

It is well documented that Pb induces arterial hypertension, and there is also a '*positive correlation between umbilical blood Pb level and the occurrence of hypertension in pregnancy*' (Poręba et al., 2010), Pb '*exerts direct constrictive effects on vascular smooth muscle'* (E.F.S.A. Panel on Contaminants in the Food Chain, 2010). It is therefore evident that current literature indicates both acute and chronic exposure to Pb can result in systemic physiological effects in humans.

2.6 Policies and guideline values

Sites such as Snailbeach Mine, Shropshire were assessed and subject to remedial works prior to the introduction of modern contaminated land legislation and policy. As such, it is necessary to review the current UK policy towards land contamination and the policy and legislation preceding the remedial works – discussed within Section 3

Scientific understanding of pollution, and land contamination has led to the introduction of legislation (EPAParliament, 1990As amended (1995)) and guidance (Defra, 2012a) to implement this understanding into common practice, particularly when assessing, developing and remediating land affected by contamination.

As scientific understanding has increased, and analytical technologies improved, fields of study have widened, and the scale of potentially affected land requiring assessment has also increased. Legislation, policy, and guidance has required development, amendment, and reform to align accordingly. With the UK's forementioned historical legacy of industrialisation and mining, legal principles have been long-established, but have been formalised, consolidated, and adapted in modern times to meet current requirements, and according to the political and geopolitical climate.

Risk-based land management is implemented via two pathways in current UK law, to address previous or historic contamination. These are outlined in Sections 2.6.1and 2.6.2 below.

2.6.1 Planning and Development

The National Planning Policy Framework (NPPF) (Ministry of Housing, 2021) sets out the UK state-level expectations for planning policy decisions across England. Paragraphs 183 and 184 define the position towards land affected by contamination. Paragraph 183 states:

> *178. Planning policies and decisions should ensure that:*
>
> a) *it is suitable for its proposed use taking account of ground conditions and any risks arising from land instability and contamination. This includes risks arising from natural hazards or former activities such as mining, and any proposals for mitigation including land remediation (as well as potential impacts on the natural environment arising from that remediation);*
>
> b) *after remediation, as a minimum, land should not be capable of being determined as contaminated land under Part IIA of the Environmental Protection Act 1990; and*
>
> c) *adequate site investigation information, prepared by a competent person, is available to inform these assessments. (pg.53)*

And:

> *184. Where a site is affected by contamination or land stability issues, responsibility for securing a safe development rests with the developer and/or landowner. (pg.53)*

In the UK, the NPPF introduces risk-based assessment of development into the planning system and forms a framework to identify land affected by contamination. This makes provision to ensure its proper assessment and remediation where required.

2.6.2 Environmental Protection Act 1990, Part 2A

The introduction of ‘Part 2A’ of The Environmental Protection Act 1990 (EPA 1990) was pivotal in shaping UK land-contamination policy. Part 2A was inserted into the EPA 1990 via Section 57 the Environment Act 2005. Prior to Part 2A, contamination was remedied and legally considered under private nuisance legislation and tort-based action. Part 2A placed a legal statutory duty upon local authorities to determine land as ‘contaminated land’ where it is found that ‘significant harm’(SH) or a ‘significant possibility of such harm’(SPOSH) from an identified contaminant. (Chartered Institute of Environmental Health, 2009, Defra, 2012a).

Statutory guidance was required to contextualise the legislation and provide a standard means, practicable by regulators, to implementing the legislation. There is anecdotal concerns that many initial assessments undertaken by Local Authorities were (overzealous), potentially unwarranted and that remedial action was being applied that was beyond the initial scope of potential ‘significant harm’ as intended in legislation. As such, further supplementary guidance was developed, and further research study commissioned to assist in assessing sites, within the Part 2a assessment scale.

The Contaminated Land Exposure Assessment (CLEA) Model is the UK-standard model that 'uses generic assumptions about the fate and transport of chemicals in the environment and a generic conceptual model for site conditions and human behaviour to estimate child and adult exposures to soil contaminants for those potentially living, working, and/or playing on contaminated sites over long time periods’ (Environment Agency et al., 2009). The framework provided by the CLEA guidance (SR2) was used to derive many current UK Guideline values, and the model is now widely used by regulators and other risk-assessment practitioners to support detailed quantitative risk assessments (DQRA’s) carried out for regulatory regimes such as the Environmental Protection Act 1990 Part 2A and the planning regime - Town and Country Planning Acts (TCPA)

(Nathanail and Earl, 2001). The CLEA guidance and ‘model’ were developed and issued through a series of Science Reports (SR) formulated by a collaboration of a number of regulatory and non-governmental bodies, and published by the Environment Agency (EA) in 2009.

2.6.3 UK and EU legislative interface

At a national level, most the most-recent widespread review and/or intervention on former metalliferous mine sites has been implemented as requirements set by EU Directives. Of the EU Directives, the two of pivotal importance are:

- European Council Directive 2006/21/EC, the Mine Waste Directive (MWD)
- European Council Directive 2000/60/EC that, along with subsequent revisions, came to be referred to as ‘The Water Framework Directive’.

The MWD brought strict requirements to address active mining and quarrying-related pollution, requiring member states to manage extractive waste and ensure that such waste, or methods used, do not cause harm to human health or the environment. Additionally, Article 20 of the directive required that member states generate and publish an inventory of closed and abandoned mining waste facilities causing, or with potential to cause, serious environmental impacts by 1 May 2012. In the UK, the MWD was implemented in to English and Welsh legislation by the Environmental Permitting (England and Wales) Regulations 2009.

2.7 UK risk-based land management

In principle, the modern UK risk-based approach to assessing land contamination consists of 4 stages - hazard identification, hazard assessment, risk estimation and, risk evaluation (Nathanail et al., 2007). Via these means the assessor seeks to clarify ‘contaminant linkages’ whereby there is a ‘source, pathway and receptor’ (Defra, 2012a). When there is deemed to be a linkage, or potential linkage, it must be assessed whether the contamination will have an impact upon the receptor, and the degree to which they will be impacted. The degree to which the impact is assessed is determined by the context, detailed above in Sections 2.6.1 and 2.6.2.

2.7.1 Generic Assessment Criteria

Soil guideline values (SGV’s), also referred to as generic assessment criteria or screening levels, provide consistent guidance determining the need to remediate a site without the expense of site-specific assessment criteria (Nathanail et al., 2007). Government-issued statutory guidance cautions the use of General Assessment Criteria (GAC) in risk assessment and contamination investigations stating: '*They should not be used as direct indicators of whether a significant possibility of significant harm to human health [The dictated threshold for a Category 3 and 4 Part 2A designations] may exist*.'(Defra, 2012a). DEFRA continue advising that '*the local authority should not view the degree by which GACs are exceeded (in itself) as being particularly relevant to this consideration, given that the degree of risk posed by land would normally depend on many factors other than simply the amount of contaminants in soil'* (Defra, 2012a, Section 3.29b). Whilst targeted to Local Authorities, this is of importance to both local authority and all land contamination practitioners - accepting the limitations and caution required in using GAC values.

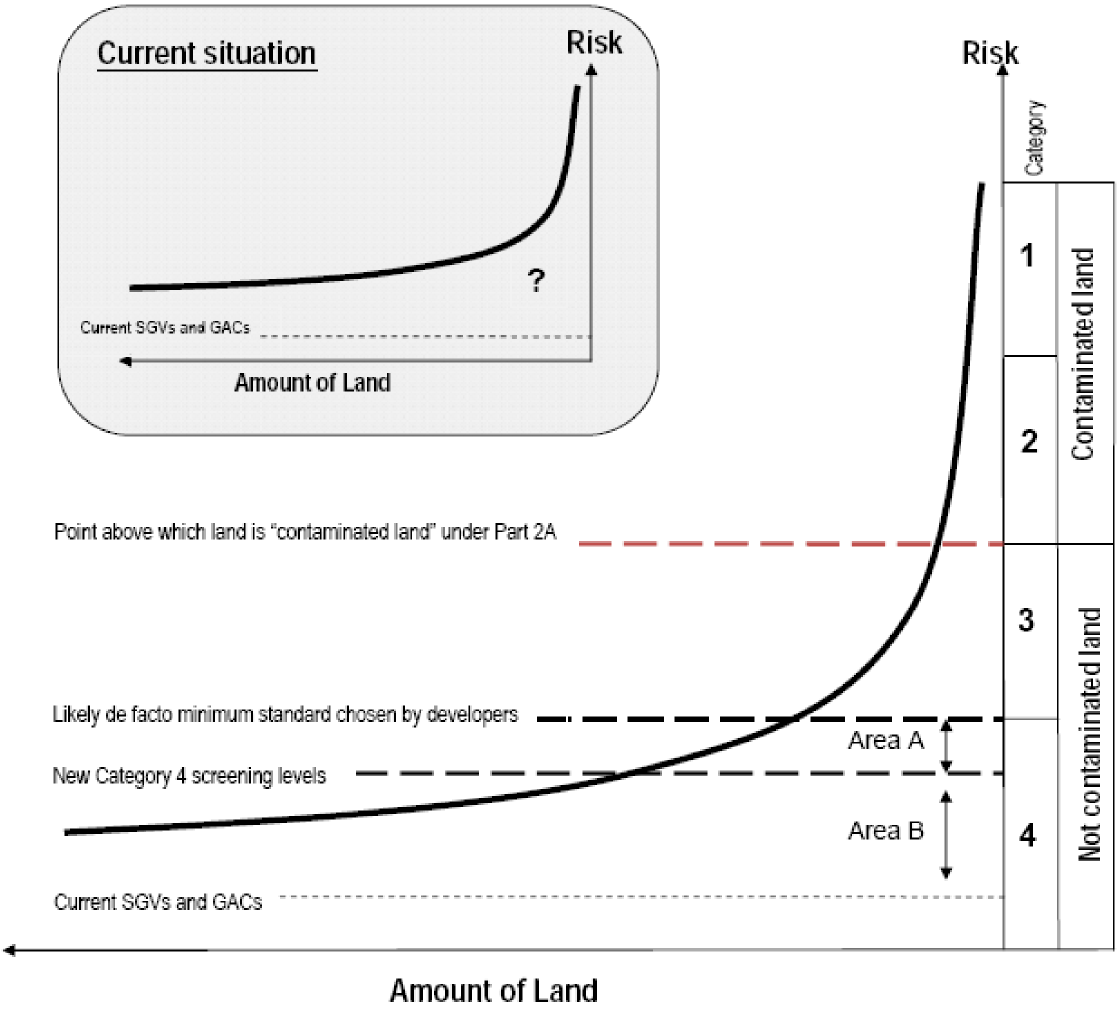

Figure 2-3 Diagram detailing the role of guideline values in determining EPA 1990 Part2A - 'Contaminated Land' categories taken from (Coles and Defra, 2011).

Figure 2-3 contextualises the determining factors in assessing land affected by contamination, to the legal categories issued within the revised statutory guidance. Figure

2-3 is taken from the Impact Assessment of the proposed changes to the guidance and makes reference to the ‘current situation’- prior to the implementation of the category system, which was introduced in 2012 (Defra, 2012a). Of notable relevance in is the marked thresholds for ‘Current SGVs and GACs’ and ‘New Category 4 screening levels’ (C4SL).

As defined by Palmer et al. (2015a) ‘*A C4SL denotes a lower tolerable limit for a contaminant in soil, beneath which human health risk is unlikely to be present’*. Notably, C4SL’s were only introduced in provisional form (pC4SL) and no final, binding levels have been issued.

The diagram (Figure 2-3) visualises the threshold of risk – for example, if a developer were to assess concentrations that were below a Category 4 Screening Level (C4SL) value the level of risk would be low enough to constitute Category 4: Human Health where the risk of SPOSH is low, and values are ‘normal’ for the area (Defra, 2012a). This is relevant when considering soil Pb concentrations given that the SGV for Pb was withdrawn (Defra and Environment Agency (EA), 2002a, lines. 77-78, as cited in Palmer et al., 2015a). A pC4SL for Pb was issued in 2012 (Defra, 2012c) and is presented and detailed in Section 6.

2.7.2 Average and background concentrations

The investigation and risk-assessment of potentially contaminated land has developed over time and dependant on the context. Accordingly, research has sought to quantify and map element concentrations in soils to define their distribution and likely source. Such definition allows risk assessors to differentiate elevated element concentrations between naturally occurring concentrations and concentrations arising from anthropogenic contamination. When considering elevated concentrations, their extent and distribution, and the risk-posed from such concentrations, it is now inherent to understand what concentrations would or should be considered ‘normal’ for that location and locality.

At a national scale, early studies sought to calculate average concentrations of particular elements. Davies (1983) estimated the normal lead content of British soils by statistical analysis of samples from four former mine sites. Using the cumulative frequency distribution from the sample set of each site, Davies (1983) identified a lower linear portion of each curve and delineated this potion as a lognormal population derived from non-contaminated soils. Based on calculations of a geometric mean and deviation of each result, Davies concluded that British uncontaminated soils are unlikely to contain more than 110 milligrams of Pb per kilogramme of dry soil, and that average soil Pb is 42 mg kg^{-1}.

As detailed in above sections, the Environmental Protection Act 1990, Part 2A and supplementary statutory guidance to for assessing potentially contaminated land sought to establish concentrations that constitute ‘contaminated land’ as legally defined. Supplementary guidance issued in 2012 (Defra, 2012a) acknowledged that elevated concentrations of some contaminants could occur naturally or be widely-elevated across a region due to historic diffuse pollution. Section 3.21 of the 2012 guidance (Defra, 2012) states that Part 2A is ‘*not intended to apply to land with levels of contaminants in soil that are commonplace and widespread throughout England or parts of it and for which in the very large majority of cases there is no reason to consider that there is an unacceptable risk.*’

The revised guidance (Defra, 2012) introduced the concept of ‘normal’ levels of contaminants in soil. Section 3 of the guidance (2012) notes that ‘normal’ presence/levels of contaminants:

- *should not be considered to cause land to qualify as contaminated land, unless there is a particular reason to consider otherwise (Section 3.22);*
- *may result from the natural presence of contaminants at levels that might be considered typical in a given area, and have not been shown to pose an unacceptable risk to health or the environment (Section 3.23(a));*
- *and are caused by low level diffuse pollution, and common human activity other than specific industrial processes (Section 3.23(b)).*

As part of a programme to support Local Authorities implement the revised SG, a research project was commissioned by Defra (Ander et al., 2013) to investigate normal concentrations of contaminants in the soil of England.

Statutory guidance for contaminated land issued in 2012 states in section 4.21 that ‘the local authority should consider the following types of land should be placed into Category 4 Human Health: …B) land with the only normal levels of contaminant in soil as explained in Section 3…’

2.8 Bioaccessibility analyses and their role within risk assessment

As established above, a contaminant linkage requires a source, pathway and receptor. The bioavailability of contaminants is dependent on a number of factors at each of those stages.

Humans are typically exposed to contamination in their individual, and the wider, environment(s) by three main pathways: oral ingestion, inhalation and by topical exposure (Environment Agency and Hosford, 2009) Much research has been undertaken into the factors influencing bioavailability in order to estimate final-exposure to humans, primarily by the oral pathway. As noted by Walraven et al. (2015), in regards to metals, bioaccessibility is initially controlled by the chemical form of the metal, and the particle size, this also determines the solubility of the metal, and therefore the pathways by which it is available.

'*The bioavailability of Pb ingested with soil by a young child due to hand-to-mouth behaviour depends on many factors including the physico-chemical properties of the ingested soil matrix, nature and solubility of the Pb present, as well as a child's nutritional status'* (Wijayawardena et al., 2015)

Most common bioaccessibility tests used today have been developed over the last twenty-five years, from approximately 1995. Bioavailability in contamination terms, can be defined as '*the fraction of a contaminant in a particular environmental matrix that Is absorbed by an organism via a specific exposure route (e.g. soil ingestion, vegetable uptake)*' (Nathanail et al., 2007). As noted by Wragg and Cave (2003) there are two key categories of bioaccessibility tests: *'chemical extraction tests that equate 'easily extractable metals… with those that are likely to be bioaccessible'* and, '*gastro or gastrointestinal analogue tests which attempt to mimic the biochemical conditions in the human/animal gastrointestinal tract'*.

Two of the most common bioaccessibility analytical methods are outlined below:

Simplified Based Extraction Test

The Simplified Based Extraction Test (SBET) form of the Physiologically Based Extraction Test reduces the analytical time required, and subsequent cost, for each test. PBET was originally developed by Ruby et al. (1996) 'approximates conditions in the human gut of a child in order to predict the bioaccessibility of metals from a solid matrix that has been ingested'(Nathanail et al., 2007). As stated by Ruby et al. (1996), '*the PBET was not* *designed to supplant bioavailability studies using animal models, but rather to estimate Pb and As bioavailability when animal studies are not available'*. The PBET was designed to allow ready estimation of lead bioavailability following the acknowledgement in the United States by the United States Environmental Protection Agency (USEPA) that a standard assumption of 30% bioaccessibility of ingested Pb, may not be applicable in all scenarios.

Unified BARGE Method

The Unified BARGE Method (UBM) has been developed by the BioAccessiblity Research Group of Europe (BARGE) as one of several international collaborations '*aimed at improving the understanding of the scientific validity of in vitro research'* (Naidu et al., 2015). The UBM was based on the Dutch Research Institute method, RIVM, which looked to '*simulate compartments of the gastrointestinal tract' incorporating 'temperature, soil-to-fluid ratio, ratio of digestive juices, transit times, centrifugation, pH values, mixing, constituents and their concentrations, and bile*.' (Oomen et al., 2003). UBM sought to adapt the RIVM methodology to ensure sufficient conservatism and ensure it was suitable for the conditions of a range of countries (Natural Environment Research Council and DTZ, 2009). UBM was evaluated by an inter-laboratory trial in 2009 and validated with in-viva data in 2012 (Denys et al., 2012) increasing its validity and acceptability by regulators.

2.8.1 Current use of bioaccessibility analyses

As late as 2005 to 2007, although widely introduced internationally the use and applicability of bioaccessibility analyses in the UK was still considered 'limited' (Environment Agency, 2007). The Land Contamination Policy Team from the UK Environment Agency summarised this view towards the use of bioaccessibility data in supporting human-health risk assessments (Environment Agency, 2007), stating that 'based on the current understanding, our views on the use of in-vitro bioaccessibility data in risk assessment have not been changed since our Science Update in 2005…'*given the current uncertainties associated with bioaccessibility testing, we consider its application to be limited'…we consider [that] this still applies…*'.

As reported by Saikat et al, 2007 in Denys et al. (2012), these views were formulated on the basis of a series of inter-laboratory 'blind' comparative analyses to compare the results from a number of UK and International laboratories from the same replicate samples. Saikat et al, 2007 in Denys et al. (2012) reported that although '*each laboratory used the same bioaccessibility method for all three contaminants, irrespective of* *concentration or matrix… The results varied between laboratories and the variability is largely attributed to the difference in the in-vitro methods used'*.

In recent years the use of bioaccessibility analyses has rapidly evolved (Dean et al., 2020). Dean et al. (2020), in their review of the application of bioaccessibility data in human health risk assessment, noted that caution needed to be exercised when utilising bioaccessibility data to relate to overall RBA advising that risk assessors should '*move away from the uncritical, blanket application of oral bioaccessibility testing and strategically target where the results of these data add real value to site determination*'.

2.8.2 In vivo and In vitro Methods

Whilst studies have been undertaken to calculate exposure and bioavailability from exposure to heavy metals, in vivo, these often incorporate several limitations. Furthermore, there are ethical concerns surrounding in vivo studies and which often both intrusive and expensive to conduct. Comparative physiological differences between humans and nearest comparator species has lead to the development of in vitro methods (Wragg and Cave, 2003). Casteel et al, (1997) herald the benefits of using a '*juvenile swine model'* to estimate a site-specific relative bioavailability of Pb in '*a mammalian species closely related to children from a physiological basis*'.

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3 Snailbeach Study Site

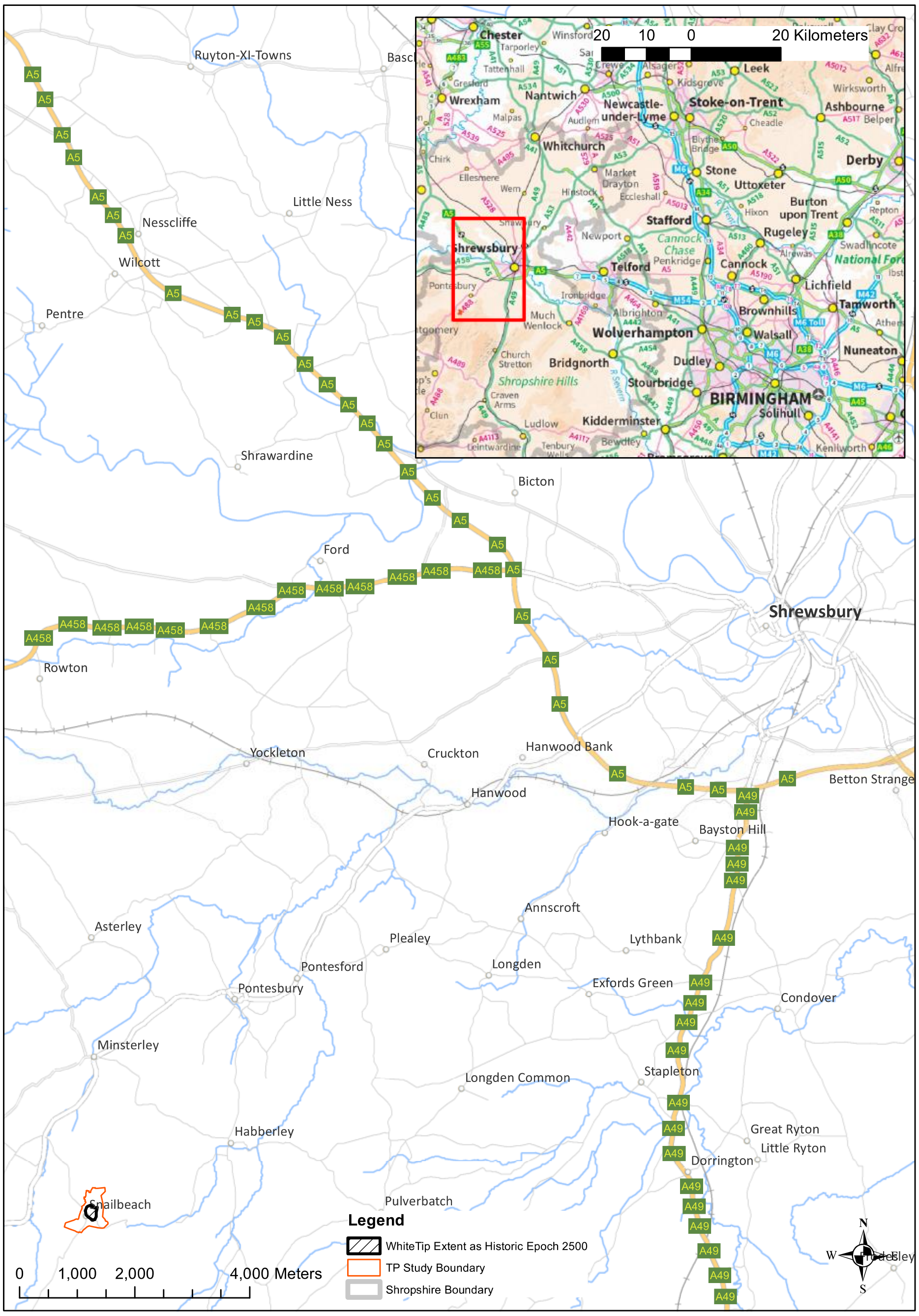

Figure 3-1 Map of Snailbeach Mine and study area in regional context.

The Snailbeach Mine Site lies within the small former-mining village of Snailbeach, Shropshire. The site is approximately 16km south-west of the county-town of Shrewsbury, and approximately 70km west of Birmingham, in the Welsh borderlands.

Snailbeach is situated at the northern end of the Stiperstones ridgeline, with parts of the village lying within the Stiperstones National Nature Reserve, (NNR) and the entire village within the Shropshire Hills Area of Outstanding Natural Beauty (AONB).

The Stiperstones ridgeline peaks at 536m with the 8 km ridgeline descending north to Snailbeach Mine. A central position of the mine, the former dressing floor, lies at approximately 250m with the surrounding village between approximately 200m and 275m. The valley topographical profile continues to descend from the village into the Hope Valley, with a known elevation of 152m at the Minsterley Brook at Water Wheel, approximately 1km west of Snailbeach.

In addition to the site and surrounding landscape sitting within the Shropshire Hill AONB, certain areas of the former mine spoil heaps are designated as a Site of Specific Scientific Interest (SSSI) due to the unique geological aspects and heritage. Most of the site lies just outside the Stiperstones NNR, though some of the key infrastructure relating to the operation of the 'Day Level' particularly the Pumping Engine house, along with the Resting Hill Chimney associated with the Site Smelter, fall within the NNR and a further SSSI site (Resting Hill North).

3.1 Geology

The county of Shropshire is well-renowned for its diverse and varied geology. As can be seen on Figure 3-2, the variation is most dramatic to the south of the county, with interspersed exposed-examples of different geology across the Shropshire Hills. Toghill (2006) notes that rocks within Shropshire represent ten of the twelve recognised periods of geological time, and that several geological epochs were named based on exposed examples of Shropshire rocks, thus bearing Shropshire names when used internationally – 'Caradoc', 'Ludlow' and 'Wenlock'.

