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Kossoff, David and Hudson-Edwards, Karen A. and Howard, A.J. and Knight, D. (2016) Industrial mining heritage and the legacy of environmental pollution in the Derbyshire Derwent catchment: quantifying contamination at a regional scale and developing integrated strategies for management of the wider historic environment. *Journal of Archaeological Science: Reports* 6 , pp. 190-199. ISSN 2352-409X.

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**Industrial Mining Heritage and the Legacy of Environmental Pollution in
the Derbyshire Derwent Catchment: Quantifying Contamination at a
Regional Scale and Developing Integrated Strategies for Management of
the wider Historic Environment**

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Accepted for publication by: *Journal of Archaeological Science Reports*

Keywords: Derwent Valley Mills World Heritage Site; Derbyshire; lead mining;
heritage; contamination; fluvial; aeolian

Abstract

The Derwent Valley Mills World Heritage Site (DVMWHS) exemplifies and records the 18th century birth of the factory or mill technology, and for the industrial spinning of cotton. The site is therefore a key global heritage asset. The Derbyshire Derwent catchment also contains another significant cultural asset with a long history – that of mining and, in particular, lead (Pb) mining. In this paper research on mining- and non-mining related Pb contamination of the Derwent catchment is reviewed and used to identify the risks it poses to the DVMWHS. The upper Derwent soils, though not impacted by mining, have high sediment-borne Pb concentrations, and the Pb is sourced from local conurbations (principally Manchester) and carried to the upper Derwent on the wind. River sediments in the middle and lower parts of the Derwent catchment are contaminated with Pb mined mainly between the 18th and 19th centuries and before, possibly as far back to the Bronze Age. The potential for large-scale, acidity-related chemical remobilization of this Pb is low in the Derwent catchment due to the largely alkaline nature of the underlying soils, but the potential for oxidation-reduction-related, and physical (flood-related), remobilization, is higher. Management guidelines for mining heritage assets and the DVMWHS are developed from the reviewed information, with the view that these will provide a framework for future work in, and management of, the DVMWHS that will be applicable to other World Heritage Sites affected by ongoing and past metal-mining. Focused collaborative work between archaeologists, geochemists, geomorphologists and mineralogists is vital if the risks to the DVMWHS and other similarly-affected World Heritage Sites are to be quantified and, if necessary, mitigated.

1. Introduction

Mining can introduce contaminants of a variety of types into the wider environment. In the case of metal mining this applies not only to the targeted metal itself, but also to those metals extracted in significant quantities as by-products and which form components of the waste stream (Lottermoser, 2010). The Earth's surface is, as a result, being continuously and increasingly contaminated with metal-bearing residues both as a function of higher demand, and as ever lower ore grades are exploited (Mudd, 2010; van Vuuren et al., 1999). In countries where metal mining forms part of the economy, its origins can often be traced back several centuries or millennia and, depending on the level of development of the country, these historic remains can be viewed in a positive or negative light. On the one hand historic mining and metal working sites form an intrinsic part of humanity's commercial and industrial history and are therefore potentially valuable heritage assets (Edwards, 1996; Palmer et al., 2012; Pyatt et al., 2005), especially if developed as part of wider geoconservation and geotourism initiatives (Larwood et al., 2013). On the other hand, these sites can constitute a serious environmental hazard because of residual contamination (Hornberger et al., 1999; Macklin et al., 1997). Therefore a tension, or dichotomy, commonly exists between cultural and environmental imperatives.

The United Kingdom (UK) affords a good example of an area where the impacts of historic mining assets are significant. During the mid-19th century the UK produced 75% of the world's copper (Cu), 60% of the tin (Sn) and 50% of the Pb (Harvey and Press, 1989; Zhang, 2008). During the latter part of the 19th and early 20th century, UK base-metal mining went into a terminal downturn due to declining domestic grades and the discovery of large, economically viable deposits overseas (Byrne et al., 2012). It has been conservatively estimated that the UK has over 3,000 abandoned metal mines (Jarvis et al., 2007). Many of