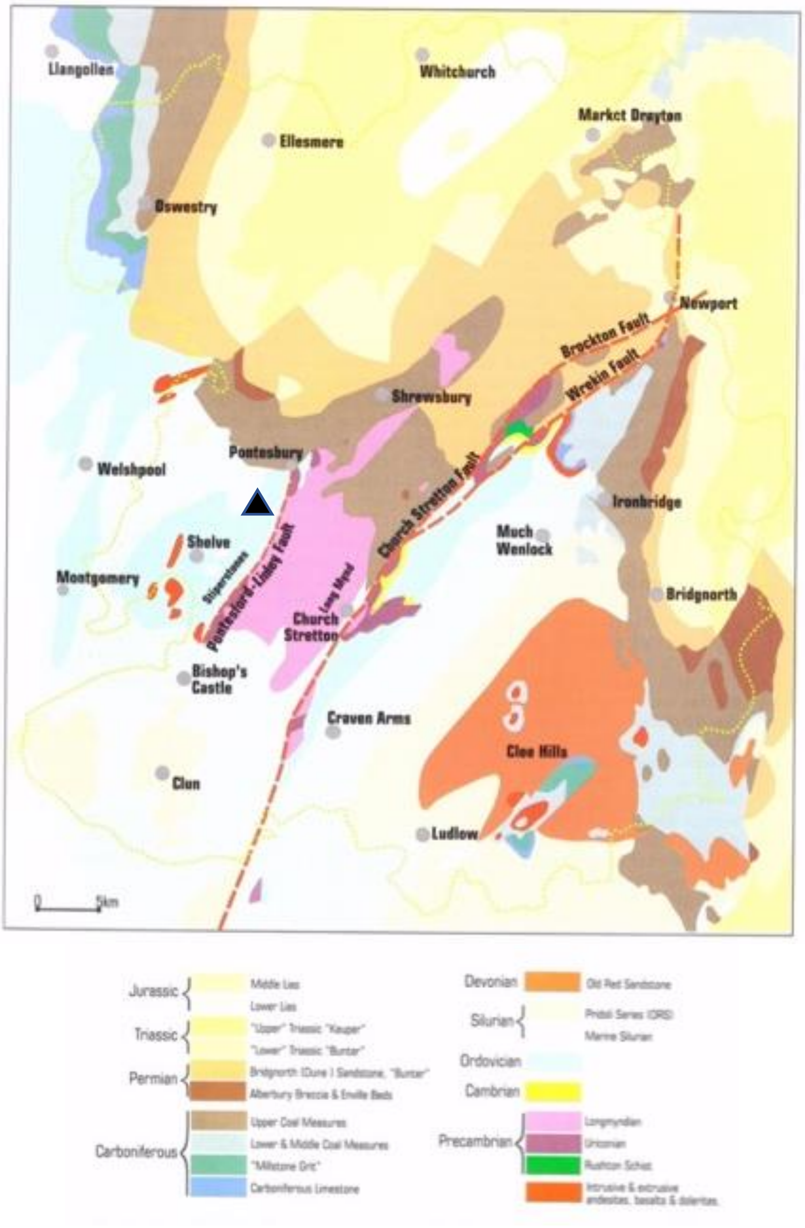

Figure 3-2 Map of Shropshire geology taken from Toghill, 2006 pp 26-27.

Given the geological diversity in Shropshire many quarries, coalfields and orefields developed to exploit these resources. Shropshire still contains many sand, gravel and mineral/aggregate workings today.

The West Shropshire Orefield which emanated within an approximate 9.5km radius of the hamlet of Shelve, within the Shropshire Hills. The orefield, shown in Figure 3-3 is considerably smaller and more compact than other typical British orefields (Brown, 2001) and concentrated on the mineralised veins within the Mytton Flags formation. Snailbeach

Mine, when active, was the largest mine operating in the orefield, and its position is marked on Figure 3-2 and Figure 3-3 by a black triangle.

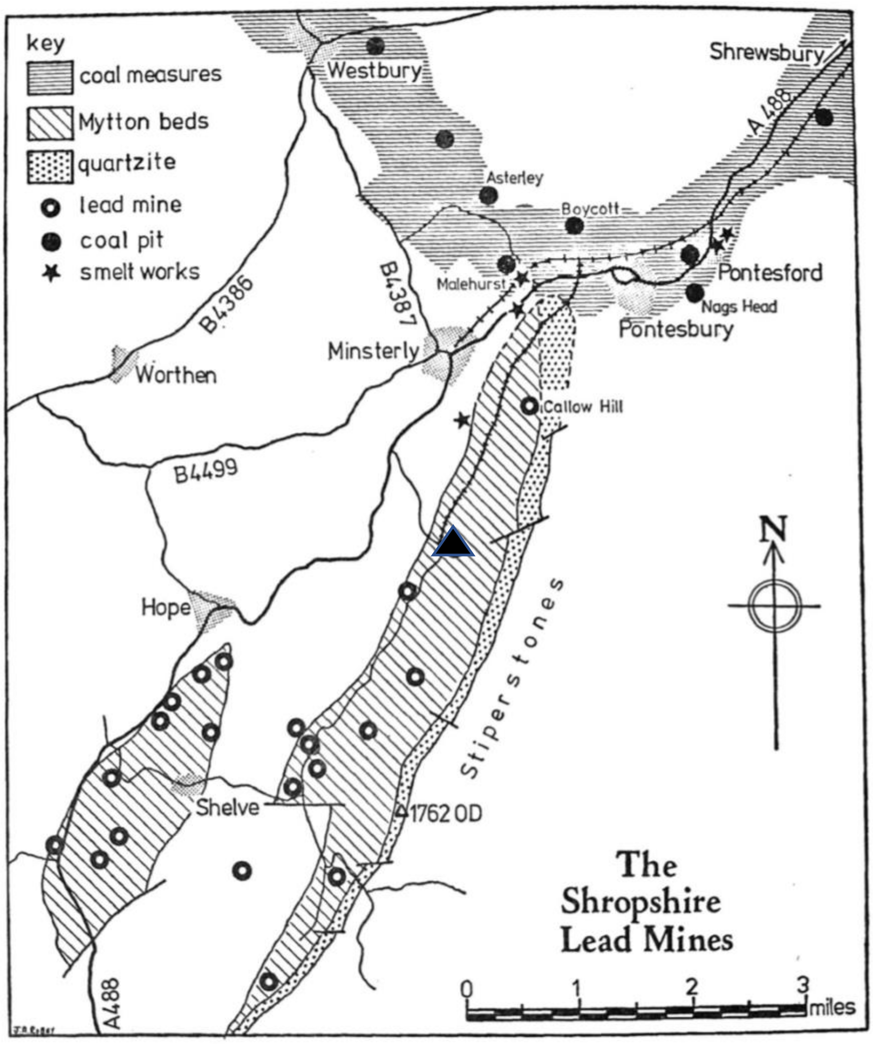

Figure 3-3 Map of the West Shropshire Orefield taken from Allbutt and Brook, 1973

It is important to note the significance of the nearby coal measures, north of the orefield and to the south-west of Shrewsbury which included pits at nearby villages of Pontesbury and Malehurst. These facilitated the development and industrialisation of the Snailbeach mine with a local cheap fuel source for both steam-driven pumping directly at the mine-works and the subsequent working and smelting of the ore.

As noted by both Brown (2001) and Brook and Allbutt (1973) the altitude and topography of the region favoured the small but rich orefield. Brook and Allbutt (1973) summarise that the combination of the relatively high local elevation and impermeable geology made the Stiperstones ridgeline a favourable orefield. '*Whilst being an obstacle to easy transport the landscape, however, facilitated mining since it allowed miners to drive along adits from* *low points in river valleys to meet the veins in the hills. By this means many mines were drained to considerable depth without requiring the use of expensive pumping machinery. It was only when the mines became too deep to drain by this method that recourse to machine pumping was necessary'(pg13).*

Brown (2001) elaborates on the benefit of the altitude further by stating '[*Altitude] also assisted in providing ventilation and draught necessary to operate early lead smelting techniques.*' This benefit is evident at the Snailbeach Mine where a 2km subterranean smelter flue was constructed beneath the main mine site and within the adjacent hillside to a chimney above the site (Historic England, 1998). The approximate route of the smelter flue is marked on Figure 4-1 Map showing location of 2019 *samples*'.

3.1.1 Geology of the Shelve/Stiperstones area.

The Shelve area and land immediately-north of the Pontesford-Linley Fault (and quartzite ridgeline of the Stiperstones) is underlain by rock formed in the Ordovician period, approximately 488 to 443 million years ago (Toghill, 2006).

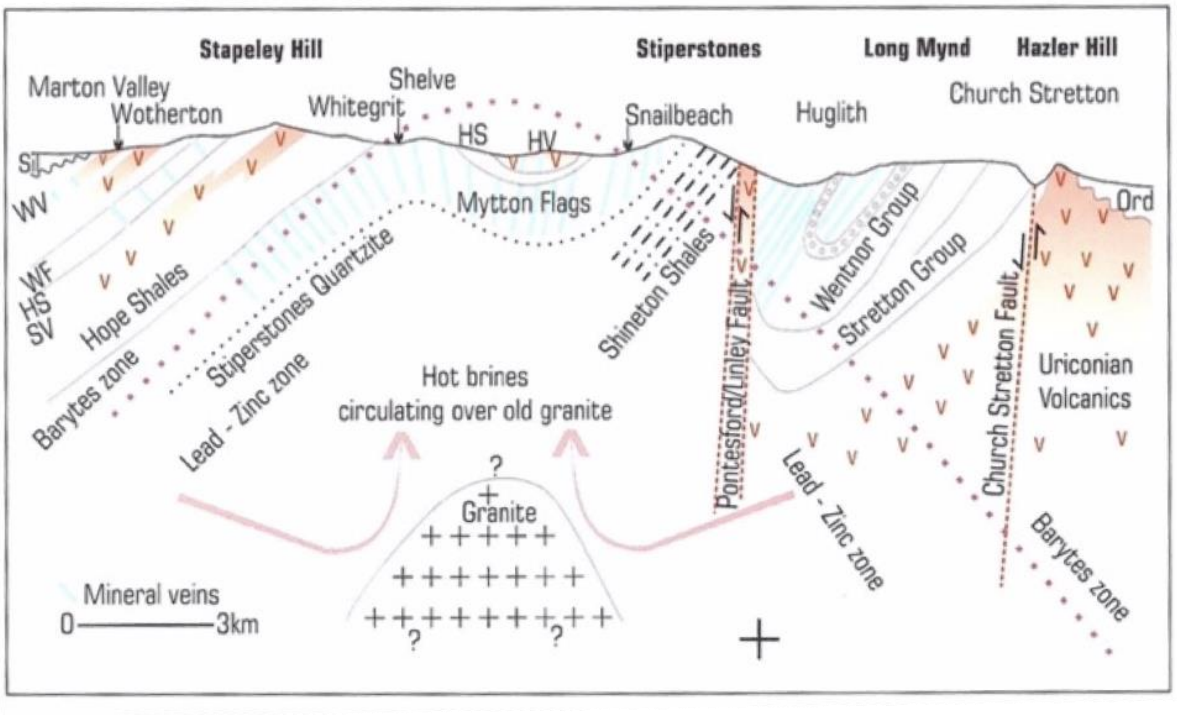

Figure 3-4 Diagram of Cross-section through the Shelve-Longmynd Area taken from Toghill, 2006 (Pg108)

It is generally accepted that tectonic movements within the Ordovician period, along and around the Pontesford/Linley and neighbouring faults, dictated the folding of rock strata.

This facilitated the formation of mineral veins within the Mytton Flags formation (Haggerty et al., 2009, Toghill, 2006) though the manner in which the veins formed remains subject to academic debate. Previous geological study hypothesised circulating sea-water, though typically downward penetrating, could be heated by older deposits and rise into faults of overlying strata, an opinion presented by Toghill (2006) and indicated in Figure 3-4. Haggerty et al. (2009), dispute the 'brines' to be the sole source of the mineralization suggest that '*the highly variable nature of the Pb-isotope data for the West Shropshire orefield excludes the possibility that the mineralizing fluid was circulating sea-water'*. They conclude that suggest that '*lead was tapped from multiple sources'*, though state there is insufficient data to confirm this.

3.1.2 Geology specific to the Snailbeach Mine site

Snailbeach, specifically, is underlain by the Hope Shale and Mytton Flags formation bedrocks, shown in Figure 3-4. The Hope Shale Formation is primarily mudstone, whilst the Mytton Flags formation is primarily Sandstone and Siltstone, subjected to igneous activity. At Snailbeach the formation is interlaid with mineralised veins. The primary minerals known to present consist of galena, sphalerite and barytes, amongst lesser quantities of cerussite, iron pyrites and witherite (Pearce, 2008, Toghill, 2006). Superficial deposits are not recorded for the majority of the Snailbeach area, it is understood that given the extensive mining activity most superficial deposits consist of weathered rock material and general 'made ground' as a result of the extensive workings.

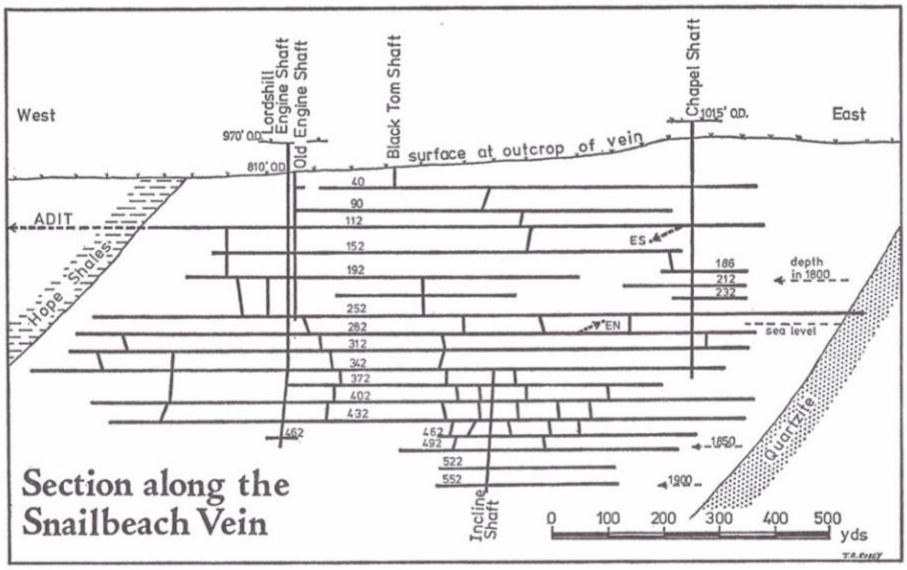

Figure 3-5 Cross-section of Snailbeach Mine workings taken from Brook (1971,pp89)

The mineral bearing veins, within the Myton Flags beds are understood to be geologically constrained between the quartzite and shales as shown in Figure 3-4 and Figure 3-5. Wardell Armstrong (1989a) summarised superficial deposits as a 'thin veneer of soil and weathered material' across the hillsides, with glacial drift (boulder clay) in the '*lower ground and valley area*', though '*several metres of mine spoil [overlay] the natural deposits*'. They describe the mineralisation as occurring principally in the 'Main Vein' and subsidiary veins - 'Black Tom' and 'South'. The corresponding 'Black Tom' shafts to meet these subsidiary veins are shown in Figure 3-5. The Main Vein is understood to have been approximately 3 metres wide, though stretched to 7 metres in places (Palumbo-Roe and Colman, 2010).

Pearce (2008) identifies the main minerals extracted at Snailbeach as:

Common Minerals

Barite – Barium Sulphate ($BaSO_4$)
Calcite – Calcium Carbonate $CaCO_3$)
Galena – Lead Sulphide (PbS)
Iron Pyrites – (FeS)
Quartz – Silicon Dioxide (SiO_2)
Sphalerite – Zinc Sulphide (ZnS)
Witherite – Barium Carbonate ($BaCO_3$)

Rare Minerals

Cerussite – Lead Carbonate ($PbCO_3$)
Chalcopyrite – Copper/Iron Sulphide ($Cu\text{-}FeS_2$)
Pyromorphite – Chloro-phosphate of Lead ($3Pb_3P_2O_8PbCl_2$)

3.2 History of Snailbeach Mine Site

Evidence of lead-mining activities in the vicinity of Snailbeach date from the early roman times, until as recently as 1955 when mining on the site ceased (Table 4-1) (Pearce, 2008, Toghill, 2006). Research suggests that Snailbeach had a reputation for a particularly high volume of Pb per unit area (Rainbow, 2018)

Table 3-1 Timeline of relevant history at Snailbeach Mine (adapted from Wardell Armstrong (1988b))

Date	Event / Summary Notes
Circa AD 120	Smelting of ore obtained from mining or surface scouring.
1552	Workings recorded at Hogstow Forest, suggested the workings at Snailbeach.
1676 and 1686	Limited records of leases with a group of Derbyshire Miners to work in the Snailbeach area.
1760's	Systematic workings along the Main vein
1769	Mapping indicates an 'engine' on site – suggesting increased development of mine workings
1782	Site leased by Thomas Lovett Snailbeach Mining Company Formed – continuous working
Early c19th	Continuous working of levels – profitable extraction. Proposal for exploration by surface trenching. Recommendation that plans and whole ground, veins, levels and mines be taken (1827).
1850's	Peak Output – 3500 tons of ore mined annually
1860	Barytes production in stopes.
1863	Mine modernisation – chimney and flue constructed. Many new workings – varied productivity, continued driving of some older levels. Smeltmill at Pontesbury abandoned with **new smelter constructed 0.5mile north of Snailbeach mine** – mill had ground flu which undercrossed the mine site to Lordshill where discharged via chimney with smoke from the Cornish engine boilers (Historic England, 1998).
1870's	Cages introduced at Ladder Shaft (Shaft No.16) and Second Engine House built. Continued exploration. Some rich pockets of ore. Barytes becoming important.
1877	Snailbeach District Railway completed – facilitates cheaper export of lead and barytes
Late c19th	Third engine house built and steam engine introduced.
1884	Mine Company makes first recorded loss, liquidates but immediately reconstitutes and continues in reduced form.
1895	Depression in industry – leading to dramatic fall in the value of lead

	Abandonment of underground exploration. Snailbeach remains as last operating mine in Shropshire Orefield
1900	Reworking of barytes from tips by Halvans [wastes] Company
1905	Only 200tons of lead. output
1910	More barytes than lead being produced.
1911	Cessation of main underground lead workings. *Mine allowed to flood to 112yd adit*
1919 – 1955	Sporadic barytes production.
1955	Cessation of underground mining. Main activity on site consists of removing fine spar from spoil heaps for use as pebble dash in the building trade
1985	First scoping structural, archaeological surveys and scoping exercises as to address local concerns

3.2.1 Early-History

Evidence of lead-mining activities in the vicinity of Snailbeach dates from the early roman times, by the means of a roman lead ingot found in the vicinity in 1976 and dated to AD117-138 (Pearce, 2008).

Earliest records of formal workings on the site originate in 1552, where records indicate a mine in ‘Hogstow Forest’ - which is believed to be Snailbeach (Pearce, 2008). There are limited records of the scale and extent of the workings in this period, with only a ‘lease to a group of Derbyshire miners’ in 1676 and 1686, as detailed in Table 3-1.

There is anecdotal evidence of crude smelters (‘boles’ – similar to a stone-lined firepit) located on the adjacent Stiperstones hillside (Pearce, 2008), indicating the rudimentary nature of the works at this period.

3.2.2 Main Production/Operation

It is generally agreed that whilst there were limited mining works at Snailbeach before the early 18th Century, Snailbeach didn’t reach importance or prominence as a productive mine site until approximately 1760 (Brown, 2001).

In 1782 the site was leased by Thomas Lovett, with the Snailbeach Mining Company being formed in December 1783. Brown (2001) advises that ‘*By 1797 mining had reached* *a depth of 180yds at Old Shaft and a drainage adit had been driven'*. Local geologist and researcher Toghill (2006) suggests that at its peak Snailbeach was '*one of the richest mines in Shropshire, and possibly Europe*'. This is substantiated by production records that indicate the site produced in the region of 139,000tons of Pb ore between 1845 – 1913 (Toghill, 2006, Armstrong, 1988).

The main centre of mining activity was located around Old Shaft which extended to the 252yd level. The deepest parts of the mine were eventually located in the winzes (or underground shafts) below the 552yd level (Brook and Allbutt, 1973).

Buddles, a lined circular pit with an inverse conical centre, were used to wash and separate ore. Heavier ore is agitated and separated from lighter gangue [waste] materials. It is noted that these early technological processes were relatively inefficient, and ore was typically passed through several buddles of varying size in order to achieve a '*satisfactory separation and purity'* (Brook and Allbutt, 1973).

Following the extraction and treatment of the ore, it was transported to Pontesbury smelter, and later to the closer Snailbeach Smeltmill. To refine and smelt the ore to workable lead.

Anecdotal reports suggest that mine waste material was used in hardcore as part of the formation of roads within the 'Lower Works' area.

3.3 Wardell Armstrong Snailbeach Mine Studies

Top photograph:(Palumbo-Roe and Colman, 2010) , Lower photograph: Google Street View Imagery (Taken 2009) https://goo.gl/maps/9Lcausw2vyMCMBbWA [Accessed 21/09/21]

Figure 3-6 Photographs of White Tip pre and post-reclamation work.

As detailed in early reports, '*the mining activity left a legacy of metal-contaminated spoil heaps, unstable ground, open and insecure mine entries and derelict buildings*' all of which posed '*a hazard to the residents of Snailbeach and to visitors*' (Wardell Armstrong, 1988b). Figure 3-6 shows photographs of the 'White Tip' circa 1980, prior to the reclamation work, above a recent photograph from Google Street View, taken in 2009. Both photos are taken facing north from the 'Dressing Floor' vicinity, the same buildings are shown in the bottom-right aspects for scale and reference.

The site was subject to an extensive series of site investigations and assessment following concerns regarding pollution and the stability of the site in 1983. Phased studies and investigation were undertaken through to 1989 whereupon a subsequent reclamation scheme was approved and commenced. Wardell Armstrong (1988b) was arguably the most-comprehensive of all studies carried out at the Snailbeach Mine Site. The report formed ‘Phase 1’ of the three perceived phases to the ‘Snailbeach Mine Reclamation Scheme’ and was commissioned to investigate the structural, environmental and archaeological security of the Snailbeach Mine site. The preceding investigations consisted of numerous surveys of the surface and sub-surface workings, with reference to the structural integrity, ecological value, biogeochemical risks and archaeological and cultural significance of the site.

As part of the biogeochemical investigation a range of data was collected, this included a sampling of topsoil and house dust within local properties. Samples and engineering surveys were undertaken on the ‘White Tip’ to determine its contents and structural stability. The investigation demonstrated that contamination from the eroding ‘Large White Tip’ was the ‘principal source of contamination’, with significant volumes of material likely to have been ‘lost’ from the Tip by wind, and water erosion (Wardell Armstrong, 1989b).

Results from the White Tip and local topsoil sampling found that ‘*The tip material has metal contents in excess of 28,000mg kg*$^{-1}$ *lead, 12,000mg kg*$^{-1}$ *zinc and 74mg kg*$^{-1}$ *cadmium, which are at least one hundred times normal background values [As determined in 1988]’*.

Across the 350 soil samples taken, ‘Total Pb’ levels range from 138,000 mg kg^{-1} in one location to only 95 mg kg^{-1} at another. The report noted that it was apparent that ‘*contamination was evident even at the furthest (distance) samples taken*’. Likewise it is reported that ‘*between 75% and 83% of the various land categories, (gardens, pastures, woodlands and vacant), within a 100 m distance of the tip, have lead values which are in excess of DoE [Department of Environment] Trigger Levels for environmental concern’* [200mg kg^{-1} for Gardens and Allotments, 2000 mg kg^{-1} for parks/playing fields] (Wardell Armstrong, 1988b).

As part of the 1988 investigation (Wardell Armstrong, 1989b), samples of house dusts were undertaken from a number of properties within the study area, as well as the nearby Stiperstones village, and a control site in Liverpool. Analysis found mean levels of 3728 ug g^{-1} within the Snailbeach properties, compared to 876 ug g^{-1} at Stiperstones, and 543 ug g^{-1} in Liverpool (Wardell Armstrong, 1989b).

3.3.1 Conclusions of the 1988 Study

Within the Phase 1 report, Wardell Armstrong (1988b) identified that the ‘White Tip’ was an ‘active’ source of pollution, and expressed concern about its centralised position within the village, and therefore the potential exposure to a significant number of local residents. They ‘*strongly recommended that the source of contamination [was] dealt with’* and proposed to import clean soil cover, underlain by a capping layer (membrane) to encapsulate the White Tip, once mineshaft stabilisation works had been completed.

Wardell Armstrong (1988b) concluded that following and capping of the White Tip *‘the health implication of the remaining historical contamination [would] not [be] serious…’.* Furthermore, they determined that *‘exposure of residents to lead and cadmium would be very much reduced and there would only be very localised potential problems.’*

With regards to human-health implications, Wardell Armstrong (1988b) stated that ‘*There [was] limited knowledge about the sub-clinical effects of long term exposure to low levels of lead and there are almost no long term studies of the effects of cadmium’.* Wardell Armstrong’s biogeochemical investigation states that ‘*The precise effects of slightly elevated blood lead levels experienced for long periods are not fully known, but concern is growing’*. In order to fully confirm the BLL they advised that a full epidemiological study of local residents would be required. However, they cautioned that ‘*, …such a study would be intrusive, alarming to local residents and also very expensive*.’

Wardell Armstrong (1988b) make recommendations with regards to future management of the site. They advise that a Trust should be established to oversee the ongoing recreational and educational aspect of the former central mine works. Furthermore, they stipulate that the cap of the tip should be protected from intrusion i.e. heavy machinery or erosion by livestock and that the newly installed drainage system and settlement ponds are regularly maintained. They concluded that the site was now suitable for its ongoing current uses as of 1995, but this should be re-assessed if usage changed in the future.

3.3.2 Reclamation Scheme

Of the 235,000 cubic metres of material estimated within the central ‘White Tip’ (Wardell Armstrong, 1988) 8000 cubic metres was moved into select derelict shafts and adits to stabilise the site and slopes of the ‘Tip’ (Shropshire Mines Trust, 2008).
Following the removal of material as part of the stabilisation works, the White Tip was reprofiled and capped according to its proposed use. Completion reports indicate that

‘*capping types included various thicknesses of imported subsoil and either a granular or geocomposite (type Enkadrain ST) capillary break*’ (Wardell Armstrong, 1995). They state that 600mm of clean cover soil was used on all new agricultural land on the reclaimed tip, and the existing agricultural land north of the tip, albeit with a granular break only for pre-existing agricultural land.

The supplementary report of the Stage 2 Reclamation Works demonstrates extensive consultation with the local residents and those with a regulatory or recreational and studious interest in the mines. This accounts for the decision to leave a certain area of ‘granular’ spoil of the Tip less open and uncovered for scientific study and education purposes.

3.3.3 Knowledge of lead and policies at the time of the Wardell Armstrong investigations

At the time of the 1988 Study, modern standardised guideline values for human health specifically for exposure pathways relating to soil, had not yet been derived. As such, the report authors used relatively ‘recent’ Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) ‘trigger values’. As noted by Wragg and Cave, 2003 the ICRCL Trigger values were ‘*derived from permissible concentrations in sewage sludge applied to farmland at soil pH values of 6.5’*. The use of such values was subject to substantial uncertainty given the variability and heterogeneity of soil characteristics - a matter that it is intended that this research will review. A study published soon after the completion of the reclamation works, Casteel et al. (1997) notes the ‘*increasing importance of quantitative risk assessment, and the associated regulations permitting some level of acceptable risk, emphasizes the necessity for greater confidence in these determinations and the need for accurate measurements of effective dose*.’

3.4 Snailbeach Farm ‘Part 2A’ Investigation 2002

Since the 1994 scheme, relatively little further study was conducted, and no evidence of validation sampling has been found to date in searches of local historical records. However, in 2002, the death of four calves in a nearby field from suspected Pb poisoning caused the local authority of the time Shrewsbury and Atcham Borough Council (SABC) to trigger an investigation. As part of this investigation, studies were carried out into the speciation of (and subsequent bioaccessibility of) Pb within material which had been deposited alongside an area of broken pipe in the field. It was identified that the pipe linked to historic drains associated with the ‘White Tip’ at Snailbeach Lead Mine. The material was characterised and subject to two extraction tests SBET and Heavy Metal

Extraction Test (HMET) to identify the potential Pb release in the soil, the report noted that '*A large proportion of Pb is bioaccessible in all soils analysed*' and that '*the minimum proportion of bioaccessible Pb , relative to the Total Pb determined, was 70%*.' The report recommends further bioavailability testing and sequential extraction for both Cd and Pb across the Snailbeach area, with particular reference to the playground area outside Snailbeach Village Hall and nearby residential gardens.

4 Methodology

4.1 Study Design

The analytical methods used were initially selected in order to comply with the original objectives and bioaccessibility analysis. This amounted primarily to total concentrations analysed by XRF and extractable concentrations undertaken on the <250 µm soil fraction by ICP-MS analysis.

Upon review, it was determined that both methods held qualities that suited the revised objectives. Samples tested by XRF require minimal pre-treatment and analyse the whole sampled-soil matrix. XRF analysis is routinely used for large-scale areas of study due to prompt and accurate analysis, whilst relatively low-cost in comparison to other methods (Fitton, 1997). Likewise, ICP-MS analysis was undertaken on the <250µm fraction to identify an extractable total concentration prior to bioaccessibility analysis, as per the UBM. It was decided that the data could continue to benefit the revised objectives given that ICP-MS provides an 'extractable concentration' and may be indicative of the concentration to which receptors could be exposed. The extent to which such conclusions could be drawn was investigated by review of recent studies and modern guidance and literature, and by analysis of the primary data collected.

Additionally, it was considered that ICP-MS allows significant accuracy across a wide range of elements, with low limits of detection – allowing greater accuracy and scrutiny in subsequent conclusions and comparison against the lower values and standards that have been provided for environmental Pb exposure.

4.2 Fieldwork

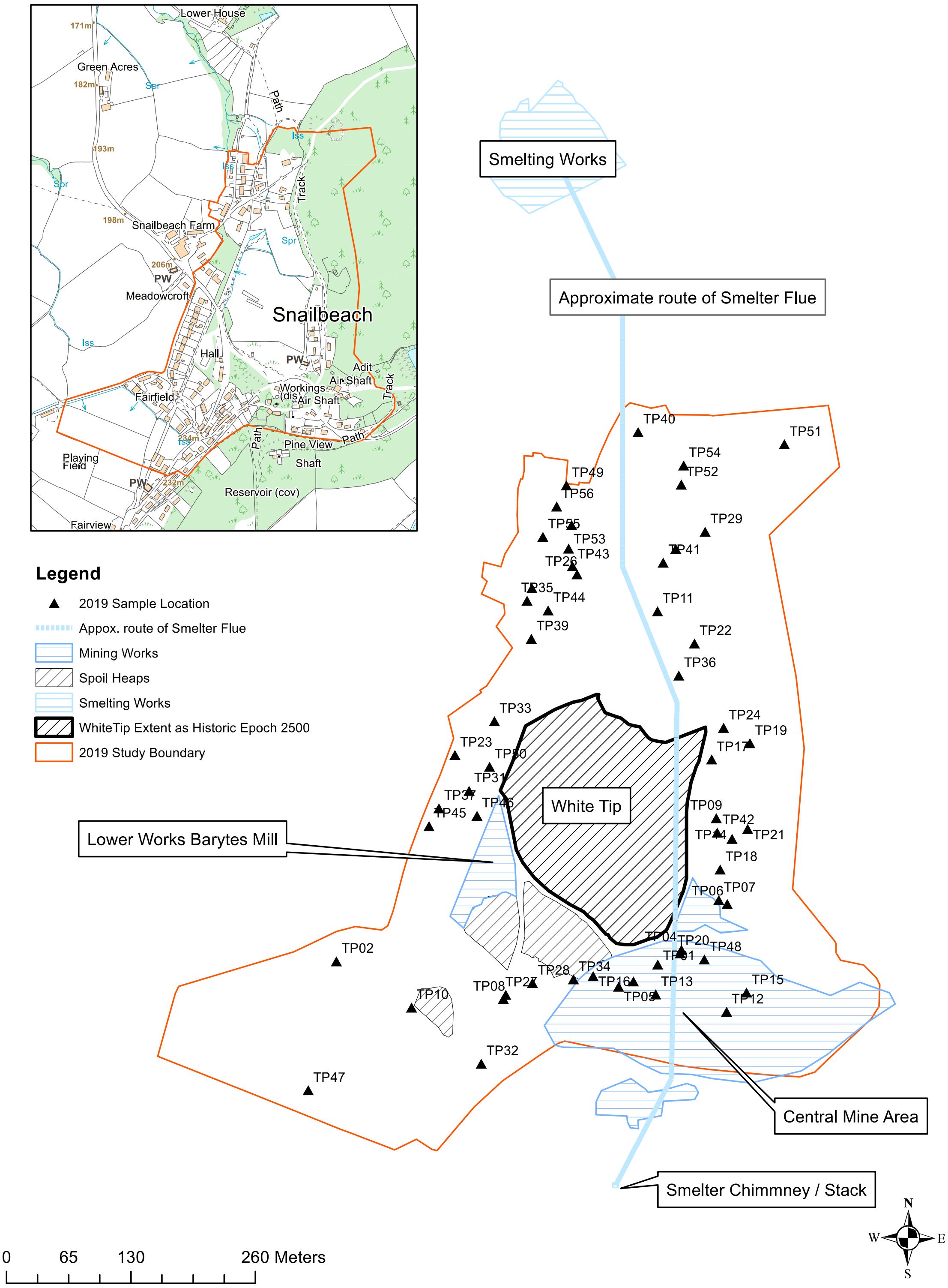

Figure 4-1 Map showing location of 2019 samples

Initial sampling locations were allocated on a stratified approach, taking account of current and historic land-use; distance and orientation from the White Tip; historic sampling locations and data; and landowner permissions. 48 sample sites were initially selected, based on the historic data available at each location. The principle of using judgment is outlined in Swyngedouw, C. in De Vivo et al. (2018) who states *'judgemental sampling is… routinely used when sufficient knowledge of the site history and activities is available'.* Judgment was exercised in the field to collect further samples where practical complications arose such as; blocked access, weather constraints, safety, new buildings etc. Permission was sought for each location by prior written or verbal arrangement with the landowner.

Ultimately 56 samples were collected, the locations of these are displayed in Figure *4-1* and are labelled as per the sample identification reference.

As discussed above, given the revised aims of the project (Table *1-1*) the limitations set by the initial sampling strategy are considered and acknowledged when assessing and drawing conclusions from the data.

Samples were taken from topsoil to a depth of 5cm at all locations and were formed of 5 consolidated subsamples across $0.5m^2$, referred to as the primary sample. Within residential properties, all efforts were made to sample 'undisturbed' land – by means of discussion with the landowner.

Approximately 0.6kg of material (conditions permitting) was collected by stainless steel trowel to clear 100mm x 140mm polythene bags. Samples were labelled by an affixed sticky-label, and by handwritten sample code in permanent marker for confirmation if labels became detached. Samples were transported to a clean cool box with freezer packs and were transferred to a refrigerator at the end of each sampling day, prior to all samples collectively being transported to the laboratory.

Sampling locations were recorded by Global Positioning System Co-ordinates (GPS) and by line-measurement to nearby identifiable features and fixtures. Photographs of each location and context were also taken on a mobile device and logged by sample location. Land-use categories were assigned based on spatial data within the ESRI ArcMap 10.4 of the ArcGIS package and verified by visual confirmation in the field.

4.3 Laboratory Work

4.3.1 Sample preparation

Primary samples were unpacked, mixed, and disaggregated by hand prior to sub-sampling. Primary samples were kept refrigerated during the lab-work period for reference in case further material was required. Primary samples were sub-sampled for approximately 100g of material to 100 x 140mm Clear Polythene bags for working material. Sub-samples were then freeze-dried prior to further analysis.

pH

Each consolidated soil was sub-sampled for analysis by a standard colorimetric field pH test.

Inductively coupled plasma mass-spectrometry (ICP-MS) preparation - Aqua-Regia Digests

Aqua regia extraction prior to ICP-MS was undertaken in the School of Geography laboratories, University of Nottingham. Aqua regia digests were prepared to the following School of Biosciences procedure (Young, 2019):

1. 1g sample weighed and transferred into a 250ml conical flask (Weights were recorded to three significant figures).
2. Within a working fume hood, 5 mL concentrated nitric acid (c. 70%) and 15 mL concentrated HCl was added to each flask.
3. Flasks were agitated slightly to wet the soil with careful attention to avoid particles migrating up the side of the flask.
4. The flasks were monitored to ensure any initial reactions to subsided (e.g. CaCO3 dissolution)
5. Flasks were then heated on the hotplate until the acid was boiling and/or emitting red fumes. Boiling was progressed until the acid volume fell to 5mL.
6. Flasks were left to cool, whereupon 20 mL deionised water was added and mixed
7. The solution was filtered through general-purpose (5 to 13 µm) filter paper into a 100 mL glass volumetric flask and progressively rinsed the flask with deionised water to quantitatively transfer all the contents to the filter paper/funnel. Care was taken to ensure the total solution volume did not exceed 100mL. Any rinsed solutions with a volume below the delineated 100mL mark were made-up with deionised water.
8. A final 1-in-100 dilution with 2% Nitric acid (e.g. Primar grade) was undertaken prior to submission to Sutton Bonnington laboratories for analysis by ICP-MS.

4.3.2 Laboratory Analysis

X-Ray Fluorescent Spectrometer (XRF) Analysis

XRF is a typical analysis to indicate the concentration of elements relative to the sample analysed. XRF requires minimal sample preparation, and does not degrade the sample, consequently it is often cheap and easily replicable, and therefore a favourable means to indicate and contamination at regional and site level.

Energy dispersive XRF differs from typical XRF analysis in that a crystal is not utilised to disperse the secondary X-Ray Beam into a spectrum. This also forms a major benefit, in that the entire primary X-Ray spectrum is measured simultaneously, this allows samples of greater thickness to be analysed, without the additional need for collimation of the X-ray beam (Fitton, 1997).

XRF Analysis was undertaken on freeze-dried sub-samples at the School of Geography laboratories, University of Nottingham using a Panalytical Epsilon3 XL Energy-Dispersive X-Ray Fluorescent Spectrometer (ED-XRF).
Samples were prepared according to the following method:

1. Sample loosely ground with an agate pestle and mortar.
2. 10g of sample in a 27ml diameter sample pot with 4.0um thickness Prolene Thin-Film.
3. The selected elements were measured using the Omnium preset calibration

Inductively Coupled Plasma-Mass-Spectrometry (ICP-MS) Analysis

Inductively coupled plasma mass spectrometry is one of the most commonly used analytical methods for determining elemental concentrations (Albanese et al., 2018). Key advantages of ICP-MS include the degree of accuracy that can be achieved, even from very minimal sample material. Analysis can be performed for multiple elements, though some matrices require chemical dissolution (Jarvis, 1998). ICP-MS equipment requires a significant capital outlay and consequently analyses can be expensive to perform, constraining the number of samples that can be analysed (Jarvis, 1998).

ICP-MS was undertaken by staff in the School of Biosciences, University of Nottingham. It was not possible to attend the measurements due to the coronavirus restrictions.

Spatial Analysis by Geospatial Information Systems (GIS).

All GIS work was undertaken utilising ESRI ArcMap 10.4 of the ArcGIS package. Data from 1988 study, current analytical data, and date from field measurements was consolidated within a geodatabase and subsequent data layers to allow visual and analytical assessment of distributional trends.

4.4 Quality Control

Certified reference material was sourced from the British Geological Survey for use within the UBM analysis as originally intended (see above). BGS102 was used within the total (XRF) and extractable (ICP-MS) concentration analyses as an independent control.

XRF analysis was undertaken on a subset of the freeze-dried and ground samples to facilitate direct comparison between XRF (<250µm) and ICP-MS (<250µm) data and provide an indication of the analytical variance.

Were the previously-discussed coronavirus constraints not in-effect, it would have been preferable to undertake ICP-MS (extractable) analysis on the whole soil-fraction equivalent samples of this subset. This would have allowed greater interrogation of the greater XRF (whole) fraction dataset, and comparison of differences by soil-fraction.

4.5 Data Analysis

The revised project objectives required the consideration and analysis of previous external datasets and primary data collected during this study. Site-specific data from previous investigations within the study area, notably from the Wardell Armstrong (1988a) study, was provided as typed data (original report); Microsoft Excel Spreadsheet (Excel); and as an ArcMap data layer with attached metadata. This data was reviewed and validated prior to introduction to this project's geodatabase. Whilst validating this data (Armstrong, 1988), a number of conflicting datapoints were identified between the typed report, and the spreadsheet. Where conflicts arose, the typed data of the original report was treated as the correct values. Consequently, new GIS Data layers were generated from the validated dataset. The Wardell Armstrong (1988) data is presented in Appendix 2 Wardell Armstrong (1988) topsoil data.

Data relating to other mine sites and relevant studies was collected from peer-reviewed and published journals and papers, and from approved governmental agency reports and guidance.

4.5.1 Primary Data

Primary data collected within the study was collated within Excel and subjected to statistical analysis. Concentration data was analysed where appropriate to allow comparison to recognised environmental standards, national background concentrations and theoretical and modelled acceptable concentrations

4.5.2 Statistical Analysis

Statistical analysis was undertaken using Excel and the IBM SPSS statistics package.

5 Results

Data presented in this section is primary data collected from this study and is hereafter termed the ‘2019 study’.

5.1 Total lead concentrations

5.1.1 Total lead – whole sample fraction.

The concentration data indicates that significantly elevated Pb concentrations exist across the study area (Figure *5-1*).

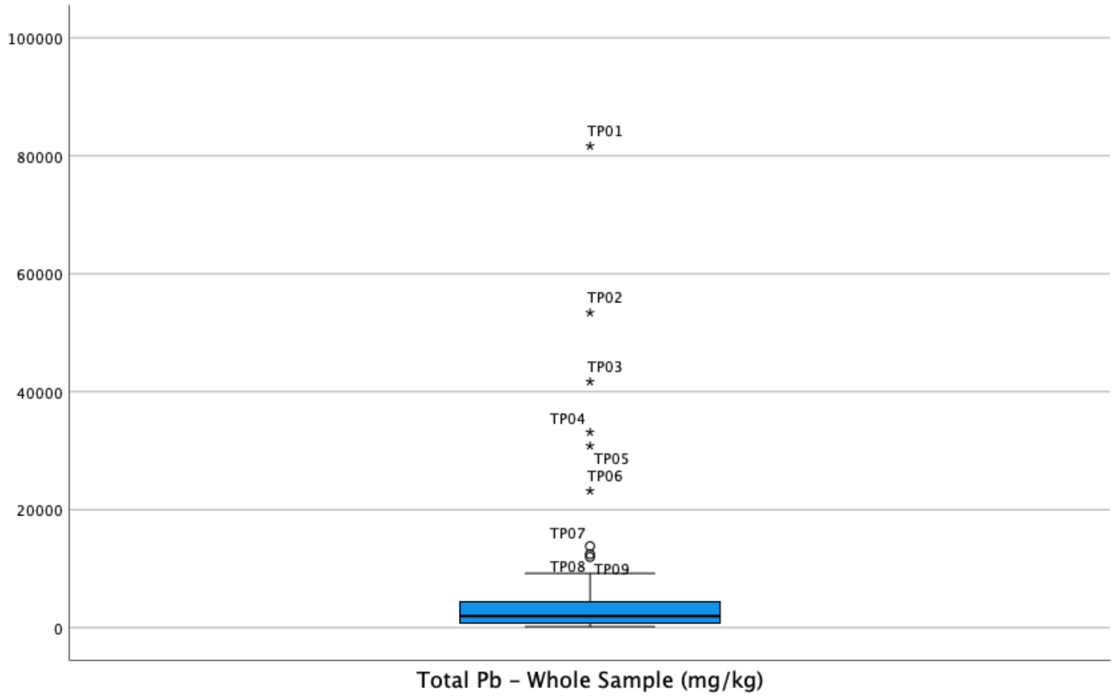

Figure 5-1 Boxplot of Total Pb Concentrations (mg/kg) of whole sample.

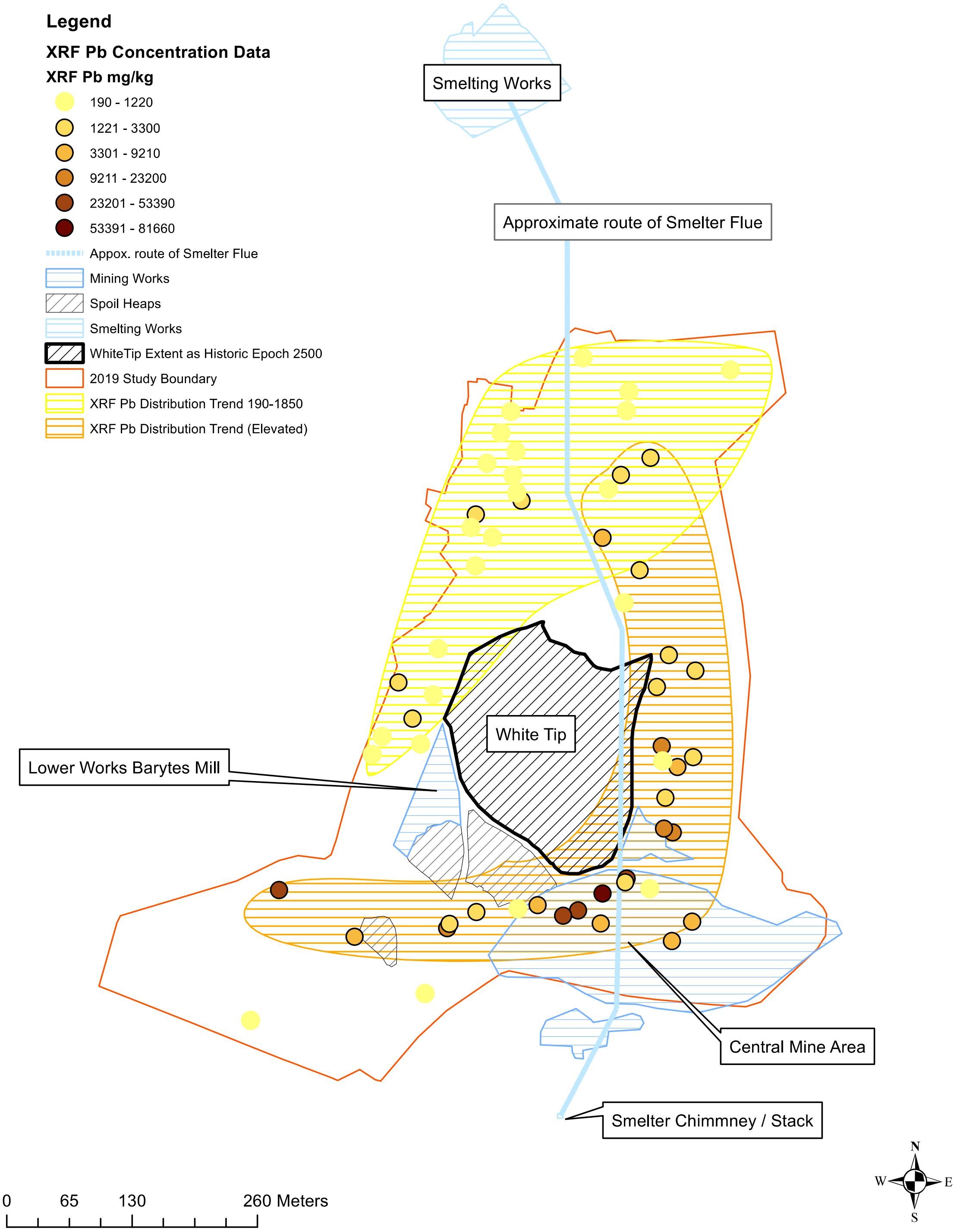

Figure 5-2 Map of total XRF Pb (Whole Fraction) concentrations across the study area.

Total concentrations within the whole soil fraction differ between the north-west and south-east aspects of the ‘White Tip’ (*Figure 5-2*) A visual trend of significantly elevated concentration can be identified, distributed in an arc from the north-east to south-west of the White Tip. This trend has been marked in orange as ‘XRF Pb Distribution Trend (Elevated)’. The most significantly elevated correlations appear to be mostly grouped within ‘Central Mine Area’ indicated by the horizontal blue hatching.

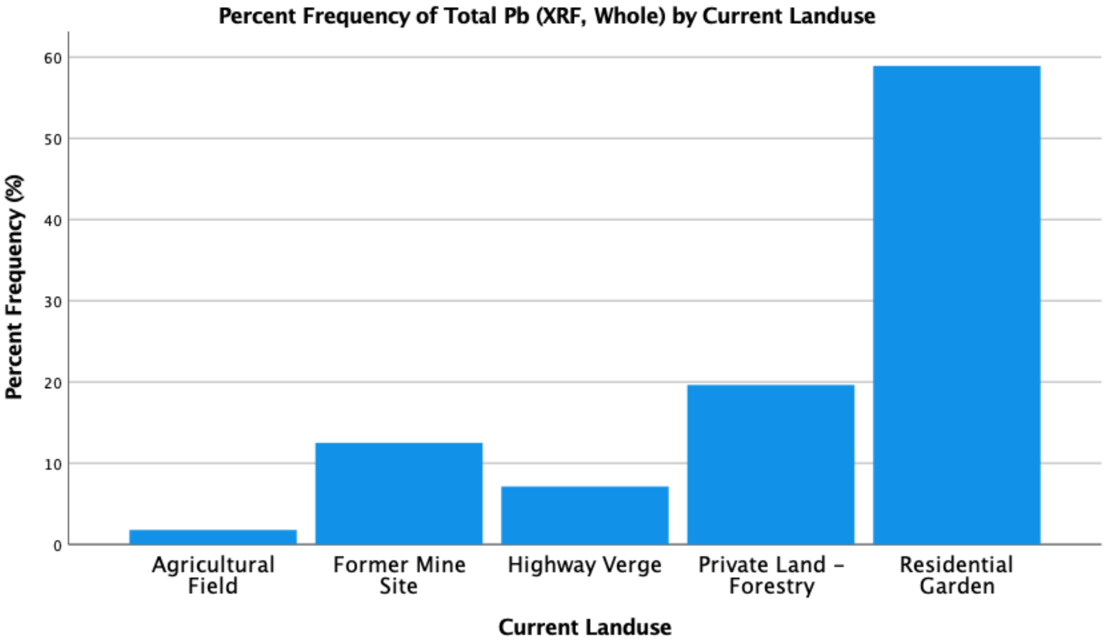

Figure 5-3 Frequency sample distribution (as % of XRF Pb (Whole) samples, n = 56) by current landuse category.