these mines and their associated adits, surface buildings, equipment and, most significantly, spoil heaps, will be contaminant sources for several centuries to come, or even longer (Davies and Lewin, 1974; Gamarra et al., 2014; Lewin et al., 1977; Younger and Wolkersdorfer, 2004). The impact of contamination may, with time, extend over a much larger scale. For example, agricultural land over a large stretch of the Swale (north Yorkshire) catchment was adversely affected by the remobilization of historic contaminants during the severe autumn flood of 2000 (Dennis et al., 2003). Additionally the wind may be a significant contaminant vector. For example, the isotopic signature of Pb detected in the Greenland ice dating between 300 -600 AD suggests that Pb is derived from Roman mining and processing activity in southern Spain (Rosman et al., 1997). Globally, many areas are impacted by the legacy of past metal mining and metal processing. A plethora of examples can be drawn from each of the continents: Mid-Welsh catchments, UK (Davies and Lewin, 1974; Lewin et al., 1977), the Matylda catchment, southern Poland (Ciszewski et al., 2012), Law Dome, Antarctica (Burn-Nunes et al., 2011), Guadalupe River and San Francisco Bay, California, USA (Thomas et al., 2002), the Pilcomayo catchment, Bolivia (Hudson Edwards et al., 2001), Endeavour Inlet, New Zealand (Wilson et al., 2004), Katanga, The Congo (Banza et al., 2009) and multiple locations in Japan (Arao et al., 2010).

The European Commission has laid out a framework for good ecological and chemical water quality (European Commission, 2015). Because water quality will be impacted upon by climate change in the future (Whitehead et al., 2009), it is important that catchment management and planning take this into account. In England and Wales, mining poses the most widespread threat, after agricultural contamination, to these water-status objectives, with 26 out of 356 groundwater bodies (7.3 %, but 14 % by land surface area) and 226 out of 5868 surface water bodies (3.9 %, but 7 % by river length) ‘at risk’ (Gandy et al.,

2007). Moreover, as a consequence of climate related increases in flooding, the problems posed by historic mining contamination are likely to continue and intensify (Foulds et al., 2014).

The ongoing management of historic mining- and associated impacted-sites poses a number of diverse challenges. Unlike current mining operations in which the operating company is often legally responsible for managing the environmental consequences of its actions, there is no such clear line of accountability with historically contaminated sites (Commission of the European Communities, 1993; Larson, 2005; Wilde, 2001). Orefields, by their very nature, are commonly associated with high background (non-anthropogenically derived) metal concentrations. Within a historic orefield, individual sites will have differing contaminant profiles as a function both of location and the type of extractive/processing activity carried out. For example, the mineralogical form and hence environmental mobility of waste materials (tailings) found within adits is likely to be significantly different from that found at smelters (Rieuwertts et al., 2000). ‘Tailings’ are defined as the residual uneconomic residue remaining after the mining- targeted material has been extracted (Hudson-Edwards et al., 2011). Over time these contaminants are disseminated into the wider environment, with fluvial process playing a leading role in such dispersions (Miller, 1997). Their distribution process may be defined as active or passive. Active transformation occurs when the mining sediment transforms the river channel; for example, in the wake of a tailings dam spill (Kossoff et al., 2014). By contrast, passive dispersion occurs when mining-contaminated particulates are disseminated as part of the normal sediment load in the fluvial regime (Macklin et al., 2006). In a global context passive dispersal is the dominant of these two processes, although in reality this is not a binary classification and a spectrum of dispersion behaviour has been reported to occur between these two end members.

Fluvial processes are the most studied, and hence understood, distributor of mining-derived contaminants. Wind-borne (aeolian) dispersion is also of significance, however, particularly both as a consequence of smelting activities and in arid climates where the soil is correspondingly dry and prone to such mobilisation (Candelone et al., 1995; Cattle et al., 2012; Csavina et al., 2012; Petavratzi et al., 2005; Razo et al., 2004). Again, as with fluvial processes, aeolian dispersion might be impacted by climate change. For example, the onset of droughts might accelerate the dispersion of contaminants; however, it should also be noted that this would tend to be mitigated by higher rainfall. Therefore the contamination pattern of a historic orefield is likely to change with time, even if industrial activity has ceased (Younger, 1997). If an understanding of such an evolution is to be attained, then knowledge of the amount and nature of the initial contaminant input and how this has been modified and distributed is required. This knowledge can then be used to model the development of future contaminant dispersal patterns, particularly in the light of their likely climate change-driven acceleration.

The UK Derbyshire Derwent catchment contains a wealth of metal-mining and associated processing sites, and these are mainly associated with Pb. These remains constitute important heritage assets, despite the growing awareness of contamination, which in itself is an historical artefact (Howard et al., 2015). In addition to the mining legacy, the middle and lower reaches of the catchment also contain the UNESCO inscribed Derwent Valley Mills World Heritage Site (DVMWHS), which encompasses a series of 18th and 19th century cotton mills recording the birth of the modern factory system, together with its associated infrastructure (e.g. workers housing, schools, churches, model farms) (UNESCO, 2014). Since the World Heritage Site lies downstream of the major former mining area, there may be a risk to these globally important historic assets from mining-related contamination.