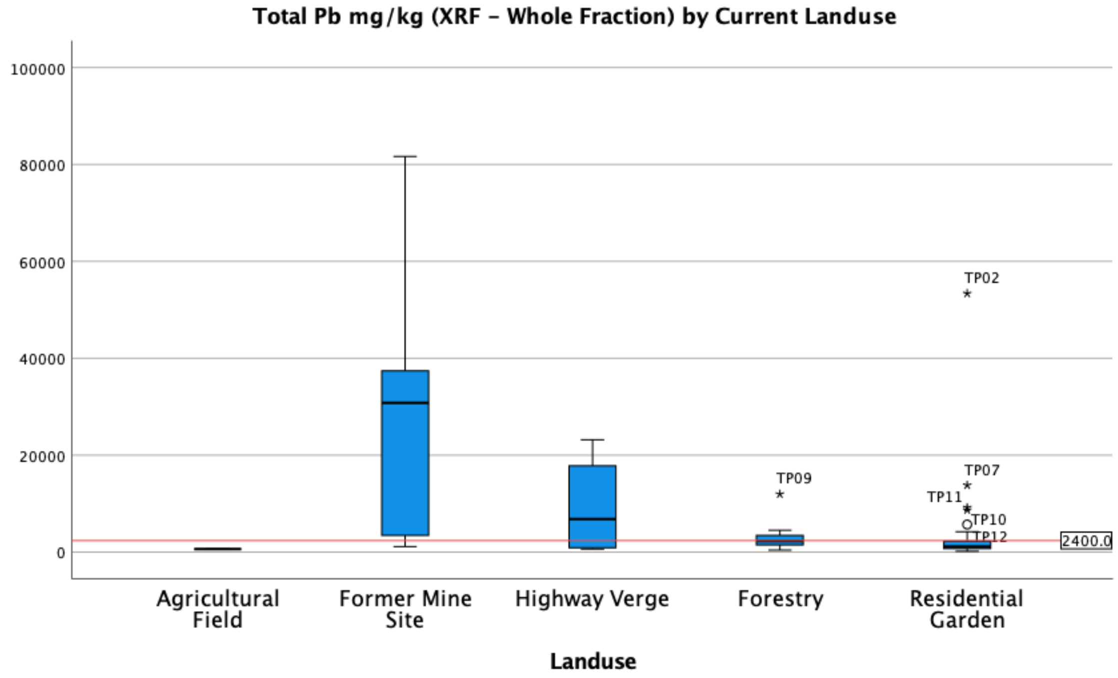

Figure 5-4 Boxplot of Total Pb (mg kg^{-1}) for whole soil fraction by current landuse type. Values shown against Normal Background Concentration for Mineralisation domain (2400 mg kg^{-1}) as per Johnson et al. (2012).

Figure *5-3* shows the number of Pb (XRF, Whole) samples within each current landuse type. When the Total Pb (XRF, Whole) concentrations are plotted by their current landuse (Figure *5-4*), it is clear that elevated concentrations fall within the ‘Former Mine Site use. Whilst only 12.5% of Total Pb (XRF, Whole) samples were within the Former Mine Site category (Figure *5-3*), the median (30,830 mg kg^{-1}) is substantially elevated in comparison to all other categories. This indicates that the population of data values with the Former Mine use, are independent from the surrounding population (across other landuse categories. It is arguable that this is to be expected given the known high volumes of mine waste across the Central Mine Area – which were not directly addressed within the 1995 remediation scheme (Wardell Armstrong, 1995) – which sought to reduce the *active* dispersal of contaminants from the mine site.

It is further notable that Figure *5-4* identifies several extreme and outlier values within the current Residential Garden categories. 60% of XRF Pb (Whole) samples were within the Residential Gardens, allowing a greater spatial resolution to the data. Considering the overall range of the Total XRF (Whole) Pb dataset, and the previously acknowledged spread of contamination beyond the boundary of direct mine workings, it is deemed reasonable to explore whether extremes and outlier values could be indicative of elevated hotspots of contamination, rather than outliers of analytical error. The range, 53200 mg kg^{-1}, within the residential garden use, is 26 times greater than the IQR, 2040 mg kg^{-1}, demonstrating the great range and variance of results, even when considering the ‘current residential garden’ use in isolation.

5.1.2 Total lead concentration within <250µm sample fraction.

When pandemic conditions permitted, a small subset of samples were sent for XRF analysis of the <250µm fraction to allow comparison of XRF concentrations between the whole and <250µm fraction. Table *5-1* shows these data alongside the corresponding sample analyses undertaken in the other analytical runs/methods. The sample subset was selected on a semi-stratified basis in order to represent the distribution of the overall datasets, and the geographic spread around the White Tip. The size of the sub-set was limited due to COVID-19 limitations, resource availability and time constraints of access to laboratory.

Table 5-1 Descriptive summary of samples with corresponding Total Pb (Whole), Total Pb (<250µm) and Extractable Pb (<250µm) analysis

Sample ID	Total Pb (mg kg^{-1}) (Whole)	Total Pb (mg kg^{-1}) (<250µm)	Total Pb <250µm as % of Total Pb Whole	Extractable Pb C (mg kg^{-1}) (<250 µm)	Extractable Pb <250 as % of Total Pb <250µm	pH	Landuse
TP01	81660	131050	160%	25520.3	19%	8	Former Mine Site
TP02	53390	60560	113%	8961.6	15%	8	Residential Garden
TP10	9210	24820	269%	6973.2	28%	7.5	Residential Garden
TP11	8700	16040	184%	4064.1	25%	5	Residential Garden
TP21	2360	17370	736%		0%	7.5	Private Land - Forestry
TP25	2150	6160	287%		0%	7	Residential Garden
TP32	1220	5090	417%	2392.9	47%	6	Highway Verge
TP46	660	3080	467%	917.3	30%	7	Residential Garden
Mean	19919	33021	329%	8138	21%	7	
Geomean	5879.1	16426.1	279%	4922.4	#NUM!	6.9	
MAX	81660	131050	736%	25520	47%		
MIN	660	3080	113%	917	0%		
Range	81000	127970	623%	24603	47%		
Count	8	8	8	6			
St.Dev	30513.3	43698.3		9010.2			
Q1	1917.5	5892.5		2810.7			
Q3	20255	33755		8464.5			
IQR	18337.5	27862.5		5653.8			

Table *5-1* displays samples for which Total Pb (whole fraction), Total Pb (<250µm) and Extractable Pb (<250µm) fraction analyses were performed. Although a small dataset, exploration of the dataset allows comparison of the analytical methods used and comparison of Total Pb and Extractable Pb concentrations within the <250µm fraction against Total Pb values of the whole soil fraction of the same sample. Of the eight corresponding Total sample pairs, five were sited in current residential garden use, with one out of the three remaining samples situated on 'Former Mine Site', 'Private Land – Forestry' and 'Highway Verge' respectively.

A geometric mean of the Total Pb (<250µm) as % Total Pb (Whole) indicates that Pb concentrations within the <250µm screened Total analyses were 279% greater than those of the whole sample. This indicates that of the Total Pb within the whole sample, the majority is situated within the <250µm fraction of the soil. This is relevant when considering the objectives of the study, as it could indicate the typical presence of Pb in a fine (<250µm) form, across all current residential gardens.

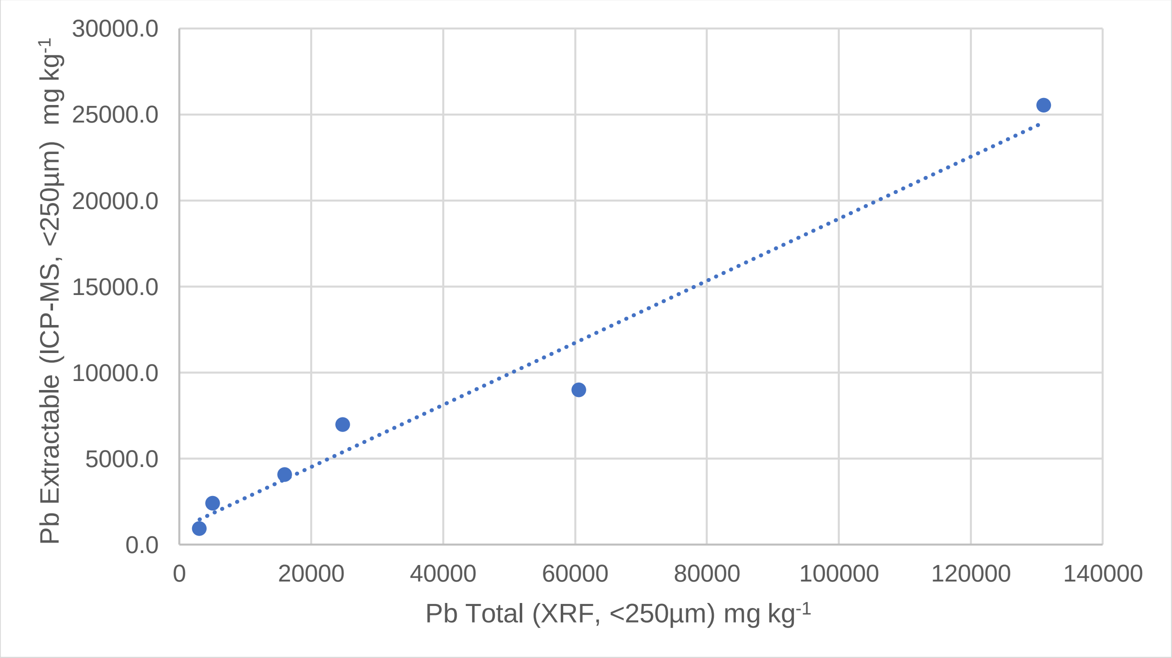

Figure 5-5 Crossplot of corresponding samples analysed for Pb Total (<250µm) and Pb Extractable (<250µm) concentrations (mg kg^{-1}) (n=6) y = 0.1803x + 905.1 R² = 0.9695

Figure 5-5 plots the corresponding values of both analytical methods performed on the <250µm fraction. It can be seen that there is a close linear relationship between the datasets, with a high R^2 value of 0.97. Whilst this indicative of a close relationship, this must be interpreted with caution given the low-number of sample points incorporated. It is further noted there is not a direct 1:1 relationship, and conversion would be required if comparing values statistically.

5.2 Extractable lead concentrations (ICP-MS) within the <250µm sample fraction.

Figure *5-6* demonstrates the distribution of Extractable Pb concentrations. The extractable (<250 µm) concentration data shows large variability in results – in agreement with the Total Pb datasets. Extremes and outliers lie significantly beyond the interquartile range (IQR), although at lower concentrations than those identified within the Total (Whole sample) analyses.

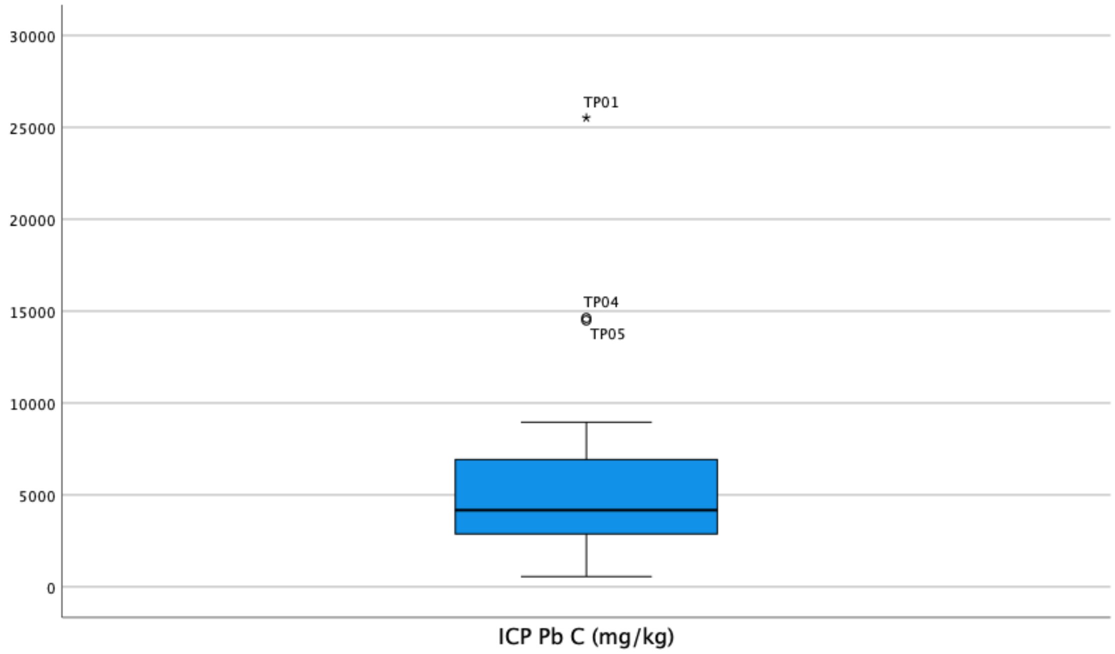

Figure 5-6 Boxplot of Extractable Pb (ICP-MS) concentrations (mg kg^{-1}) within the <250µm fraction.

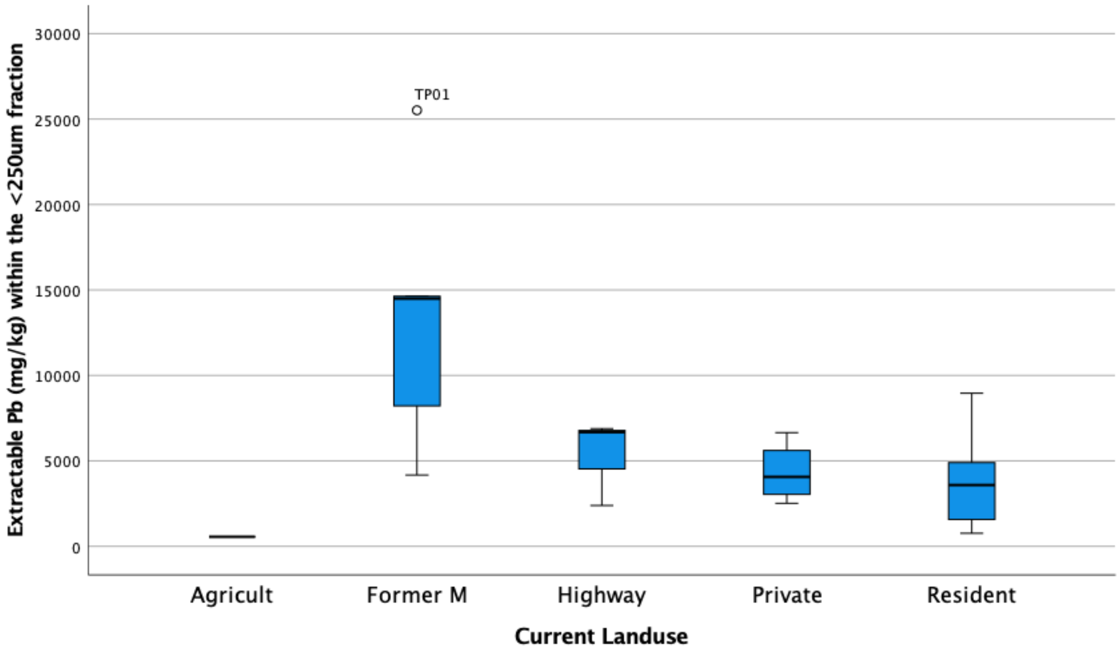

Figure 5-7 Boxplot of Extractable ICP-MS concentrations (mg kg^{-1}) by current landuse type

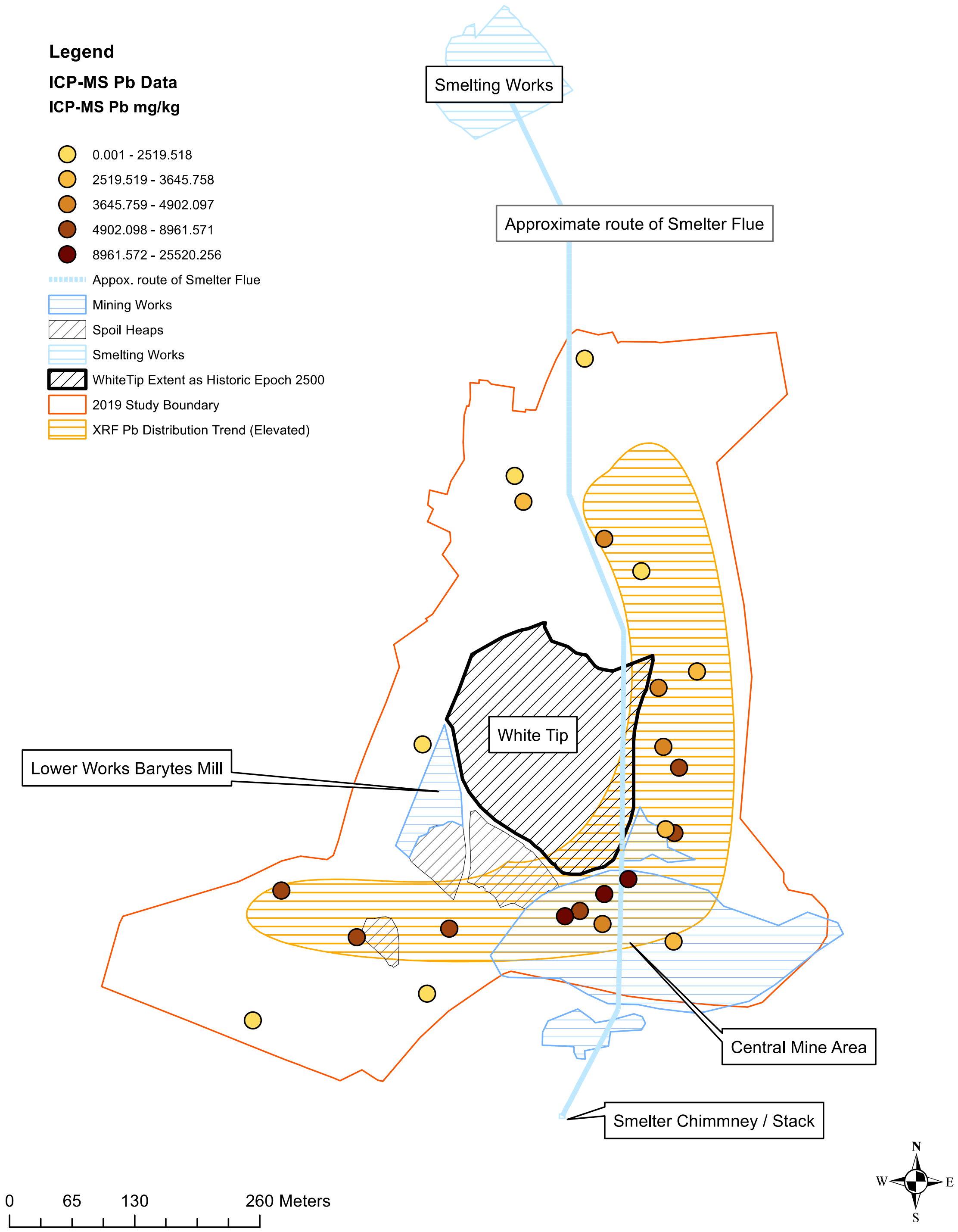

Figure 5-8 Map showing ICP-MS Pb concentrations (mg kg^{-1}) by sample location

Figure *5-8* similarly conveys the spatial distribution of ICP-MS Pb concentrations within the study area. As can be seen, ICP-MS analysis was undertaken at fewer sample points (n=23) than XRF Pb (n=56).

Elevated concentrations visually follow similar spatial distribution to those displayed by XRF Pb (Whole Sample) concentrations - split between the northwest and southeast of the study area. This has been identified by the overlay of the 'XRF Pb Distribution Trend (Elevated)' shapefile. As identified within Figure *5-6* to Figure *5-8*, ICP-MS Pb concentrations are visibly lower, than the XRF Pb concentrations at the same south-eastern locations, within the Central Mine Area. This can be seen in more clarity when comparing the data.

5.3 Comparison of Total (XRF, Whole) with Extractable (ICP-MS, <250µm) data.

Table 5-2 displays the summary statistics of the raw data from the largest datasets by XRF (Whole Fraction) and ICP-MS (<250µm). Maximum extractable concentrations (as determined by ICP-MS Pb) (25520.3 mg kg^{-1}) are elevated but significantly lower than the Total (XRF) Pb (81660 mg kg^{-1}), which was located within the Central Mine Area.

Table 5-2 Summary Statistics of all raw XRF Pb (Whole) and ICP-MS (<250µm) concentration data

	Whole Fraction XRF Pb (mg kg^{-1})	**<250µm Fraction ICP-MS Pb (mg kg^{-1})**
Geomean (GM)	2208.399	4167.425
Mean	7082.143	6063.219
Standard Error	1965.390	1182.124
Median	1965.000	4177.270
Mode	2360.000	#N/A
Standard Deviation	14707.634	5669.268
Sample Variance	216314504.416	32140604.856
Kurtosis	13.242	5.636
Skewness	3.457	2.161
Range	81470.000	24955.573
Minimum	190.000	564.683
Maximum	81660.000	25520.256
Sum	396600.000	139454.040
Count	56	23

'-' indicates non-calculable result

GM = geometric mean

It is clear from Table 5-2 that both Pb XRF (Whole) Pb ICP-MS (<250µm). concentration data has a non-normal statistical distribution. Kurtosis and Skewness outputs that the distribution of both analytical method data is leptokurtic (Kurtosis = >1.0) (XRF Pb Kurtosis: 13.242, ICP Pb Kurtosis: 5.636) and positively (right) skewed (Skewness = >1.0) (XRF Pb Skewness: 3.457, ICP-MS Pb Skewness: 2.161).

Geometric means (GM) have been determined to account for the exponential nature of concentration trends. The geometric mean therefore provides a more-representative ‘average’ of each Pb’s concentration values (XRF Pb GM: 2208.4 mg kg^{-1} n = 56, ICP-MS Pb GM: 4167.4mg kg^{-1} n = 23). Likewise, the minimum ICP-MS Pb value (564.7 mg kg^{-1}) exceeds the minimum XRF Pb Value (190 mg kg^{-1} by a substantial margin.

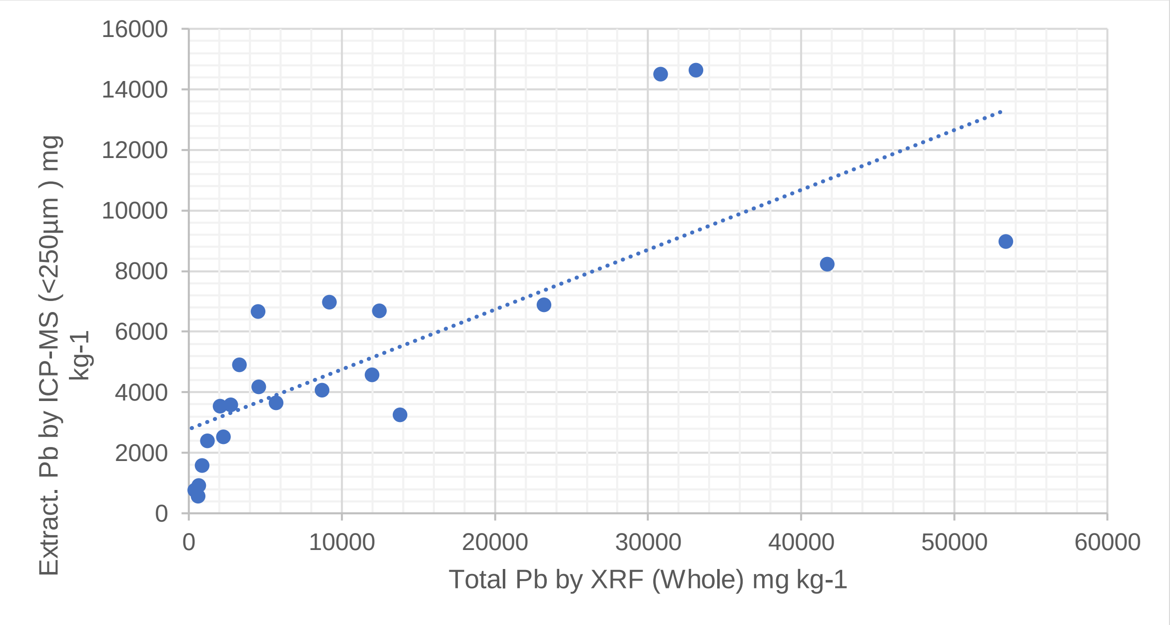

Figure 5-9 Crossplot of Total Pb (XRF, Whole Sample) and Extractable Pb (ICP-MS, <250µm) concentrations (mg kg^{-1}) y = 0.2448x + 2347.2 R² = 0.7886

XRF Pb samples (n=56) were most frequently determined between 2000 mg kg^{-1} and 6000 mg kg^{-1}. In contrast ICP Pb samples (n=23) occurred frequently between 4000 mg kg^{-1} and 7000 mg kg^{-1}. Figure 5-9 plots the distribution of sample concentrations of Total Pb (XRF, Whole) and Extractable Pb (ICP-MS, <250µm) across the concentration scale. It is clear that there is loose linear correlation between the datasets, with a substantial offset. The R^2 value indicates 0.79 of the variance is attributable to the model (Equation: y = 0.2448x + 2347.2) although as acknowledged previously, the judgemental nature of the sampling limits the confidence and statistical significance that can be found in this correlation.