However, the risk, and its implications for management and protection of the resource, has not been determined.

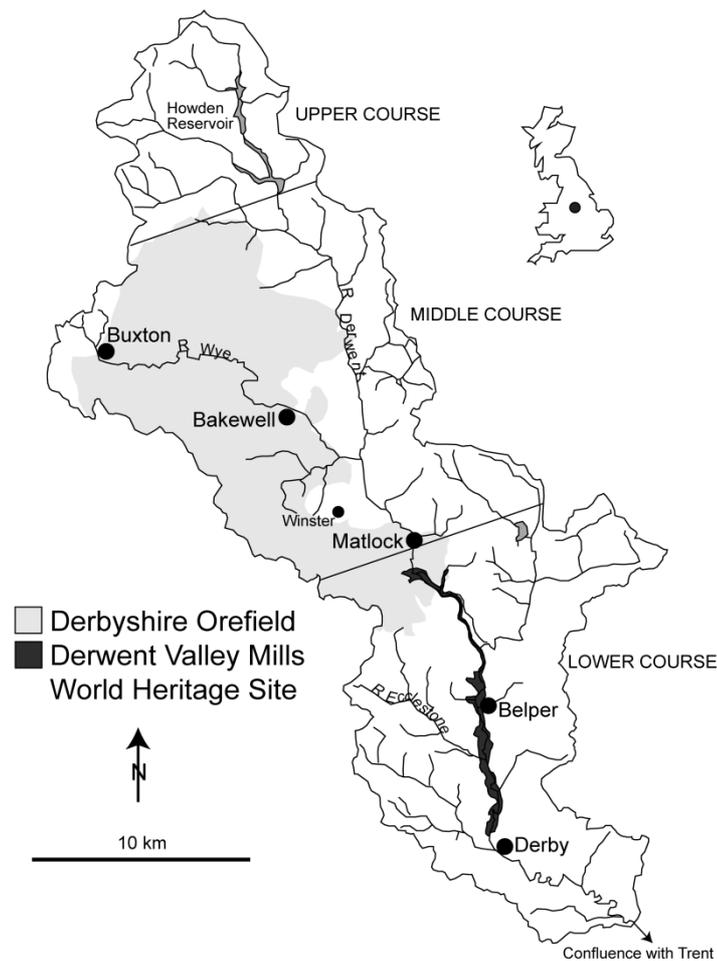
The aims of this paper are to review the literature on the geology, physiography, lead mining history, metal contamination and heritage in the Derwent catchment, and to use this information to provide a framework for future work in, and management of, the DVMWHS that will be applicable to other World Heritage Sites affected by ongoing and past metal-mining, both in the UK (e.g. Cocks, 2010) and globally (e.g., Potosí, Bolivia, Gtai, 2010; Guanajuato, Mexico, López-Doncel et al., 2013; Gauteng Province, South Africa, Durand et al., 2010). As well as exploring the issues of contamination and heritage, we also consider the opportunities for heritage to be a driver for sustainable development and ecotourism. Lead is the principal contaminant in the Derwent catchment and its risk to the DVMWHS therefore forms the focus of this paper.

2. Physiography and Mining History of the Derwent catchment

The River Derwent rises in the Peak District on Bowden Moor at 590 m OD and has a catchment area of 1,194 km². It flows for 80 km in a southerly direction until it joins the River Trent, just to the south of Derby (Figure 1). Physiographically, the river can be divided into three parts. The upper course comprises the high Carboniferous gritstone moorlands and blanket peat cover above the Derwent reservoirs, which were constructed during the early-mid 20th century. For example, Ladybower, the largest of the three reservoirs, was completed in 1945, although the reservoir took a further two years to fill. The moorlands are subject to very high annual rainfall, in excess of 1,450 mm per year. The middle course comprises the reach downstream of the reservoirs as far as the head of the Matlock Gorge, a Carboniferous limestone feature. In this part of the system, the Derwent is joined by an important tributary,

the Wye, which flows off the limestone uplands draining the western part of the catchment. The lower course comprises the length between the end of the Matlock Gorge and the Trent confluence; it includes the 24 km reach designated as the DVMWHS (Figure 1) between the Masson Mills near Cromford and the Silk Mill in central Derby. At Duffield, within the DVMWHS, the Derwent is again joined by an important west bank tributary, the Ecclesbourne River, which drains the historically significant lead-mining areas around Wirksworth and Carsington. The terms upper-, middle- and lower-course will henceforth be used when talking about specific reaches of the Valley floor (Figure 1).

Figure 1. Location of the Derwent catchment, showing the Derbyshire Orefield and the Derwent Valley Mills World Heritage Site (DVMWHS).



The orebodies that were mined for Pb in the Derwent catchment occur where hydrothermally-derived mineralized veins occur along bedding planes, faults and joints within the limestone and between adjacent bedded strata (Cox and Singer, 1986; Ineson and Ford, 1982). These bodies are *c.* metre-wide, ribbon-like veins of limited vertical extent that extend laterally for up to a kilometre (Ineson and Mitchell, 1972; Palumbo-Roe and Colman, 2010), as well as more massive bodies that infill pre-existing activities and structural zones of weakness within limestone (Ford, 2001; Quirk, 1993). In contrast to copper which, from excavations at Ecton Hill in Staffordshire (Barnett et al., 2013) is known to have been mined in the Peak District since the Early Bronze Age, the case for lead mining in the Peak District prior to the mediaeval period rests currently on indirect evidence, including rare prehistoric artifacts (Barnatt 1999; Barnatt and Smith 2004; Guilbert 1996; Barnatt et al., 2013) and in Roman period discoveries of inscribed lead ingots and traces of ore processing activities (Barnatt 1999; Dearne 1990). This provides circumstantial evidence for lead mining in the region from the late prehistoric period, but direct evidence for lead mining is currently firmly focused upon the medieval and later periods (Blanchard 1971; Kiernan 1989; White 1991). By the 17th century, Pb was second only to wool in value as a British export (Slack, 2000; Willies and Parker, 1999). Until the advent of the Industrial Revolution, however, mining enterprises were small, with outputs from mines and smelters often no more than a few tons per year. The large topographical footprint of the mines and associated processing facilities, coupled with the small-scale of the individual enterprises, has therefore resulted in a multitude of small Pb point sources.

During the 18th and 19th centuries, as industrialisation proceeded apace, greater outputs were produced by fewer mines. By 1760, the seven largest mines in the Derwent catchment belonged to major companies and produced six times the combined production of

the 22 other mines in the local mining area jurisdiction (Willies, 1986). The Mill Close Mine at Darley Bridge produced around 70 % of the total Derbyshire Pb during the late 19th- and early 20th-century – a very significant proportion of total production before it closed in 1939 (Brearley, 1977). For the Derbyshire Orefield as a whole, overall ore production has been estimated to be in the millions of tons, with the bulk of this sourced from within the Derwent catchment (3-6 million tons of Pb; Ford and Rieuwerts, 2000), with maximum Pb production being reported as having occurred during the 18th century. Therefore, mining since the Industrial Revolution has produced additional hotspots of Pb-rich material.

3. Pb Contamination Legacy of the Derwent Catchment

3.1. Distribution of Pb in the Derwent Catchment

The Derwent catchment hosts sediment-borne Pb hotspots that have the highest concentrations of Pb (3,960-10,000 mg/kg) recorded in England and Wales (Table 1). Many of these concentrations exceed internationally agreed safety levels for sediments and soils (Table 1). An extensive survey of Derbyshire surficial deposits and associated underlying geology carried out in 1970s, which encompassed the Derwent catchment (Burek and Cubitt, 1979), showed that most of the catchment's surficial deposits exhibit Pb concentrations of *c.* 400 mg/kg. In five former Pb mining areas, however, concentrations reach as high as 1,200 mg/kg. The sampling methodology of this study aimed to avoid areas of obvious Pb mineralisation; hence, these data most probably underestimate the degree of mining-derived contamination of the surficial deposits. Subsequent work by the British Geological Survey for their Geochemical Baseline Survey of the Environment, also showed extensive Pb contamination of river sediments (Figure 2). On a local scale, however, Pb distribution in

soils is not homogeneous and is difficult to predict (e.g. Winster village, 53.1419° N, 1.6399° W, Figures 1, 3).

Figure 2. Lead (Pb) concentrations in stream sediments in the Derwent catchment. Adapted from British Geological Survey (2010).