It is notable that at lower concentrations (<5000 mg kg^{-1}) there is a tighter correlation. This is displayed on Figure 5-10, which has a higher R^2 value of 0.85.

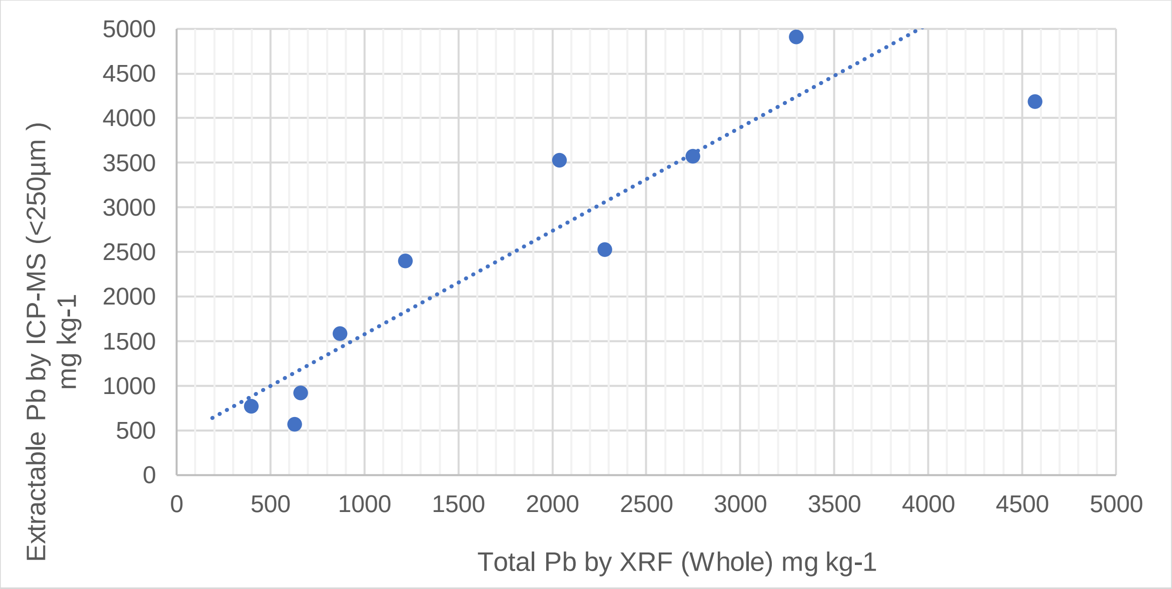

Figure 5-10 Crossplot of Total Pb (XRF, Whole) and Extractable Pb (ICP-MS, <250µm) concentrations to 5000mg kg^{-1}, $y = 1.1581x + 420.45$ $R^2 = 0.8538$

Table 5-3 Descriptive summary values of XRF Pb (Whole) and ICP-MS Pb (<250µm) by current landuse

		Agricultural Field	**Former Mine Site**	**Highway Verge**	**Private Land - Forestry**	**Residential Garden**
Sample Count		1	7	4	11	33
XRF Pb (mg kg^{-1}) (Whole)	Mean	630	27921	9383	3078	3913
	Geomean	**630**	**12340**	**3862**	**2041**	**1528**
	Max.	630	81660	23200	11990	53390
	Min.	630	1160	630	430	190
Sample Count		1	4	3	4	10
ICP-MS Pb (mg kg^{-1}) (<250µm)	Mean	565	13411	5321	4326	3857
	Geomean	**565**	**11322**	**4793**	**4064**	**2991**
	Max.	565	25520	6887	6660	8962
	Min.	565	4177	2393	2520	764

Table *5-3* details the geometric mean, arithmetic mean, maximum and minimum of Pb as determined by XRF and ICP-MS. The values are categorised by the current landuse of the sample location for closer interrogation. The arithmetic mean value for the 7 samples undertaken on Former Mine site by XRF for Pb is 27921 mg kg^{-1} but only half that when calculated by geometric mean (12340 mg kg^{-1}) demonstrating the exponential variability of XRF Pb concentrations on this land form.

5.4 Background concentration of Study Area.

Background values within topsoil were calculated for the study area based on the XRF Pb total concentrations. The upper 95% confidence limit of the 95th percentile was used to derive the background value.

To generate a localised ‘background’ value for the study area, it was decided to exclude outlier results on the basis of subjective assessment and consideration of the individual merits of each sample and sample location. Given the complexities of soil heterogeneity; evolving land-use in the area; and the varied potential dispersion sources within the locality, it was decided to exclude sample points which directly overlayed former mining works and related infrastructure where direct point-source contamination could be reasonably suspected. The methodology for determining a background possible was adapted from ISO 19258:2018 (British Standards Institution, 2018). Statistical outliers were identified within the concentration datasets via box-plot analysis.

Background values varied dependent upon the available data; criteria applied to determine outliers; and the judgment of other relevant characteristics (i.e. sample location, proximity to point sources) applied to accept of remove outliers and extremes from the dataset. Two different background values are presented below.

5.4.1 Background Value - Pb XRF (Whole) data

Background concentration Option 1 was calculated on the XRF Pb concentration dataset, excluding samples within the ‘Central Mine area’ as identified in Table 5-5(A). These values (Table 5-5, (A) Central Mine) were excluded, on the knowledge that the core features of the mine remain unaltered today. Furthermore, they are likely to have been unduly influenced by the direct core functions of the mine, such as the processing of ore within the dressing floor and crushing house. It is therefore argued that they are not representative of the ‘background’ area within the study area.

The remaining dataset was then represented on a boxplot (Figure 5-11) to identify remaining outlier values. These outliers (Table 5-5 (B) Statistical Outliers / Judgemental Approach) were further excluded following close examination of relevant factors that including sample location, proximity to former mining works infrastructure and the likelihood that the result was a hotspot of contamination.

Descriptive statistics were calculated on the remaining dataset to calculate the Upper 95% Confidence interval of the 95th percentile and determine a background value of 3563 mg kg^{-1} (Table *5-4*, value in bold).

Option 1 results infers the background concentration of the study area to range from (190 mg kg^{-1} to 4540 mg^{-1}) of with a calculable background value of 3563 mg kg^{-1}.

Table 5-4 Descriptive Statistics of 'Background Concentration – Pb XRF (Whole)

	XRF Pb (mg kg^{-1})
Mean	1405
Standard Error	157
Median	1120
Mode	#N/A
Standard Deviation	979
Sample Variance	958662
Kurtosis	1
Skewness	1
Range	4350
Minimum	190
Maximum	4540
Sum	54800
Count	39
Confidence Level(95.0%)	317
95th Percentile	3246
90th Percentile	2438
75th Percentile	2025
50th Percentile	1120
25th Percentile	680
10th Percentile	424
95th Percentile	
Upper CI (95%)	**3563**
Lower CI (95%)	2929

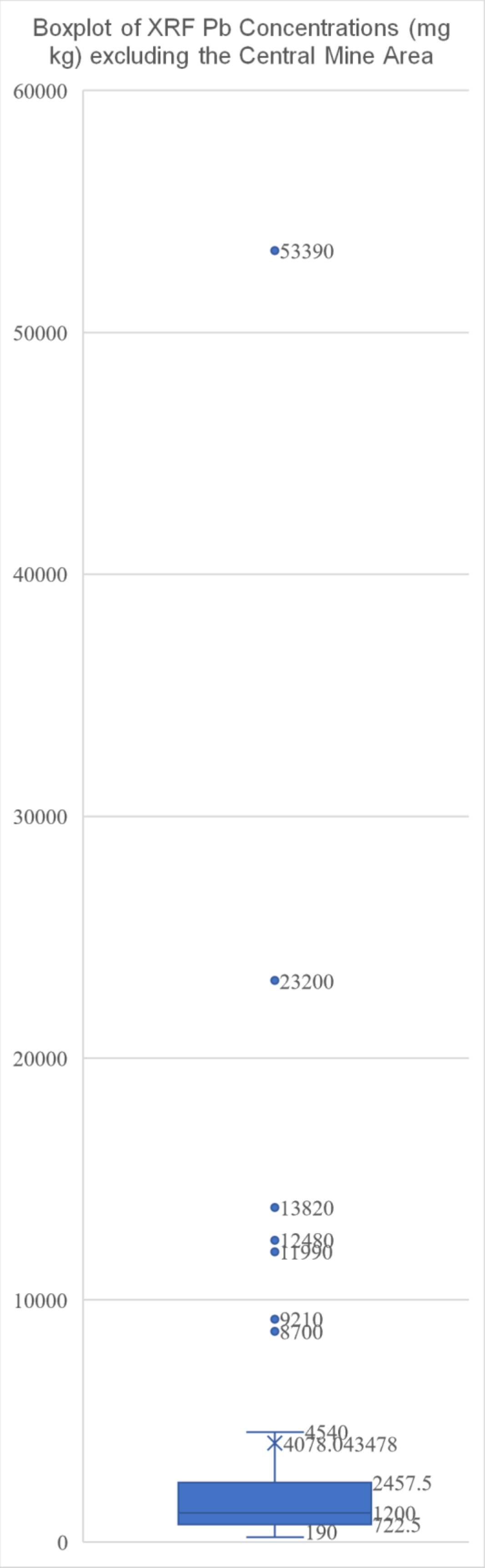

Figure 5-11 Boxplot of XRF Values without excluded values as per 'Background Value – Pb XRF (Whole)

Table 5-5 Table of excluded values for ‘Background Value - Pb XRF (Whole)

(A) Central Mine Area	
TP01	81660
TP03	41720
TP04	33150
TP05	30830
TP12	5710
TP13	4750
TP15	4230
TP16	4150
TP20	2360
TP48	630

(B) Statistical Outliers / Judgmental Approach	
TP02	53390
TP06	23200
TP07	13820
TP08	12480
TP09	11990
TP10	9210
TP11	8700

5.4.2 Background Value – Pb ICP-MS (<250µm) data

Extractable Pb (ICP-MS, <250µm) data was analysed via the same methodology as above - removal of sample points within the Central Mine Area and then removal of statistical and judgmental outliers.

There are insufficient samples (<30) within the Pb ICP-MS (<250µm) data to derive a true background concentration, with the upper confidence level of the 95th percentile exceeding the maximum value.

The upper confidence level (US95) of the mean of the data, minus the Central Mine area, and both judgemental and statistical outliers is 5133 mg kg^{-1}. The boxplot and summary tables for this data are presented in Appendix 4 Tables and Boxplot for Background Value - Pb (ICP-MS, <250µm) data.

5.5 Soil description and landuse

The distribution of sampled soil types within in each landuse category is detailed in Table 5-6. 48% of residential gardens contained soils classified as 'silty clay loam', with 'sandy loam' and 'sandy clay loam' classes jointly identified as next most populous in gardens. Soils sampled on 'former mine site' land were predominantly 'loamy sand' or 'sandy clay loam'.

Several clusters of adjacent-corresponding soil types can be see identified within Figure *5-12*.There is a cluster of 'silty clay loam' categorised samples at the northern extent of the site. Likewise, at the southern extent, the linear sampling pattern (unintentional) details a tight spectrum of the 'sandy clay loam' to 'Sandy Loam' aspect of the scale. It is arguable that this may correlate to granular waste spoil associated with the dressing floor and spoil, which would exhibit as sand-sized particles (coarse processed material). This is further supported by samples located on the former 'Dressing floor' which are consistently determined as 'loamy sand' despite minimal topsoil evident in this area.

Table 5-6 Soil descriptions by landuse category

	Agricultural Field		Former Mine Site		Highway Verge		Private Land - Forestry		Residential Garden	
Sample Soil Description	**Number of Samples**	**Percentage of Soil Description**	**Number of Samples**	**Percentage of Soil Description**	**Number of Samples**	**Percentage of Soil Description**	**Number of Samples**	**Percentage of Soil Description**	**Number of Samples**	**Percentage of Soil Description**
CLAY		0.00%		0.00%		0.00%		0.00%	1	3.03%
CLAY LOAM		0.00%		0.00%		0.00%	1	9.09%	3	9.09%
LOAMY SAND		0.00%	2	28.57%	2	50.00%		0.00%	1	3.03%
SAND		0.00%	1	14.29%		0.00%		0.00%		0.00%
SANDY CLAY		0.00%		0.00%		0.00%		0.00%	1	3.03%
SANDY CLAY LOAM		0.00%	2	28.57%		0.00%	3	27.27%	4	12.12%
SANDY LOAM		0.00%	1	14.29%		0.00%		0.00%	4	12.12%
SILT-LOAM		0.00%		0.00%	1	25.00%	1	9.09%	1	3.03%
SILTY CLAY		0.00%		0.00%		0.00%		0.00%	2	6.06%
SILTY CLAY LOAM	1	100.00%	1	14.29%	1	25.00%	6	54.55%	16	48.48%
Total	1		7		4		11		33	

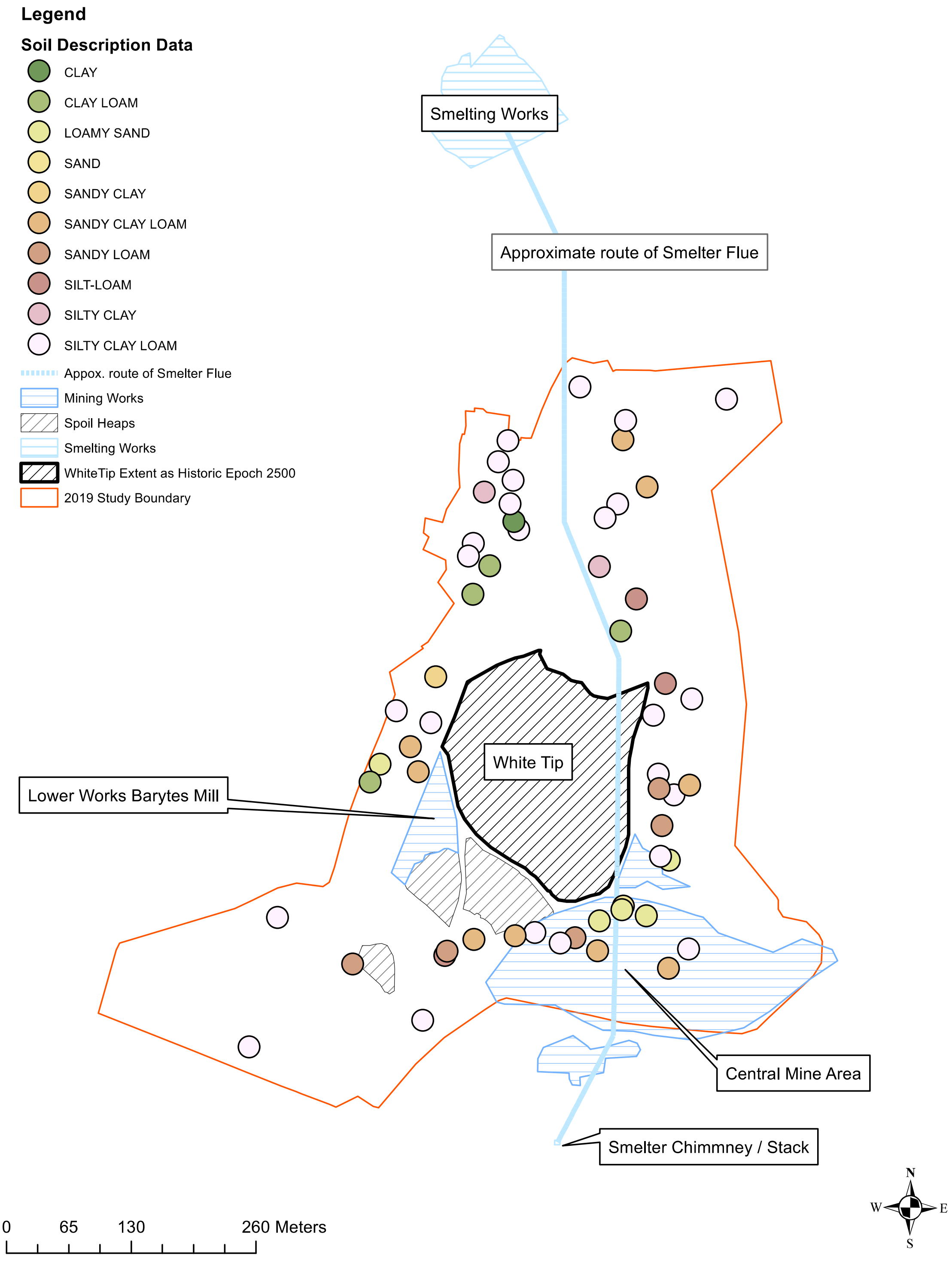

Figure 5-12 Map showing spatial distribution of soil description data

5.6 pH

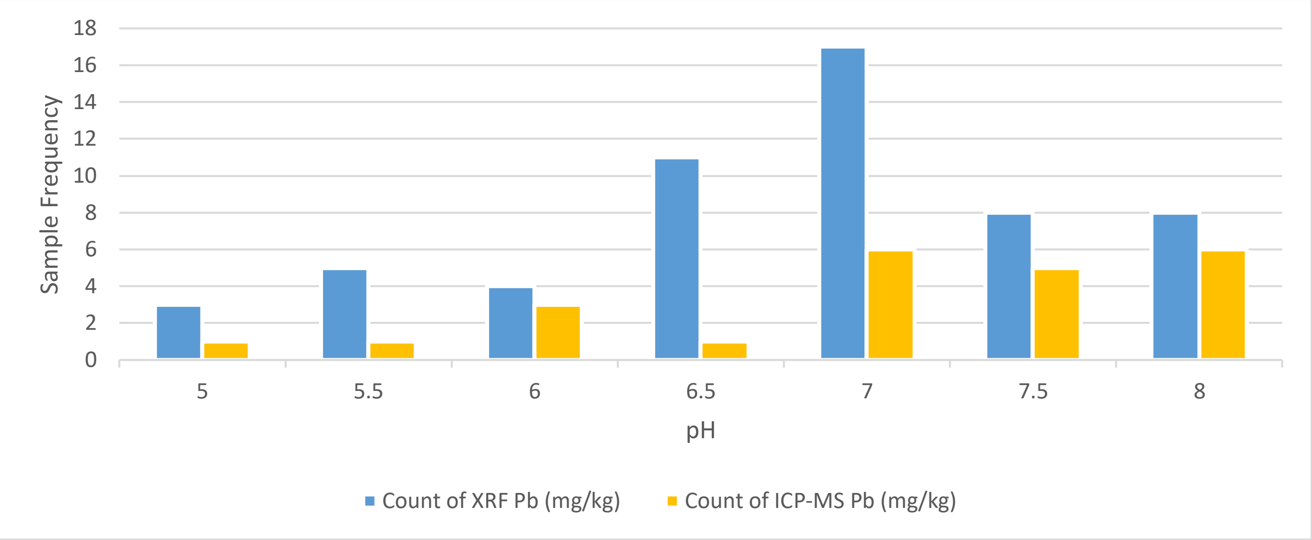

Figure 5-13 Chart of XRF Pb and ICP-MS Pb frequency by pH. Samples undertaken by XRF analysis (Total = 56). ICP-MS analysis undertaken on 23 samples.

31% of all samples were neutral, with mildly acidic soils (20%) and mildly alkaline soil (14%) as the next most frequently-occurring. Figure 5-13 displays the frequency of samples across the pH scale, the frequency of samples by each Pb analytical method are displayed separately. Of the sampled soils analysed by XRF (Total: 56) were Neutral (pH 7, 17), with 16 samples at values greater than pH 7 (pH 7.5 n= 8, pH 8 n=8). In contrast, of the 23 samples analysed by ICP-MS, 11 were determined as alkaline (pH 7.5 n=5, pH 8 n=6).

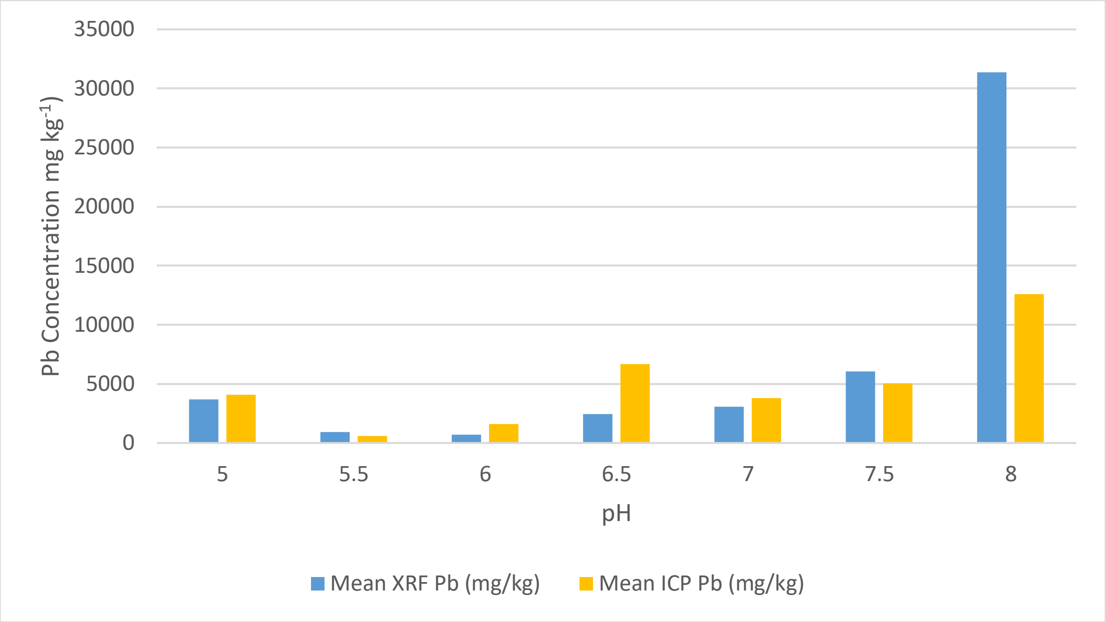

Figure 5-14 Mean XRF Pb and mean ICP-MS Pb Concentrations (mg kg^{-1}) by pH

The mean concentrations of each Pb analytical method (as identified against pH scale intervals) are displayed above in Figure 5-14. It is notable that mean Pb concentrations as determined by XRF are significantly elevated. Of the 8 XRF Pb samples in strong alkaline soils (pH 8), the arithmetic mean concentration is 31358 mg kg^{-1}. In context, 6 samples were undertaken in pH 8 soils by ICP-MS compiling an arithmetic mean of 12580 mg kg^{-1}. Acknowledging that ICP-MS analysis was undertaken on the <250µm soil fraction (See Methodology) The results indicate that elevated concentrations as determined by both methods were significantly elevated in alkaline soils/material.

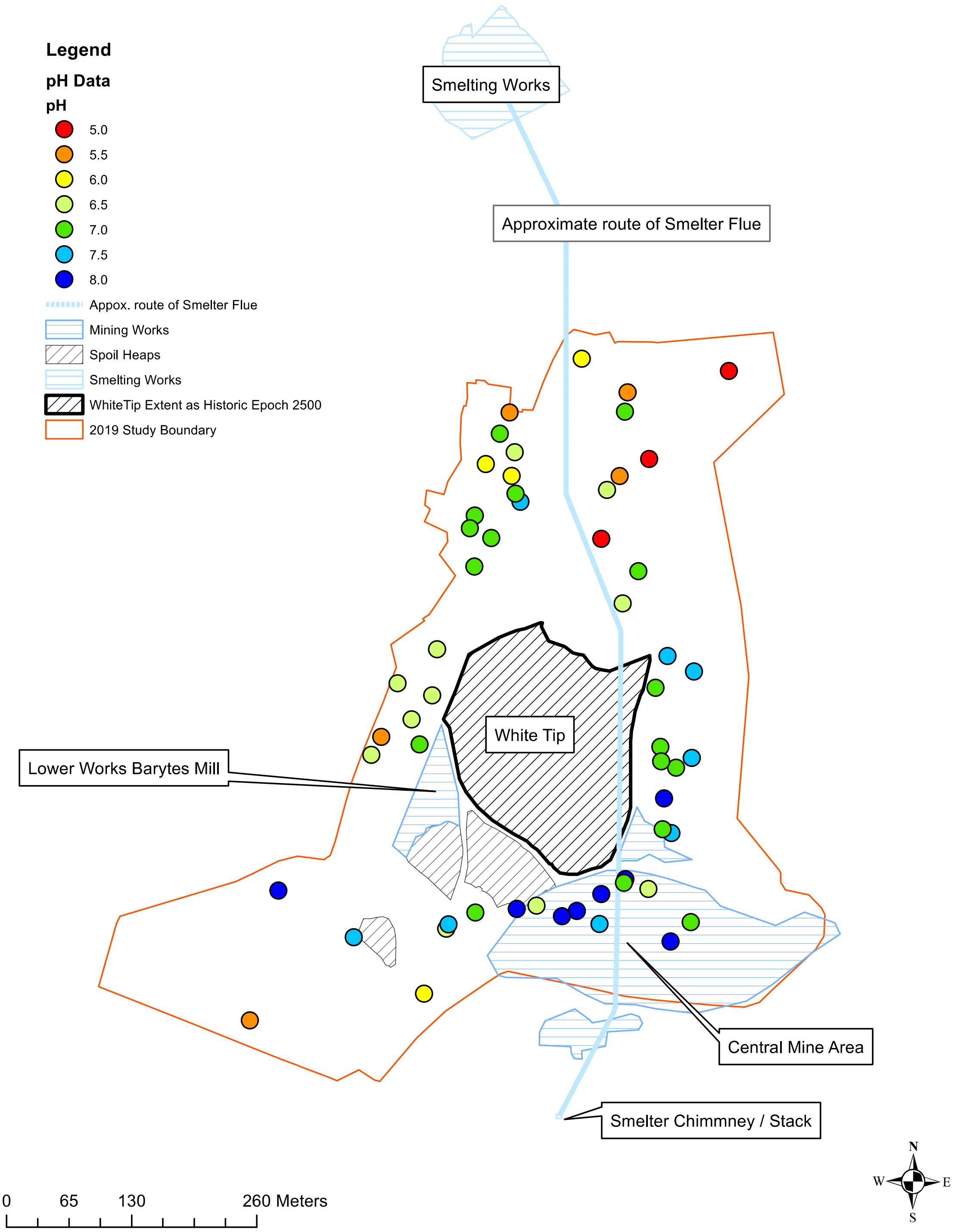

Figure 5-15 Map showing spatial distribution of pH levels across the study area

Most alkali (> pH 7.5) soils follow the same SE trend as identified by Figure *5-2* and Figure *5-8*. Most residential gardens appear to be neutral (pH 7) or mildly-weighted acidic or alkali (i.e. pH 6.5 or pH 7.5).

5.7 Additional data

Additional data was collected during the course of the research. The full primary dataset is disclosed in Appendix 1 All 2019 Data and includes field estimations of organic matter content, stones (by prominent size) as well as location co-ordinates.

5.8 Quality control

As part of the original study design, a Certified Reference Material (CRM) was included in the analyses to act as a control to reference the data.

Table 5-7 Table of Certificate of Analysis Mean Values and 2019 Measured Values

	BGS102 C.O.A	**St. Dev**	**2019 XRF**
	mg kg-^{1}		mg kg-^{1}
Mn	7330	± 49	9710
As	104	± 1	0
Cd	0.275	± 49	0
Co	40	± 1.1	690
Cr	225	± 3	320
Cu	26	± 1.5	50
Ni	80	± 1.1	120
Pb	79.4	± 1.4	500
V	356	± 3	450
Zn	191	± 2	280

Table *5-7* shows the CRM guidance concentrations as stated in the Certificate of Analysis (COA)(British Geological Survey, 2009) expressed as an arithmetic mean, compared with the corresponding measured values within this study. Measured values exceed the CRM values by approximately 40% (mean percentage difference) except for Co and Lead Pb which substantially exceed by a factor of 17 and 6 respectively. This highlights potential analytical error and increased variance within the collected datasets, explored further below.

6 Discussion

6.1 The ‘2019 data’ and confidence therein

High background and elevated hotspot concentrations within the study area were identified. When assessing the validity and significance of the conclusions of the study, there are several factors to consider, including: study design, quality control, appropriate means of comparison.

Amongst other factors, the onset of the coronavirus pandemic severely impacted available laboratory resources and changed the course of the study as detailed above. Consequently, the design of the study had to re-evaluated to utilise the data collected and analysed prior to the onset of the pandemic. As a result, data originally collected on a stratified/judgemental approach for the analysis of bioaccessibility has limited available statistical analyses which could be applied. Notwithstanding that, revising the project to assess and characterise spatial distribution was still deemed applicable given that there was existing data sets and previously documented site history which could be enhanced by this study. As confirmed by Swyngedouw, C. in De Vivo et al. (2018) *‘judgemental sampling is… routinely used when sufficient knowledge of the site history and activities is available’.*

Both total measurements within the BGS102 CRM report (British Geological Survey, 2009) and the total measurements in figure Table *5-7* were determined by XRF spectrometry. XRF as a direct measurement, allows measurement without any loss or deterioration of material. As with any direct total measurement, XRF can be sensitive to analytical error when analysing non-homogenous samples. Samples containing coarser grains introduce a greater potential for a single ‘nugget’ which will give rise to greater variability (Defra, 2012c). Croffie et al. (2020) noted the influence of ‘*particle size and matrix effects*’ within sandy or high-quartz soils particularly compared to other soils. This is of relevance to Snailbeach, where most mine waste contains significant levels of quartz (silicon dioxide) and where significant amounts of mine waste have been transported and otherwise mobilised around the locality.

Research into the application of ED-XRF in the assessment of contaminated soils has highlighted the difficulty of distinguishing analytical (measurement) variance, as detailed above, and from location variance (the heterogenous distribution) of Pb (Vanhoof et al., 2004).

A further explanation for the Co and Pb difference in Table *5-7* could be the influence of other samples within the same XRF sample run. Given the exceedingly high values found within the 2019 measured dataset, and within the same sample run, it is possible that typical calibration of the machine was offset against the other measured values leading to an overall amplification of measured results.

Due to the COVID-19 pandemic restrictions, the second subset of XRF samples were sent by mail to Nottingham for analysis by laboratory staff. It was therefore not feasible to run repeated separate analyses given the time and resource constraints. If operating under different circumstances, this would have been interrogated in further detail.

Acknowledging the above, it is arguable that elevated concentrations within the whole and <250µm XRF datasets may have been subject to similar effects, particularly within the Central Mine Area where they may have been influenced by 'nugget' variability and the influence of particle size.

This is supported by the difference between results for Sample TP01, within the dressing floor of the Central Mine Area. XRF analyses determined total concentrations of 81660 mg kg^{-1} in the whole sample, 131050 mg kg^{-1} within the <250µm fraction and yet only 25520 mg kg^{-1} within the <250µm fraction when determined by pseudo-total aqua-regia digest by ICP-MS.

To increase confidence in the dataset, the number of replicate samples including both the <250µm fraction and the whole sample would need to be increased. It is difficult to analyse variance, though extreme values raise questions as to the cause of the variance. Careful consideration is required to distinguish analytical variance or genuine site heterogeneity.

Results for the 2019 study ranged from 190 mg kg^{-1} to 81000 mg kg^{-1} (XRF Pb, whole), whilst Wardell Armstrong (1988) ranged from 95 mg kg^{-1} to 138000 mg kg^{-1}. The similarly scaled ranges suggest that the results gained are consistent with previous studies. This study used a laboratory specification XRF instrument and carried out pre-treatment as per good practice. Despite this it is possible that the coarse and granular nature of the mine spoil may have introduced analytical variance. In order to confirm this further replicate samples would be required.

6.2 The ‘2019 data’ in relation to previous investigations and relevant guidelines.

Table 6-1 provides the summarised data from this study, termed the ‘2019 study’, alongside key data from Wardell Armstrong (1988), Normal Background Concentrations ((Ander et al., 2013) and relevant guidance values.

Table 6-1 Table of summary 2019 study data in relation to previous site investigation, background, and guidance levels

	Source	**Details**	**Count**	**Pb mg kg^{-1}**			
Normal Background Concentration (NBC) for Pb	(Ander et al., 2013)	Urban domain	7529	820			
		Principal domain	34257	180			
		Mineralisation domain	347	2400			
					Residential Garden	**No HG Produce**	**pOS**
pC4SL	(Defra, 2012b)	pC4SL with exposure parameters as SR3 (3.5)	-	-	190	310	-
		pC4SL with changes in exposure 2 (3.5)	-	-	200	310	1300
Withdrawn SGV	(Palmer et al., 2015a)				450	450	-
Wardell Armstrong (1988) Study		Geomean Extractable (Whole)	331	3810			
		Geomean Available (Whole)	38	156.6			
					‘Residential Garden’		**‘Former Mine Site’**
2019 Snailbeach Data		US95 – ICP-MS Extractable Pb		5133	-		-
		Background Value – XRF Pb Data		3563	-		-
		Geomean Total (Whole)	56	2208	1528 (33)		12340 (7)
		Geomean Extractable (<250um)	23	4167	2991 (10)		11322 (5)

6.2.1 Total and Extractable lead concentrations

Background Values

The US95 value derived from the '2019 Extractable (ICP-MS) 'Pb data, 5133 mg kg^{-1}, indicates that average values across the study area are elevated in the <250µm fraction. Notably, this value is based on just 15 stratified sample points, and consequential limitations of a small dataset. This study's '2019 Total' Pb (XRF) (Table 6-1) data has statistically determined a background value for the whole sample fraction, 3563 mg kg^{-1}, that exceeds the NBC for Mineralisation domain (Johnson et al., 2012) by 33% and the Principle domain by 115%. The '2019 Background Value – XRF Pb Data' is argued to be the most appropriate current assessment of the 'ambient background' level within the study area, as it incorporates a wider sample base. The value is based on the UCL of the 95th percentile of the date, and therefore a more encompassing but conservative value. As stated by Johnson et al. (2012) *'…the 95th [percentile] captures a high proportion of the data and is likely to exclude the very high results that would be associated with point source data.*'.

As identified, by Defra (2012c) '*When investigating a result in the context of a NBC it is important to as whether localised variability (scales at less than 1:50000) say within the principle domain, has been truly captured during the determination of the NBC*'. This study has concluded that the ambient background concentrations are closer aligned to that of the Mineralisation domain.

Further study should undertake additional sampling and analysis to clarify the background concentrations at Snailbeach and across the region.

At Snailbeach, undertaking additional Pb ICP-MS (extractable) analysis on the whole soil fraction could reduce uncertainty in the 2019 Pb XRF (Total, whole fraction) data. Linear regression analysis could model the relationship identified and generate a wider and validated dataset upon which to derive a local ambient background value. This process was established by Ander et al. (2013) who compared XRF data and ICP-MS analyses of aqua regia extractions. They determined a minimal offset between the two datasets in arable and pastoral soil samples. (R^2 = 93 % n=65 $[Pb_{XRFS}] = 4.67 + (0.953 \times [Pb_{\text{aqua regia}}])$. They further note that *'regression equations can be used as a tool to estimate total concentrations of Pb for aqua regia/ICP-MS determined samples, though an awareness of the analytical error range must be maintained, particularly at higher concentrations'* (pg.6)

At the regional level, higher resolution sampling, would clarify the context of Snailbeach concentrations within the regional ‘ambient background’. This would confirm whether the elevated concentrations at Snailbeach amount to ‘diffuse geogenic background pollution’ as defined with the Part 2A statutory guidance (Defra, 2012a) or represents an atypically polluted site – i.e. impacted substantially more than the surrounding region.

Spatial Distribution

The spatial distribution of the Wardell Armstrong (1998) data is presented in Figure 6-1 and Figure 6-2. Figure 6-1 displays total Pb data collected as part of the Wardell Armstrong (1988) investigation at Snailbeach. There are significantly elevated concentrations surrounding the vicinity of the White Tip. Elevated concentrations follow a similar spatial trend to those found in the XRF data (Total Whole) from this study. Figure 6-2 plots the Wardell Armstrong (1988) Available Pb concentrations. It is notable that this data was collected at a much-reduced density of samples. Concentrations are substantially lower than the total data reaching a maximum of 2100 mg kg^{-1}.

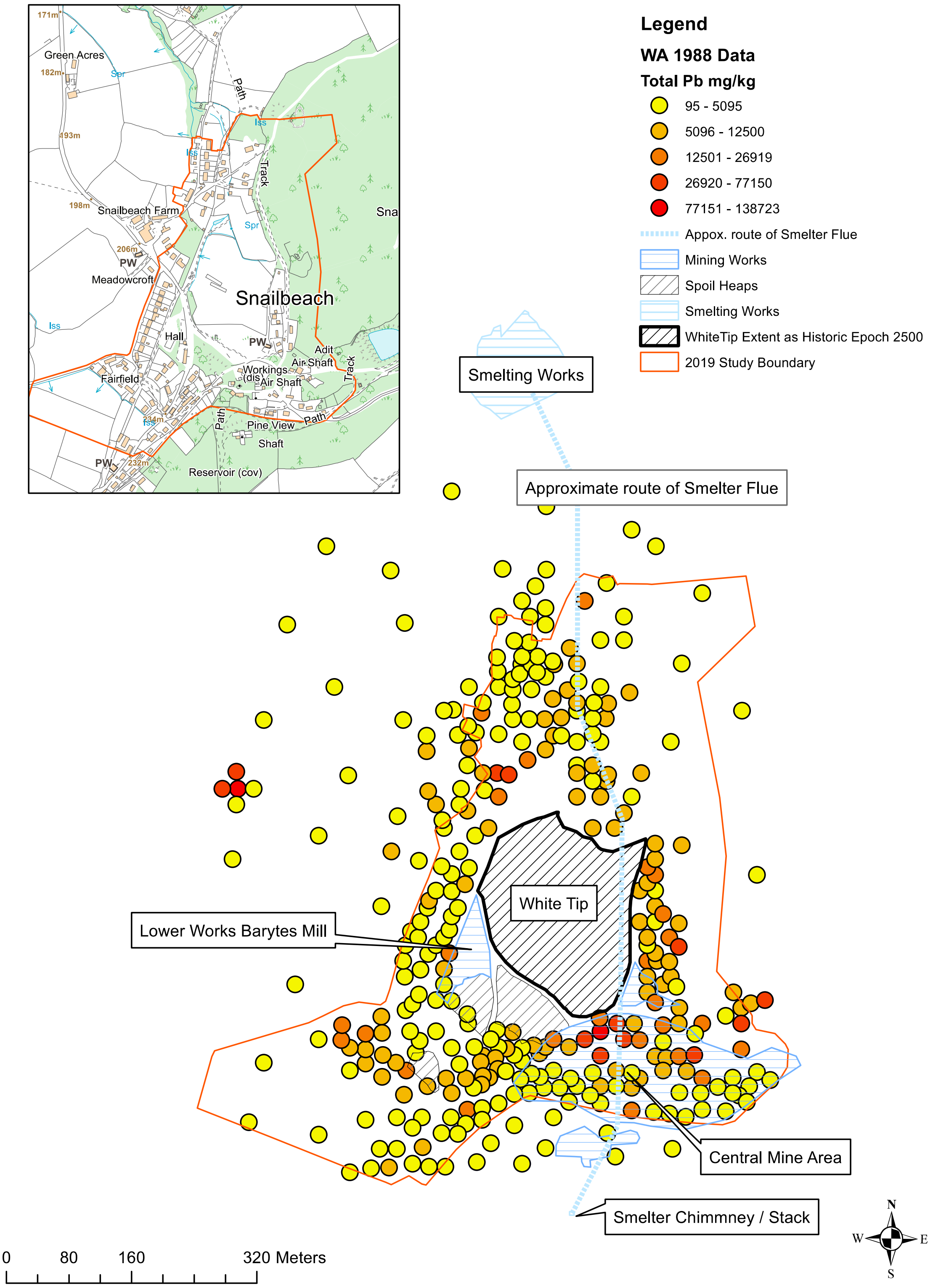

Figure 6-1 Map showing Wardell Armstrong (1988) Total Pb (mg kg^{-1}) spatial distribution and concentrations

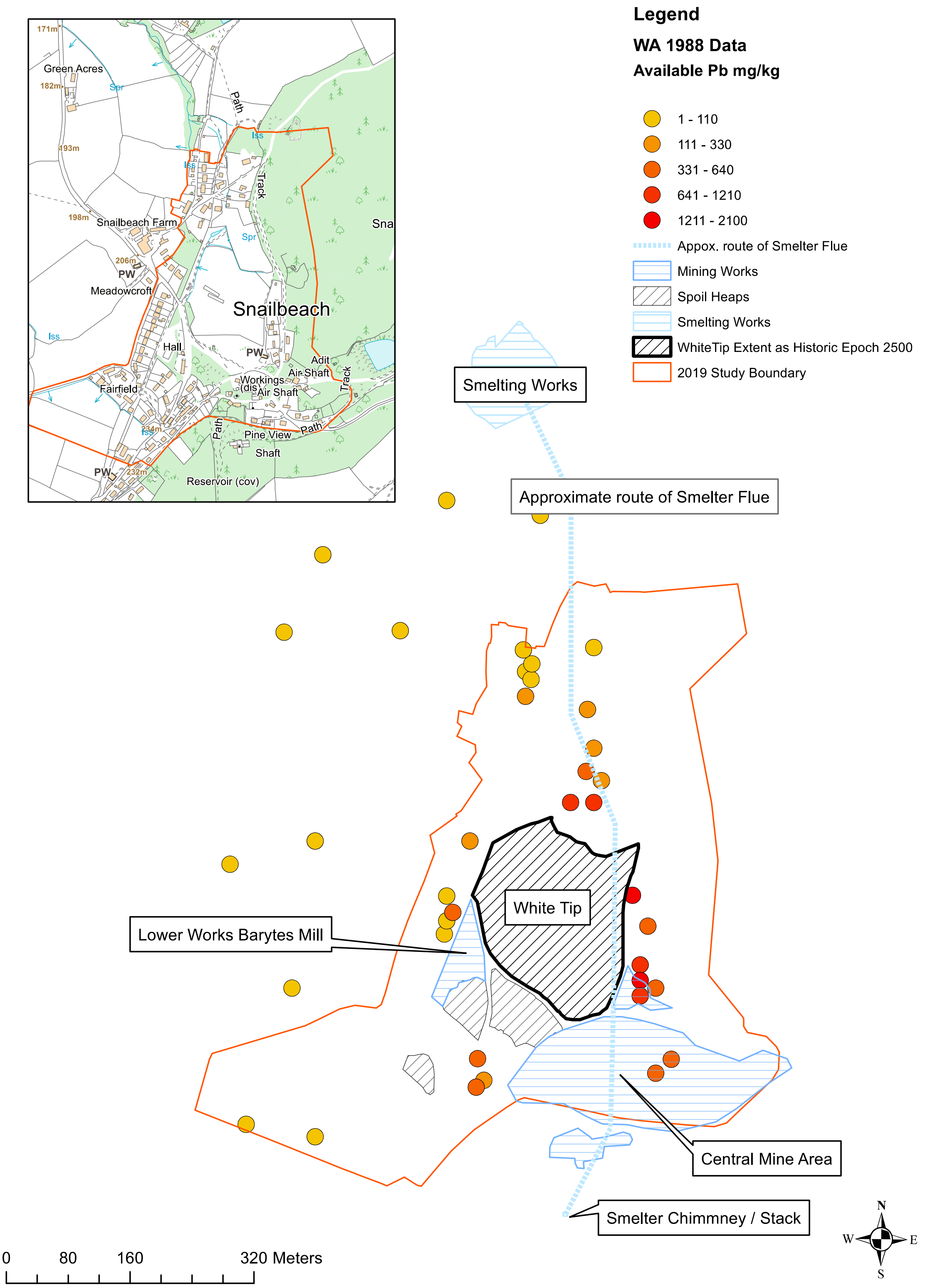

Figure 6-2 - Map showing Wardell Armstrong (1988) Available Pb (mg kg^{-1}) spatial distribution and concentrations

Statistical Interrogation of ‘2019 data’ and comparison with guideline values

This study has had to rely on qualitative assessment of summary statistics and visual analysis of the spatial trends. As detailed, deviation from the original study design impeded the level of statistical analysis and interrogation which could be applied to the datasets. During the course of the study, professional guidance relating to the comparison of soil values, to a critical concentration, was updated (CL:AIRE, 2020). The 2020 guidance states ‘Only, once assessors are confident that their datasets adequately capture the characteristics of the site being sampled, can a reliable answer be given to the planning or Part 2A questions being asked about the site…’. As has been highlighted earlier, most generic assessment criteria such as C4SL’s are developed innately to confirm and enact such decisions, and are delineated by land-use category. CL:AIRE (2020) further cautions that assessors should ensure sample datasets are ‘relatively evenly spread across the area and are not clustered… [as this may give] …undue weight to some parts of the site over others in the calculated statistics..’.

The study design of the 2019 study, for which sampling was originally undertaken, was on a judgmental approach, targeting locations and features of interest surrounding the ‘White Tip’. As a consequence, certain land-use categories received skewed density of samples, and were in locations not necessarily representative of that landuse category i.e residential gardens overlying former mine site features. This can be evidenced in Table *5-3* which displays sample counts of XRF Pb (Whole) and ICP-MS Pb (<250µm) analysis by landuse categories. The range of factors (analytical method, soil fraction size, landuse category) when considered alongside the differing sampling strategy and low and/or skewed sample counts makes robust statistical interrogation problematic, and risks unreasonable impacts on the reliability, and confidence in, the result. It is for these reasons that it has been deemed that the study had been unable to meet Objective 3 as detailed in Table *1-1*. Recommendations are made and detailed below, as to how such matters could be addressed in future study.

6.3 Soil-bound lead mobility at Snailbeach

Wardell Armstrong (1988b) concluded that mobility of Pb was likely to be low, given the high levels of calcites within the spoil, resulting in widespread alkaline soils. The pH levels identified within this study found alkaline samples (≥7.5), on the south and eastern aspects of the White Tip (Figure *5-15*), and a substantially elevated total Pb concentration (mean) of pH 8.0 compared to the other pH values identified across the study site (pH5 to pH8). The map (Figure *5-15*) shows a tight cluster of alkaline values surrounding the

Central Mine Area. As the central area of the mine activities, where a significant proportion of ore treatment and refining was undertaken, these elevated concentrations, likely relate to mine spoil in this area.

Wardell Armstrong (1988b) report the White Tip constituents, as “*waste mineral associated with the ore which forms the larger portion of the spoil tip material is mainly calcite* [calcium carbonate $CaCO_3$*]. The metals are therefore present in an alkaline environment” (pg123)*. This is further clarified with the ‘gangue’ [waste] minerals constituents stated as Calcite (Calcium Carbonate, $CaCO_3$) Quartz i.e. (Silicon Dioxide, SiO_2) and Barites (Barium Sulphate, $BaSO_4$) (Wardell Armstrong, 1988b).

In the absence of organic matter, for example in mine waste, Pb adsorbs (to silicates and clays (Steinnes, 2013)) thus reducing mobility and subsequent bioavailability. It is arguable that the alkaline nature of the waste material limits the mobility of Pb, particularly in the Central Mine Area.

Wardell Armstrong (1988b) assessed that the ‘White Tip’ contained up to 10% Pb across its extent, and it is reasonable to assume that residual minerals within the waste included those stated above, albeit in varying quantities. Future study should seek to explore the speciation of Pb within the White Tip material, and surrounding soils, to better characterize the extent and mineral distribution.

6.4 Bioavailability and Exposure of soil-bound lead at Snailbeach

In this study’s ‘2019 data’, the exceedingly elevated Pb concentrations directly contained within mine waste (Former Mine Site areas) appear to be within an alkaline matrix and encapsulated inside insoluble material. This would suggest, the bioavailability of such concentrations is likely to be substantially lower in comparison to the total values recorded. This validates the conclusions of the 1988 report, in that exposure to Pb in a readily available form from direct and un-altered mine spoil is low, and substantially lower since the capping of the White Tip in 1995 (Wardell Armstrong, 1995). Notwithstanding, this study has identified potential hotspots of high total Pb concentrations in areas beyond in Central Mine Area with varying pH values as low as 5 and has calculated an overall background Pb value (3563 mg kg^{-1}) that exceeds the normal background concentration for areas of mineralisation (Johnson et al., 2012).

Previous investigation (Pearce et al., 2002) undertaken on ‘White Tip’ material identified cerussite and galena minerals within its waste spoil that was located on agricultural land adjacent to the ‘Lower Works Lane’. A background sample and duplicate were taken beyond the core area of investigation, to benchmark the study site against the locality. These samples were pH 5.1 and pH 5.7 respectively. Each background sample displayed different proportions of heavy minerals (by x-ray diffraction (XRD) analysis), with one sample stated as containing 3% galena, 7% cerussite, 3% sphalerite and 32% barite in the 63mm - 250mm soil fraction. Simple SBET analysis was undertaken from a Total Pb (extractable) 2289 mg kg^{-1} sample, 1612mg kg^{-1} was found to be bioaccessible, resulting in a RBA of 70% and 87.5%. Smelter slag particles were also identified in both background particles displaying ‘low-density silicate mineralogy’ common to those from smelter-flue fallout, this was further explored by energy-dispersive x-ray analysis (EDXA) which indicated detectable (<5%) Pb-phosphates. Pearce et al. (2002) noted that some bioaccessible fractions were greater than the ‘Total’ values and were confirmed by repeated analysis. They note the organo-Pb complexes can be volatilised during the total digest process and thus some Pb may be lost. Pearce et al. (2002) caution that total analyses may not be a reliable guide to the true amount of Pb in the soil.

Pearce et al. (2002) theorised that sand and silt-sized galena and cerussite was unlikely to have been deposited by wind-borne deposition in large quantities from the White Tip, predicting that the material was most likely transported to the location – this corroborates with other local anecdotal reports of waste spoil being transported and repurposed locally. Rainbow (2018) details the impact of weathering upon galena stating that some *‘lead lodes [formed] may include cerussite, pyromorphite, anglesite, and/or mimetite (a lead arsenate chloride formed by the oxidation of galena and arsenopyrite’.* Given the lack of speciation and source apportionment analyses carried out elsewhere on the site, we are unable to confirm the distribution of Pb by mineral speciation, and this should be prioritised in further study.

The only localised and available information regarding the speciation of the mine spoil minerals, is from the Snailbeach Farm investigation (Pearce et al., 2002), and likewise the single background sample and its duplicate, are the only samples indicative of land not directly overlaying mine infrastructure or workings. These speciation analyses, highlight the *potential* bioaccessible nature of Pb in the area, albeit dependant on the manner it is mobilised i.e. spoil had been directly (physically) transported, and was likely weathered under atypical conditions for the current use of the area.

As detailed above, Pearce et al. (2002) further identified Pb minerals associated with smelter emissions. Whilst emissions from the smelter flue were discussed in the Snailbeach Mine study reports (Wardell Armstrong, 1988b), no details of any determination or Pb source apportionment has been identified. It is however feasible that, Pb identified by this study, could be associated with either and/or windborne fine mine spoil material, or aerially deposited Pb from the Smelter flue. Figure 6-2 includes an approximate route of the smelter flue in relation to other site features. The smelter stack on 'Lordshill' is still standing today. From this location, south of the mine site (and elevated on an adjacent hillside), together with the predominant wind direction (south westerly), flue emissions would have been predominantly emitted across the study area and beyond. (Linzon et al, 1976 as cited in Rieuwerts and Farago, 1995) found concentrations from aerially deposited smelter emissions to be 21200 mg kg^{-1} within 100m of the smelter stack, which decreased exponentially with distance to 1180mg kg^{-1}. Rieuwerts and Farago (1995), in their review of smelting environments, found maximum levels of 20000ppm (mg kg^{-1}) and 60000ppm (mg kg^{-1}), within 400m or less of smelter stacks.

Notably, this study found widespread elevated concentration in the <250µm fraction, that were typically 178% of the whole fraction when assessed by XRF. When assessed by digestion (aqua regia) methods, extractable Pb for the <250µm fraction determined values which were 73% less, than XRF on <250µm (Figures based on corresponding-samples subset, Table *5-1*).

Given that galena was the primary mineral extracted on the site, and that potential sub-products (species) of the weathering of galena were identified during the Snailbeach Farm investigation (Pearce et al., 2002) it is deemed that the potential for bioaccessible Pb to be present surrounding Snailbeach cannot yet be disproven and requires further investigation. Whilst this study identified typically lower extractable values, it has identified widespread elevated Pb concentrations in the <250µm fraction. Discussion of the confidence in such datasets has been reviewed above and likewise recommendations are made later as to further investigation to apportion the Pb by species and source.

6.5 Previous biological uptake of lead at Snailbeach and success of the 1988 works

As detailed in Wardell Armstrong (1989b) several instances of elevated blood lead levels greater than (40 ug/dL) were found, although no evidence of human health impacts were, or have been, recorded. Wardell Armstrong (1989b) also noted that some residential properties within the village utilised private water supplies which drew directly from the Mine Adits, at concentrations reported as being '*eight times the recommended limit…for potable water*'.

The deaths of young bullocks in the fields west of the White Tip triggered the Snailbeach Farm (Pearce et al., 2002) investigation. Whilst the study determined high levels of bioaccessibility within the suspected source material, they attributed the likely exposure to have been direct-ingestion of raw 'White Tip' material thought to have been transported to the location. The vulnerability of livestock to elevated metal concentrations in agricultural soils has been reviewed by Thornton (2002). Livestock deaths have been reported from other mining locations e.g. Silvermines (Garavan et al., 2008) and Derbyshire (Cotter-Howells and Thornton, 1991) and yet paradoxically, low community level human impacts were identified.

Wardell Armstrong (1989b) also identified substantially elevated concentrations of lead in house dust (discussed above) suggesting potentially high levels of community level exposure to lead, likewise reference is made to multiple activities being carried out on the exposed white tip at the time of the study prior to remediation (off-road motorcycling, children playing). Anecdotal evidence was received during the course of this investigation which stated knowledge of *'…children crawling through the smelter flue!*'.
Wardell Armstrong (1989b) established that significant amounts of fine mine-waste material were, and had been for many years, actively dispersing across the area by windblow. Elevated BLL's could therefore be explained by inhalation of fine mineral waste containing fine galena particles. To explain, the inhalation pathway is discussed in reference to particle size in the earlier review - Chaney et al (1988) in Thornton et al. (2001) where it is established that '*smaller particles… [are] more bioavailable since, when ingested they [are] more easily dissolved or reach the alveoli and are subsequently… dissolved in the blood stream, when inhaled*'. In contrast, galena currently ingested via the oral pathway would not be readily bioaccessible due to acidity in the gastrointestinal system, whereas directly-inhaled fine galena particles could be mobilised to the bloodstream via the inhalation pathway. This would explain why no further elevated BLL's have been highlighted in the community but would require BLL testing to clarify this further.

Notwithstanding the above pre-existing indications of exposure, it is highly likely that the efforts of the 1988 remediation scheme: capping the spoil heap, stabilising the site and securing the open features, were successful in reducing the capacity for exposure within the community.

This study found high extractable Pb concentrations (max: 25550 mg kg^{-1}) in <250µm fraction across study area. Directly comparable sample locations indicated Extractable ICP-MS concentrations were typically 73% (Mean, Range: 53 to 85%) less than the Total <250µm concentration – although this increased to up to maximum of 85% less at higher Pb concentration values. As established, previous studies (Pearce et al., 2002) identified minerals likely sourced from smelter emissions in 'background' agricultural soils. This is arguably confirmation of the presence of wider regional elevated background concentrations as indicated by the nationwide normal background concentration data (BGS). BGS Data suggest large area of elevated soil surface Pb including up to 20km^2 north of from southern extent of Snailbeach (and encompassing Snailbeach, plus other know Pb smelter at Pontesbury) (Figure 9-2) indicative of widespread diffuse pollution. Maps containing BGS interpolated values are included in Appendix 3 British Geological Survey – NBC Pb Contaminant Distributions as per Ander et al. (2013).

On the basis of the 2019 data, there is insufficient data to draw conclusions regarding current levels of exposure. But there clearly remains substantially elevated Pb concentrations within fine topsoil fractions across the study area. There is therefore potential for exposure to these concentrations which require further investigation.

6.6 Management of Pb at Snailbeach and the legislative context

At the time of the 1988 study, there was no legal requirement to address historic contamination. Consequently, the investigation of Snailbeach Mine sought only to address 'active' dispersal routes. In conducting 'a reclamation project' and remedial works on the mine site, this may be open to misinterpretation by interested non-technical parties; specifically, it may not be clear, without thorough review, that whilst capping and reducing the 'White Tip' would inhibit ongoing dispersal, the legacy of elevated soil-Pb concentrations would not be addressed.

Consideration of the soil chemistry and conditions has identified ongoing potential/theoretical availability of Pb in soils surrounding Snailbeach. Yet no recent or additional indicators of harmful Pb uptake have been identified. As noted in Table 2-1, (Literature Review) other mining sites have similarly noted high potential Pb availability yet limited recorded impacts to human health. It has further been established that the reputed ‘richness’ of the ore extracted at Snailbeach was substantiated as recorded by the levels of Pb within White Tip material and surrounding the vicinity of the site. The case for further characterisation at a regional scale is supported in order to clarify the theoretical bioavailability with informed ‘actual’ bioavailability. As discussed above there is insufficient evidence to attribute previous indicators of bioavailable uptake (BLL, Livestock deaths) to soil-bound Pb concentrations and that other historic pathways (transported mine spoil and direct access to exposed mine infrastructure) could be source to these indications.

Such matters could only be truly quantified by (exposure) epidemiological studies of the local population. The 1988 study determined that such study would be ‘*costly, intrusive, and may cause unnecessary stress to local residents’*(Wardell Armstrong, 1989a, Wardell Armstrong, 1988b) It is probable that the same consequences would likely arise today. Therefore, it is considered more favourable and proportionate to carry out validated bioaccessibility analyses in order to assess bioavailability in the area, and wider region. This is in accordance with the conclusions of the Snailbeach Farm assessment which noted the potential availability of Pb in the wider Snailbeach region (based on the available concentration within the material in the agricultural field) and recommended prompt review of the wider Snailbeach area via the same analytical methods used.

As highlighted in this study’s literature review, there has been concern over the ‘blanket application of oral bioaccessibility analyses’ in recent risk assessment (Dean et al., 2020). However, it is deemed that sufficiently targeted study, in the context of Snailbeach Mine, could provide valuable clarity to characterising the bioaccessibility of Pb in the area. This study, has noted the value of both previously collected data (Wardell Armstrong, 1988b, Pearce et al., 2002) to inform characterisations of the area at a local scale. Collating new datasets, and that of this study, could be utilised to form a semi-stratified (zonal) strategy to estimate bioavailability across the study area.

7 Conclusions

This research aimed to characterise the concentration and distribution of soil-bound lead (Pb) at Snailbeach, Shropshire. The study has successfully identified elevated Total and Extractable Pb concentrations surrounding the Central Mine Area. It was further identified that there are localised elevated concentrations across all the varied current-landuse types surrounding the 'White Tip'. Analysis established that these elevated concentrations persist, in a similar range and spatial distribution to that identified by Wardell Armstrong in 1988. A background concentration has been derived for the study area with a value of 3563 mg kg-1. This exceeds the NBC Mineralisation domain value by 32%, indicating that Snailbeach concentrations exceed typical values of other mineralisation regions. Analysis of the Extractable Pb within the <250µm fraction, found elevated extractable Pb concentrations as an average of the study area (US95: 5133 mg kg-1). Whilst speculative of wider elevated concentrations within the <250µm fraction, the accuracy of this figure is caveated given the small dataset available for the size averaging area. The data found substantially elevated Pb concentrations in alkaline (>pH7.5) soils and mine waste, and these appear to spatially correlate to the Central Mine Area and areas impacted by waste spoil. Soil descriptions show some spatial trends, which could be indicative of particle size and therefore indicative of mine spoil beyond the White Tip and Central Mine Areas. Whilst beneficial to the understanding of the site these correlations are only indicative; the limitations of the study design prevent independent statistical interrogation of these correlations.

With regards to the study methodology, the research aims were amended due to the coronavirus pandemic. This resulted in a change to the purpose of the sampling data that had already been collected. This new purpose was not the primary intention of the original sampling strategy, and this has therefore the reduced the ability to determine the statistical significance of the results. Notwithstanding this, the research has highlighted the complexity of the Snailbeach Lead Mine, and the surrounding area. Additionally, the data enhances and updates current knowledge and characterisation of the site. The 2019 data, in combination with previous site investigation, should prove beneficial for future specialised research - recommendations for which are made below.

This study is the first site-scale research undertaken at Snailbeach, known to the author, that specifically considers soil-bound Pb since the Wardell Armstrong (1988) investigation, and post-completion of the 1995 reclamation scheme. It has been discussed that the correlating Total Pb trends between the Wardell Armstrong (1988) data and this study's

(2019) data could be interpreted to demonstrate the stability of soil bound Pb in the area. This could be seen to confirm the success of the capping works in limiting ‘active dispersal’ across the area. Whilst indicative of this conclusion, this study has not confirmed the source or speciation of the topsoil Pb concentrations. It has been identified that both the former smelter chimney and mining activity, are likely to have contributed to background topsoil Pb concentrations in the study area. However, speciation and mineral-form analysis are required to clarify and apportion these sources.

It has been noted that both Wardell Armstrong (1988), and ‘2019’ concentrations, exceed normal background concentrations and guidance values. Given that Pb is now identified as a non-threshold toxin (Public Health England, 2017), it is arguable that elevated Pb concentrations remain a theoretical cause for concern. However, this concern, is only deemed valid if there are viable pathways by which receptors can be become exposed, and that this exposure then results in uptake of the contaminant. There is insufficient evidence to confirm this uncertainty, and analysis of exposure was beyond the scope of the revised research aims.

The risk posed from such concentrations must not be overstated. The discussion has highlighted other potential sources and pathways that may have caused indications of biological uptake previously. No further indications of uptake have yet been identified at Snailbeach and it has been concluded that the area should be managed accordingly, until otherwise evidenced. It has not been possible to quantify the risk posed from such exposure. Acknowledging this, and the forementioned elevated Total Pb and elevated background, there is a strong case for further characterisation of the area to reduce uncertainty. As such, it is concluded that the use of bioaccessibility analyses in further work is justified.

The following recommendations are made:

- Future work should seek to clarify the distribution and mineral composition of soil Pb across the wider region, south-west of Shrewsbury, and encompassing the former West Shropshire Orefield. Data of a higher spatial resolution would enhance current characterisation at the regional scale.
- At Snailbeach, undertaking additional Pb ICP-MS (extractable) analysis on the whole soil fraction could reduce uncertainty in the 2019 Pb XRF (Total, whole fraction) data. Linear regression analysis could then model any correlation identified and generate a wider and validated dataset upon which to derive an accurate local ambient background value within the study area.

- In addition to the above, further sampling should be undertaken surrounding Snailbeach and analysed as per the recommendations of Pearce et al. (2002). Validated bioaccessibility analyses such as the Unified BARGE Methodology (UBM) are recommended as a proportionate means to assess potential bioaccessibility of Pb at Snailbeach and have been used to the same purpose in other former mining regions (Palmer et al., 2015, Appleton et al., 2013).

It is argued that both this research, and previous investigation, have recognised the Pb-rich nature of waste spoil associated with Snailbeach. It is clear that the reputation of the mine as ‘one of the richest in Europe’ (Brook and Allbutt, 1973), is well-deserved, and that inefficiencies in early processing and refining techniques left significant quantities of Pb in the waste material that is present on site and around the Snailbeach area today. This study has utilised previous datasets to interpret and enhance current Pb contamination trends and identify further areas requiring investigation. Acknowledging this, caution must be exercised when interpreting these values, given their respective pitfalls which can misrepresent concentrations.

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9 Appendices

9.1 Appendix 1 All 2019 Data

Table 9-1 Appendix 1 - All 2019 data

Sample	**XRF Zn (mg kg^{-1})**	**XRF Cd (mg kg^{-1})**	**XRF Pb (mg kg^{-1})**	**ICP Zn (mg kg^{-1})**	**ICP Cd (mg kg^{-1})**	**ICP Pb (mg kg^{-1})**	**ICP Sample Wt. (g**	**pH**	**Landuse**	**Sample Soil Descripti**	**Stones**	**OM**	**Latitude DD**	**Longitude DD**
TP01	1424	13	81660	2464.322207	14.16444469	25520.25595	1.2706	8	Former Mine Site	LOAMY SAND	Small Stones (6mm to 2cm)	None	52.613911	-2.924911
TP02	231	2	53390	394.7234128	4.9669402	8961.571142	1.4666	8	Residential Garden	SILTY CLAY LOAM	Very Small Stones (2mm to 6mm)	None	52.613904	-2.929869
TP03	1035	5	41720	2534.839181	37.63097428	8225.021056	0.9995	8	Former Mine Site	SANDY LOAM	Medium Stones (2cm to 6cm)	20%	52.613750	-2.925283
TP04	1305	4	33150	2318.81539	22.38498913	14633.85614	1.0553	8	Former Mine Site	SAND	Medium Stones (2cm to 6cm)	None	52.614054	-2.924547
TP05	388	2	30830	1281.993719	8.656485518	14496.5157	1.0453	8	Former Mine Site	SILTY CLAY LOAM	None / Negligible	20%	52.613699	-2.925511

TP06	770	2	23200	1859.220954	23.13181566	6886.785771	1.0418	7.5	Highway Verge	LOAMY SAND	Very Small Stones (2mm to 6mm)	<5%	52.614489	-2.923850
TP07	335	1	13820	657.9973271	6.254815051	3240.861633	1.0029	7	Residential Garden	SILTY CLAY LOAM	Small Stones (6mm to 2cm)	<5%	52.614523	-2.923984
TP08	635	2	12480	1640.75078	18.71103333	6683.331837	0.9885	6.5	Highway Verge	SILT-LOAM	Very Small Stones (2mm to 6mm)	<5%	52.613569	-2.927285
TP09	631	2	11990	1287.400377	16.55951903	4560.736276	1.0976	7	Private Land - Forestry	SILTY CLAY LOAM	None / Negligible	<5%	52.615293	-2.924036
TP10	364	1	9210	1340.997993	14.47281415	6973.239646	0.9849	7.5	Residential Garden	SANDY LOAM	Small Stones (6mm to 2cm)	<5%	52.613489	-2.931473
TP11	380	1	8700	1132.71061	8.621453166	4064.101001	1.0584	5	Residential Garden	SILTY CLAY	None / Negligible	<5%	52.617228	-2.924984
TP12	167	0	5710	730.8419222	5.626231956	3645.757657	1.0262	8	Residential Garden	SANDY CLAY LOAM	Small Stones (6mm to 2cm)	<5%	52.613476	-2.923840
TP13	56	0	4570	356.6846384	4.253384579	4177.270477	1.0468	7.5	Former Mine Site	SANDY CLAY LOAM	None / Negligible	<5%	52.613631	-2.924936

TP14	287	1	4540	2173.721691	25.67486227	6659.921438	1.0118	7	Private Land - Forestry	SILTY CLAY LOAM	None / Negligible	> 50%	52.615100	-2.923789
TP15	192	0	4230	#N/A	#N/A	#N/A		7	Residential Garden	SILTY CLAY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.613659	-2.923535
TP16	170	0	4150	#N/A	#N/A	#N/A		6.5	Private Land - Forestry	SILTY CLAY LOAM	None / Negligible	> 50%	52.613796	-2.925905
TP17	184	0	3300	1262.30085	19.10453266	4902.096518	1.029	7	Residential Garden	SILTY CLAY LOAM	None / Negligible	<5%	52.615843	-2.924121
TP18	204	0	3240	#N/A	#N/A	#N/A		8	Residential Garden	SANDY LOAM	Small Stones (6mm to 2cm)	<5%	52.614812	-2.923967
TP19	235	1	2750	1842.056357	26.413175	3564.039353	1.0189	7.5	Private Land - Forestry	SILTY CLAY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.616000	-2.923533
TP20	105	0	2360	#N/A	#N/A	#N/A		7	Former Mine Site	LOAMY SAND	Very Small Stones (2mm to 6mm)	20%	52.614019	-2.924567
TP21	123	0	2360	#N/A	#N/A	#N/A		7.5	Private Land - Forestry	SANDY CLAY LOAM	Very Small Stones (2mm to 6mm)	20%	52.615194	-2.923550

TP22	94	0	2280	638.4301696	9.008583351	2519.517544	1.0344	7	Private Land - Forestry	SILT-LOAM	Small Stones (6mm to 2cm)	20%	52.616931	-2.924408
TP23	78	0	2270	#N/A	#N/A	#N/A		6.5	Residential Garden	SILTY CLAY LOAM	None / Negligible	20%	52.615854	-2.928081
TP24	139	0	2220	#N/A	#N/A	#N/A		7.5	Residential Garden	SILT-LOAM	None / Negligible	<5%	52.616142	-2.923942
TP25	146	0	2150	#N/A	#N/A	#N/A		7	Residential Garden	SILTY CLAY LOAM	None / Negligible	<5%	52.617431	-2.926928
TP26	141	0	2040	1087.326576	11.55772993	3523.987808	1.0512	7.5	Residential Garden	SILTY CLAY LOAM	Small Stones (6mm to 2cm)	None	52.617565	-2.926232
TP27	124	0	2010	#N/A	#N/A	#N/A		7.5	Residential Garden	SANDY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.613609	-2.927250
TP28	111	0	1980	#N/A	#N/A	#N/A		7	Residential Garden	SANDY CLAY LOAM	Medium Stones (2cm to 6cm)	<5%	52.613723	-2.926840
TP29	24	0	1950	#N/A	#N/A	#N/A		5	Private Land - Forestry	SANDY CLAY LOAM	Small Stones (6mm to 2cm)	<5%	52.617981	-2.924264

TP30	75	0	1850	#N/A	#N/A	#N/A		5.5	Private Land - Forestry	SILTY CLAY LOAM	None / Negligible	20%	52.617817	-2.924714
TP31	48	0	1810	#N/A	#N/A	#N/A		6.5	Residential Garden	SANDY CLAY LOAM	None / Negligible	<5%	52.615520	-2.927857
TP32	38	0	1220	328.0742123	3.459516133	2392.897385	1.5697	6	Highway Verge	SILTY CLAY LOAM	Medium Stones (2cm to 6cm)	<5%	52.612960	-2.927614
TP33	71	0	1180	#N/A	#N/A	#N/A		6.5	Residential Garden	SANDY CLAY	Small Stones (6mm to 2cm)	<5%	52.616177	-2.927480
TP34	33	0	1160	#N/A	#N/A	#N/A		8	Former Mine Site	SANDY CLAY LOAM	Small Stones (6mm to 2cm)	20%	52.613762	-2.926208
TP35	91	0	1140	#N/A	#N/A	#N/A		7	Residential Garden	SILTY CLAY LOAM	None / Negligible	<5%	52.617312	-2.927001
TP36	43	0	1120	#N/A	#N/A	#N/A		6.5	Private Land - Forestry	CLAY LOAM	None / Negligible	<5%	52.616628	-2.924642
TP37	34	0	1090	#N/A	#N/A	#N/A		5.5	Residential Garden	LOAMY SAND	None / Negligible	<5%	52.615352	-2.928319

TP38	65	0	1020	#N/A	#N/A	#N/A		6.5	Residential Garden	SILTY CLAY LOAM	None / Negligible	<5%	52.618027	-2.926328
TP39	79	0	900	#N/A	#N/A	#N/A		7	Residential Garden	CLAY LOAM	None / Negligible	<5%	52.616954	-2.926925
TP40	56	0	870	433.3093465	4.597281511	1576.201358	1.0631	6	Residential Garden	SILTY CLAY LOAM	None / Negligible	50%	52.618908	-2.925319
TP41	46	0	850	#N/A	#N/A	#N/A		6.5	Residential Garden	SILTY CLAY LOAM	Small Stones (6mm to 2cm)	<5%	52.617686	-2.924906
TP42	39	0	790	#N/A	#N/A	#N/A		7	Residential Garden	SANDY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.615158	-2.924019
TP43	56	0	750	#N/A	#N/A	#N/A		7	Residential Garden	CLAY	None / Negligible	<5%	52.617641	-2.926307
TP44	56	0	730	#N/A	#N/A	#N/A		7	Residential Garden	CLAY LOAM	None / Negligible	<5%	52.617223	-2.926671
TP45	27	0	700	#N/A	#N/A	#N/A		6.5	Residential Garden	CLAY LOAM	None / Negligible	<5%	52.615184	-2.928468

TP46	40	0	660	288.1569821	2.086213125	917.2644376	1.0483	7	Residential Garden	SANDY CLAY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.615286	-2.927730
TP47	25	0	630	207.5641335	1.650980698	564.6830944	1.1609	5.5	Agricultural Field	SILTY CLAY LOAM	None / Negligible	20%	52.612689	-2.930280
TP48	24	0	630	#N/A	#N/A	#N/A		6.5	Highway Verge	LOAMY SAND	None / Negligible	<5%	52.613964	-2.924192
TP49	46	0	580	#N/A	#N/A	#N/A		5.5	Residential Garden	SILTY CLAY LOAM	None / Negligible	20%	52.618398	-2.926415
TP50	70	0	550	#N/A	#N/A	#N/A		6.5	Residential Garden	SILTY CLAY LOAM	None / Negligible	> 50%	52.615748	-2.927546
TP51	6	0	440	#N/A	#N/A	#N/A		5	Private Land - Forestry	SILTY CLAY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.618811	-2.923058
TP52	29	0	430	#N/A	#N/A	#N/A		7	Private Land - Forestry	SANDY CLAY LOAM	Very Small Stones (2mm to 6mm)	<5%	52.618419	-2.924644
TP53	35	0	400	324.2155487	2.558782446	764.1269634	1.1261	6	Residential Garden	SILTY CLAY LOAM	None / Minimal	<5%	52.617806	-2.926370

TP54	13	0	390	#N/A	#N/A	#N/A		5.5	Residential Garden	SILTY CLAY LOAM	Small Stones (6mm to 2cm)	<5%	52.618600	-2.924608
TP55	23	0	260	#N/A	#N/A	#N/A		6	Residential Garden	SILTY CLAY	None / Negligible	<5%	52.617913	-2.926769
TP56	23	0	190	#N/A	#N/A	#N/A		7	Residential Garden	SILTY CLAY LOAM	Small Stones (6mm to 2cm)	20%	52.618199	-2.926562

9.2 Appendix 2 Wardell Armstrong (1988) topsoil data

Table 9-2 Table of Wardell Armstrong (1988) topsoil concentration data

Report - Sample Code	**Excel - Sample Code**	**Grid Ref.**	**Grid Ref. 1**	**Pb (mg kg^{-1})**	**Cd (mg kg^{-1})**	**Zn (mg kg^{-1})**	**Av. Pb (mg kg^{-1})**	**Av. Cd (mg kg^{-1})**	**Av. Zn (mg kg^{-1})**
1		337525	302285	17335	51.1	8016	1210	16.7	1500
2		337537	302285	8283	35.9	3992			
3	1	337535	302295	9241	42	4645			
4	2	337525	302305	4795	16	2098			
5	3	337553	302315	20180	41	5994			
6	4	337525	302315	10070	33.9	4187			
7	5	337515	302335	11200	40	5100			
8	6	337535	302335	4000	15	1900	510	7.3	365
9	7	337535	302355	8076	35.9	3589			
10	8	337535	302375	5095	23	2597			
11	9	337515	302375	10500	74	8000	1960	12.5	1050
12	10	337525	302385	11200	85	9000			
13	11	337535	302395	13900	92	10000			
14	12	337525	302405	12736	55.7	6965			
15	13	337535	302415	10490	37	3796			
16	14	337535	302435	10390	29	3696			
17	15	337545	302345	17500	44	4800			
18	16	337525	302265	6743	20	2597	2100	8.8	700
19	17	337545	302255	8932	16	2395	406	6.4	420
20	18	337525	302245	8300	20	3000	1029	8.7	440
21	19	337535	302232	14600	14	1800			
22	20	337555	302265	6600	15	2300			
23	21	337553	302284	6082	14	1894			
24		337565	302303	31437	24	3443			
25		337562	302252	778	1	329			
26	22	337545	302203	19119	55.1	5506			
27	23	337566	302225	10900	27	2400			
28	26	337565	302205	11776	26.9	2395			
29	27	337595	302205	17400	9	1200			
30	28	337625	302215	4800	14	1900			
31	29	337645	302225	7307	10	1552			

32	30	337657	302231	7100	13	1000			
33	31	337675	302235	38961	33	3546			
34	32	337645	302205	45637	9	903			
35	33	337586	302192	200	0.5	90			
36	34	337545	302182	3896	7	899			
37	35	337535	302163	9590	13	1998			
38	36	337549	302161	10978	25.9	3393			
39	37	337565	302163	13914	67.1	9009	580	4.1	420
40	38	337585	302165	33500	30	2400			
41	39	337575	302144	5195	12	1698			
42	40	337545	302145	12500	22	3300	640	8	470
43	41	337595	302135	26919	60.8	6979			
44	42	337645	302172	15753	51.8	6979			
45	43	337634	302136	3493	12	998			
46	44	337665	302143	2994	5	798			
47	45	337682	302133	2700	7	410			
48	46	337655	302125	2797	6	799			
49	47	337642	302113	3500	5	600			
50	48	337634	302116	3187	3	797			
51	49	337652	302105	1209	3	360			
52		337615	302124	1150	3	850			
53		337625	302093	1562	3	601			
54	50	337593	302116	3500	7	1900			
55	51	337595	302095	1848	3	599			
56	54	337566	302117	1978	9	1299			
57	55	337574	302086	1160	1	300			
58	56	337553	302090	550	0	180			
59	57	337533	302092	180	0	140			
60	58	337505	302094	15538	2	279			
61	59	337505	302123	8724	11	2293			
62	60	337485	302125	4860	11	2104			
63	61	337515	302135	10070	32.9	4038			
64	62	337505	302142	4705	11	1301			
65	63	337485	302145	6537	24	2495			
66	64	337465	302125	7627	61.8	7976			
67	65	337465	302103	4387	6	1097			
68	66	337455	302142	3707	11	1503			
69	67	337452	302113	1184	2	491			
70	68	337435	302125	4691	6	3842			

71	69	337427	302135	3194	4	599			
72	70	337405	302145	4505	9	1001			
73	71	337387	302167	9700	20	4700			
74	72	337395	302175	7193	21	2597			
75	73	337380	302177	8900	14	3200			
76	74	337405	302185	12913	29	2352			
77	75	337425	302175	6693	28	2098			
78	76	337445	302185	34930	109.8	9980			
79	77	337465	302164	49401	106.8	9980			
80		337495	302185	37111	262.8	29087			
81		337515	302184	17632	44	4895			
82	78	337508	302205	10568	98.7	10967			
83	79	337486	302205	30938	239.5	24950			
84	82	337465	302195	138723	103.8	10978			
85	83	337464	302212	21722	82.1	9510			
86	84	337413	302123	2036	3	399			
87	85	337393	302123	1658	4	699			
88	86	337388	302137	3497	10	1848			
89	87	337377	302141	2909	6	1805			
90	88	337374	302116	863	2	391			
91	89	337363	302134	1394	3	602			
92	90	337365	302157	460	3	300			
93	91	337365	302174	2066	5	798			
94	92	337353	302194	6169	20.9	3333			
95	93	337355	302165	3586	116.5	1295			
96	94	337345	302173	5856	12	2202			
97	95	337333	302197	2847	11	1399			
98	96	337335	302175	3504	8	1401			
99	97	337325	302185	2653	9	1802			
100	98	337315	302164	9300	26	3200	470	8	900
101	99	337331	302161	6100	16	3000			
102	100	337334	302147	5500	17	2700			
103	101	337344	302144	4354	12	2603			
104	102	337355	302115	647	2	338			
105	103	337323	302136	7450	18	2400	300	5.3	1100
106	104	337312	302156	12040	39.8	4179			
107	105	337315	302138	7777	18.9	3290			
108		337313	302127	9341	18	3946	360	5.3	1100
109		337303	302123	910	4	800			

110	106	337293	302135	5918	11	1805			
111	107	337304	302175	2900	10	1800			
112	110	337285	302153	3000	7	1300			
113	111	337268	302135	5938	11	2395			
114	112	337275	302116	5633	15	2592			
115	113	337295	302095	15784	10	1299			
116	114	337314	302097	3100	10	2200			
117	115	337335	302103	1122	4	1303			
118	116	337314	302082	1548	5	1099			
119	117	337293	302077	2390	11	2390			
120	118	337325	302052	1397	1	150			
121	119	337355	302075	1128	0	100			
122	120	337365	302026	888	2	210			
123	121	337395	302046	978	1	105			
124	122	337405	302085	1130	0	130			
125	123	337425	302105	2008	0.5	210			
126	124	337474	302065	2198	9	1499			
127	125	337484	302035	1471	0.5	180			
128	126	337557	302045	1240	0	150			
129	127	337615	302033	1220	0.5	180			
130	128	337307	302028	510	1	220			
131	129	337267	302022	510	0	120			
132	130	337246	302022	1642	8	1401			
133	131	337225	302026	1270	6	1300			
134	132	337238	302047	5544	10.5	1698			
135	133	337262	302065	1269	3	699			
136		337283	302064	4204	28	3203			
137		337274	302085	820	3	440			
138	134	337237	302085	4004	8	1301			
139	135	337225	302072	4900	9	1600			
140	138	337205	302045	3197	7	999			
141	139	337195	302021	6914	8	902			
142	140	337172	302020	1274	6	903			
143	141	337183	302045	2495	6	749			
144	142	337205	302085	1894	6	997			
145	143	337214	302114	6406	13	2703			
146	144	337244	302125	10421	22	3307			
147	145	337217	302145	17100	18	3050			
148	146	337229	302168	2894	9	1397			

149	147	337234	302183	511	1	265			
150	148	337275	302174	1140	2	460			
151	149	337255	302195	531	1	190			
152	150	337296	302205	95	0.5	85			
153	151	337295	302217	215	0	180			
154	152	337275	302234	1128	22	1248			
155	153	337255	302235	719	0	170			
156	154	337265	302255	859	14	1099			
157	155	337145	302015	1440	7	1000			
158	156	337165	302082	2603	8	1401			
159	157	337186	302137	11011	18	3403			
160	158	337204	302155	5289	8	1796			
161	159	337222	302195	989	3	380			
162	160	337187	302165	12000	17	3300			
163	161	337165	302154	9990	7	1199			
164		337165	302172	10611	14	2452			
165		337145	302174	11266	8	1795			
166	162	337134	302184	14671	30.9	3593			
167	163	337165	302192	12774	18	1996			
168	166	337186	302193	7385	34.9	4092			
169	167	337185	302214	7700	16	2700			
170	168	337216	302222	1190	6	3300			
171	169	337225	302230	1812	6	1201			
172	170	337233	302242	469	1	210			
173	171	337215	302265	1738	3	360			
174	172	337235	302274	1956	4	499			
175	173	337213	302285	2398	8	1798			
176	174	337216	302305	1000	7	1500			
177	175	337223	302323	519	2	269			
178	176	337232	302315	1467	5	798			
179	177	337245	302294	1147	4	399			
180	178	337255	302305	1357	6	998			
181	179	337265	302315	1940	15	4000			
182	180	337265	302275	6750	69	7000			
183	181	337272	302295	19381	31	11988			
184	182	337272	302325	2708	7	1103	84	2.2	200
185	183	337235	302335	1920	6	800			
186	184	337244	302353	2550	3	380			
187	185	337275	302342	2207	4	441	80	1.2	31

188	186	337283	302353	3996	2	385	430	1	31
189	187	337246	302362	8492	4	475			
190	188	337255	302375	1180	3	320			
191	189	337275	302374	2503	6	571	103	1.3	54
192		337292	302383	5300	6	900			
193		337275	302396	3800	6	700			
194	190	337262	302406	3400	7	800			
195	191	337285	302425	3403	7	1101			
196	194	337297	302404	4304	12	1401			
197	195	337305	302445	3604	14	1702	176	4.6	165
198	196	337265	302455	1916	7	1697			
199	197	337322	302455	6356	40	3303			
200	198	337295	302477	5611	19	2405			
201	199	337317	302503	4404	21	3203			
202	200	337335	302495	13573	48.9	4790			
203	201	337333	302525	44132	144.4	34604			
204	202	337348	302523	31062	132.3	16032			
205	203	373315	302545	15800	132	22000			
206	204	337335	302575	3800	18	2200			
207	205	337365	302565	2988	14.9	1494			
208	206	337372	302542	15100	84	10000			
209	207	337395	302555	9118	66.1	8016			
210	208	337405	302573	5289	25	2395			
211	209	337394	302594	7984	25.9	4591			
212	210	337374	302594	4004	116.1	13013			
213	211	337353	302594	4400	19	2200			
214	212	337415	302596	6094	27	2697			
215	213	337415	302573	4108	18	1804			
216	214	337435	302565	3992	16	1697			
217	215	337435	302535	4790	20	2295			
218	216	337435	302525	6000	23	3000			
219	217	337435	302495	6857	36	3604	1050	18.2	700
220		337455	302455	10900	84	9000			
221		337483	302455	8709	50.1	5105			
222	218	337495	302474	7086	36.9	4192			
223	219	337505	302495	4200	25	2600			
224	222	337473	302515	5656	20	2503			
225	223	337465	302495	8124	43.1	4413	1100	21	1000
226	224	337455	302515	3700	18	1900			

227	225	337475	302523	7493	22	4795	330	6.6	700
228	226	337455	302535	7086	32.9	3743	440	9.4	440
229	227	337465	302565	3097	16	1898	168	4.3	200
230	228	337455	302575	3643	13	1647			
231	229	337472	302595	10010	70.1	8008			
232	230	337475	302614	6144	30	3097			
233	231	337455	302595	4309	13	1904			
234	232	337435	302605	3504	13	2002			
235	233	337457	302615	2794	6	998	198	1.9	90
236	234	337423	302631	5700	34	5400			
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238	236	337437	302642	2603	5	1001			
239	237	337465	302635	4700	15	1400			
240	238	337364	302664	1998	5	803			
241	239	337435	302665	8308	35	3303			
242	240	337135	302203	24500	12	1300			
243	241	337263	302465	3403	4	901			
244	242	337285	302485	2100	7	900			
245	243	337255	302485	5912	16	1503			
246	244	337287	302505	3938	9	1296			
247	245	337315	302525	5506	21	1902			
248		337295	302535	4088	9	1296			
249		337297	302557	5305	59.1	5255			
250	246	337283	302574	3900	13	2100			
251	247	337306	302577	4304	13	2352			
252	250	337296	302585	2597	10	3497			
253	251	337313	302602	20618	12	3287			
254	252	337315	302615	4672	23.9	5268			
255	253	337335	302635	4313	14	2307			
256	254	337277	302606	2689	6	1096			
257	255	337352	302613	1804	8	1403			
258	256	337353	302632	1363	6	802			
259	257	337377	302632	3490	11	1396	174	3.5	150
260	258	337404	302620	7178	22.9	2493			
261	259	337395	302648	4995	38	4496			
262	260	337406	302664	8425	26.1	3711			
263	261	337404	302668	4208	16	1904			
264	262	337426	302685	6106	14	2102			
265	263	337465	302695	2400	7	1300	110	2.4	130

266	264	337495	302695	3190	11	1097			
267	265	337495	302725	4192	5	699			
268	266	337445	302745	22954	22	3792			
269	267	337473	302768	1386	3	409			
270	268	337353	302645	1380	4	700			
271	269	337362	302652	448	1	239			
272	270	337377	302664	2020	7	995	45	1.9	120
273	271	337384	302654	2792	9	1246	68	2.7	150
274	272	337385	302674	2200	6	800	72	1.8	70
275	273	337365	302674	1128	3.5	479			
276		337374	302692	1710	5	800	48	1.4	80
277		337355	302694	1770	4	700			
278	274	337334	302655	341	1	271			
279	275	337333	302673	1552	6	796			
280	278	337395	302715	2124	6	902			
281	279	337395	302736	1962	6	801			
282	280	337375	302725	2888	6	896			
283	281	337365	302745	1610	5	800			
284	282	337382	302764	2038	7	799			
285	283	337335	302725	1650	3	600			
286	284	337340	302786	2503	23	2803			
287	285	337105	302063	810	0.5	220	24	0.6	24
288	286	337016	302079	669	1	279	13	0.5	21
289	287	337035	302155	888	1	279			
290	288	337105	302185	1433	3	411			
291	289	337145	302145	1872	1	410			
292	290	337075	302255	1329	1	370	53	1	43
293	291	337185	302355	1693	2	697			
294	292	337233	302413	3490	3	698			
295	293	337105	302445	1030	1	350	30	0.7	24
296	294	336995	302415	980	0	260	25	0.5	11
297	295	337198	302425	7415	5	802			
298	296	337206	302470	1423	1	501			
299	297	337143	302522	1715	2	698			
300	298	337035	302593	4935	9.5	1396			
301	299	337245	302502	8818	30.1	3257			
302	300	337243	302553	6757	34	5305			
303	301	337243	302573	1916	4	1098			
304		337265	302605	1638	4	1099			

305		337213	302593	2014	4	997			
306	302	337125	302635	1011	0.5	360			
307	303	337297	302635	1878	5	703			
308	306	337215	302717	1317	0	359	42	0.7	32
309	307	337065	302715	1125	2	418	29	0.8	29
310	308	337115	302815	1502	2	390	45	0.9	54
311	309	337197	302784	518	0	269			
312	310	337275	302885	588	0	279	9	0.4	26
313	311	337396	302785	3353	10	1201			
314	312	337396	302866	922	2	411	35	1	26
315	313	337505	302836	1306	4	598			
316	314	337536	302815	578	4	648			
317	315	337595	302755	2455	2	271			
318	316	337569	302665	2645	2	269			
319	317	337502	302628	5400	19	1700			
320	318	337646	302605	2856	2	331			
321	319	337517	302525	6807	21	2553			
322	320	337569	302433	6269	18.9	1791			
323	321	337565	302333	8809	30	3103			
324	322	337635	302245	7515	19	1703			
325	323	337665	302395	4304	7	541			
326	324	337555	302565	3888	9	798			
500	500	337002	302505	113000	111	11667			
501	501	337000	302485	1468	2	370			
502	502	336982	302505	48100	89.2	7014			
503	503	337000	302527	77150	119.2	9018			
504	504	337022	302505	2407	3	542			

9.3 Appendix 3 British Geological Survey – NBC Pb Contaminant Distributions as per Ander et al. (2013)

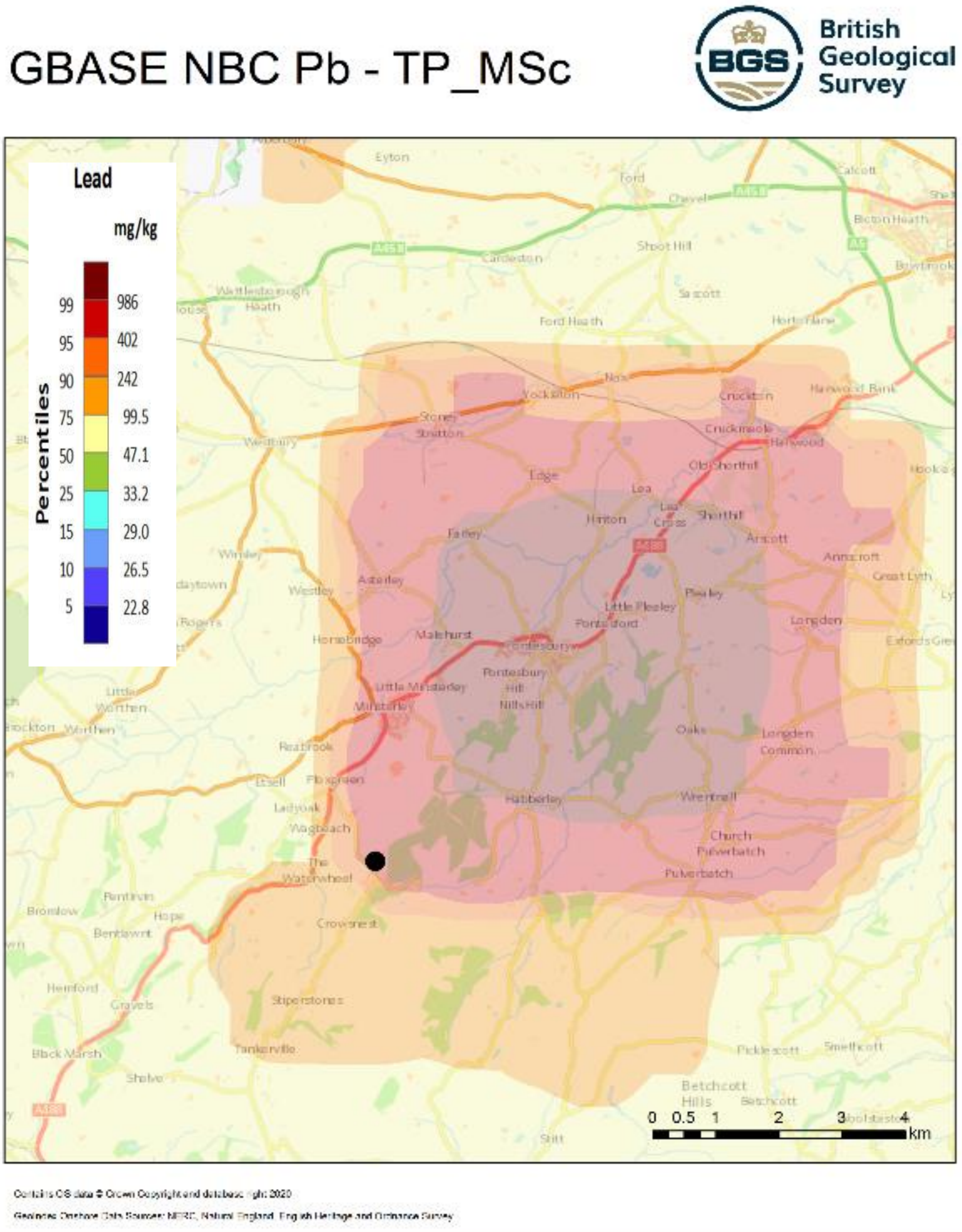
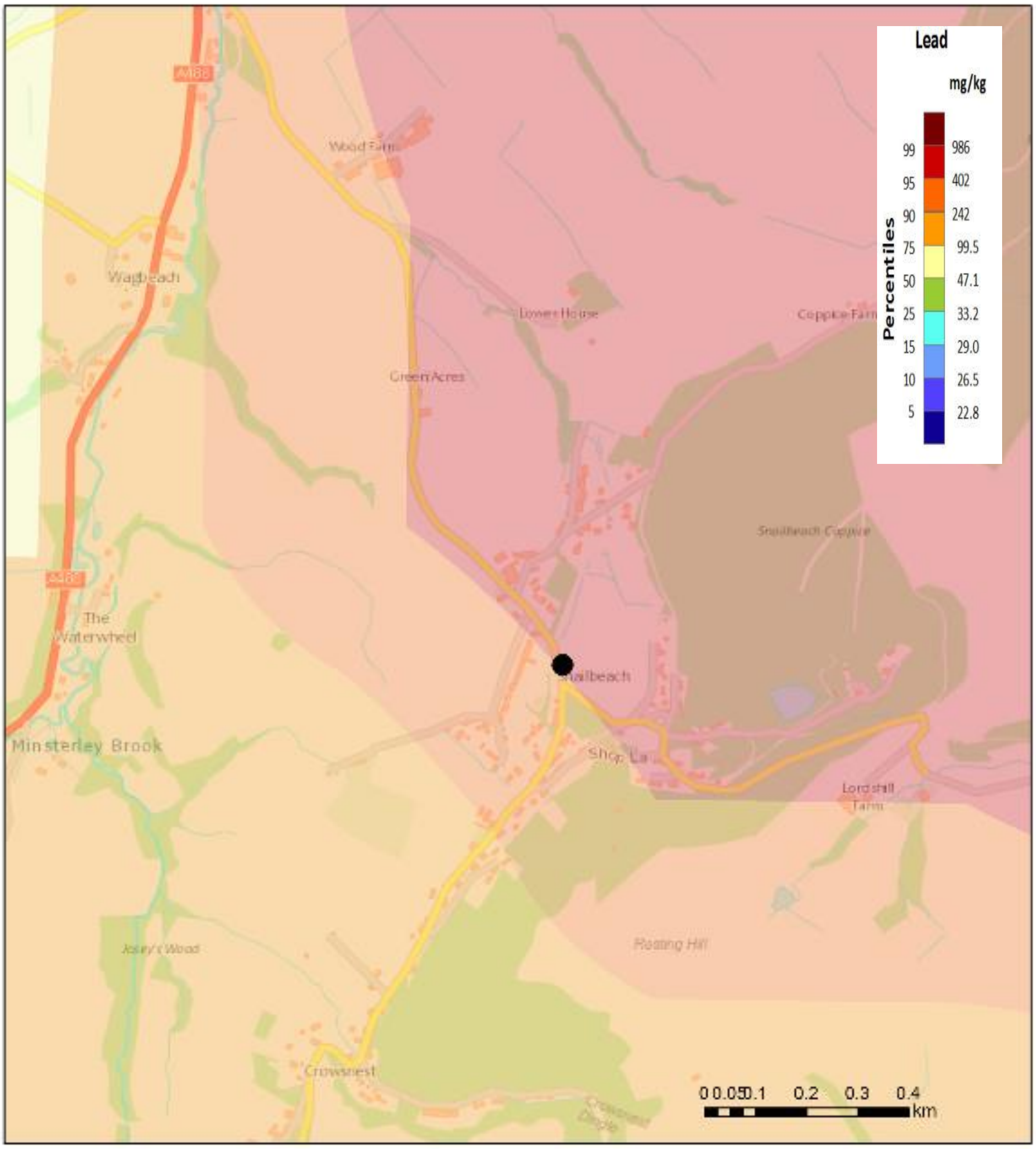


Figure 9-1 Map of West Shropshire Orefield - British Geolological Survey - Interpolated NBC data as derived by Ander et al. (2013) (URL: https://mapapps2.bgs.ac.uk/geoindex/Service.asmx/GeneratePDF) Accessed: 09/09/21

GBASE NBC Pb - TP MSc



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GeoIndex Onshore Data Sources: NERC, Natural England, English Heritage and Ordnance Survey

Figure 9-2 Map of Snailbeach - British Geolological Survey - Interpolated NBC data as derived by Ander et al. (2013) (URL: https://mapapps2.bgs.ac.uk/geoindex/Service.asmx/GeneratePDF) Accessed: 09/09/21

9.4 Appendix 4 Tables and Boxplot for Background Value - Pb (ICP-MS, <250µm) data

Table 9-3 Table of summary data for Background Value - Pb (ICP-MS, <250um) data

ICP-MS Pb Data - Central Mine Area and Outliers	
Mean	3935.3
Standard Error	558.3
Median	3564.0
Mode	#N/A
Standard Deviation	2162.4
Sample Variance	4676120.6
Kurtosis	-1.1
Skewness	0.1
Range	6408.6
Minimum	564.7
Maximum	6973.2
Sum	59029.7
Count	15.0
Confidence Level(95.0%)	1197.5
95th Percentile	6908.4
90th Percentile	6785.1
75th Percentile	5341.6
50th Percentile	3544.0
25th Percentile	2188.7
10th Percentile	840.7
UCL MEAN	**5132.8**
Upper CI (95%)	**8105.9**
Lower CI (95%)	5710.9

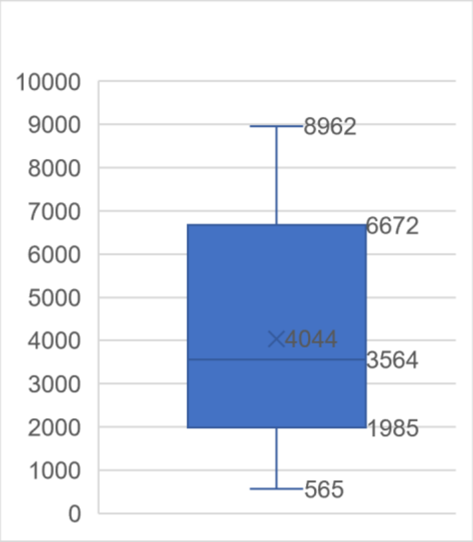

Figure 9-3 Boxplot of ICP-MS Pb Extractable (<250um) concentrations minus the Central Mine Area.

Table 9-4 Table of Central Mine Values (A), ICP-MS Pb (<250) data minus Central Mine Area (B) and Statistical / Judgmental Outliers (B).

(A) Central Mine Area Values	
TP05	14496.5
TP12	3645.8
TP13	4177.3
(B) ICP-MS Pb (<250um) Data - Central Mine Area	
TP53	764
TP47	565
TP46	917
TP40	1576
TP32	2393
TP26	3524
TP22	2520
TP19	3564
TP17	4902
TP14	6660
TP11	4064
TP10	6973
TP09	4561
TP08	6683
TP07	3241
TP06	6887
(C) Judgemental Outlier	
TP02	8962