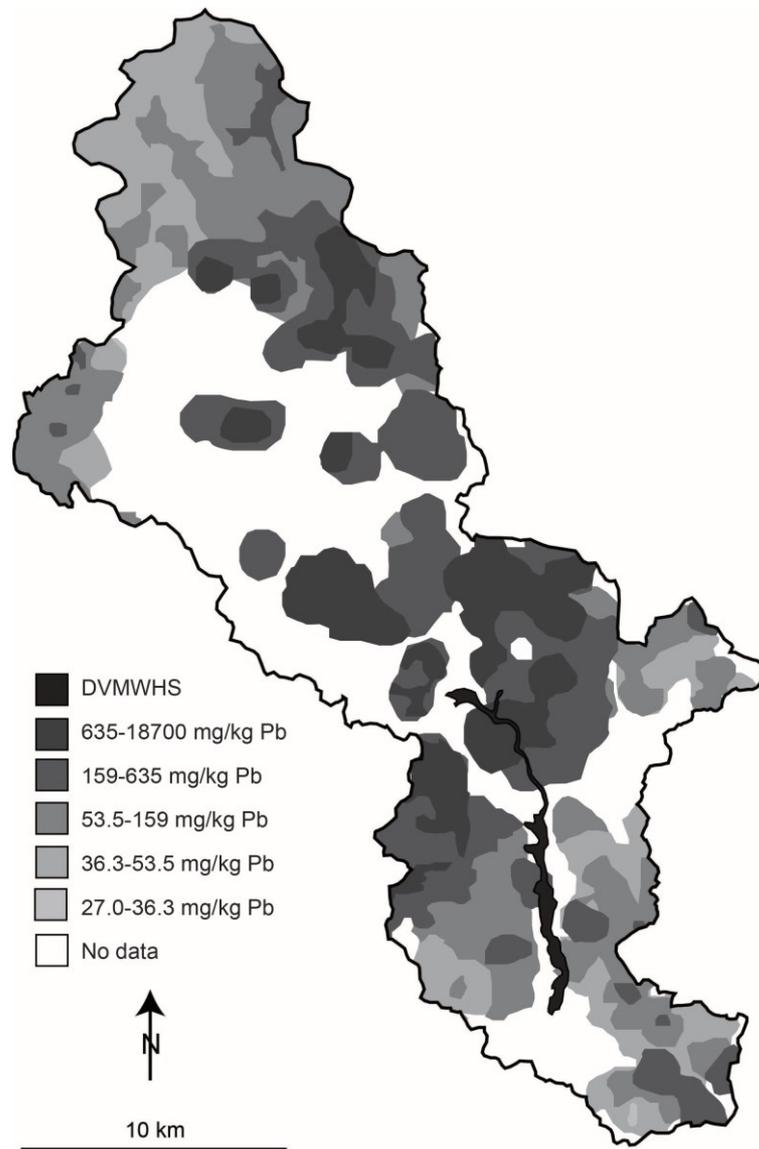
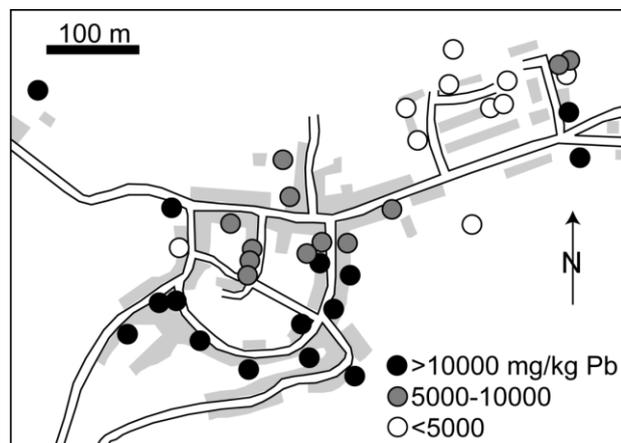


Figure 3. Variable distribution of Pb in garden soil, Winster. Adapted from Cotter-Howells and Thornton (1991).



3.2. Introduction of Pb into the Derwent catchment by fluvial processes

Fluvial processes are responsible for introducing metals such as Pb into catchments. This occurs by the stream erosion of Pb-bearing natural soils, the direct discharge of Pb-bearing mine or industrial wastes into rivers, and the remobilisation of mine or industrial wastes and mining-contaminated alluvium (Dennis et al., 2003; Leenaers, 1989; Talbot 1983). An example of natural erosion occurs in the upper Derwent catchment. Here the, often aeolian-contaminated, peat catchment soils are the most eroded in Britain, with large areas of bare flats and dissected gullies (Tallis, 1997, Moors For The Future, 2015). Concentrations of Pb in the near-surface peat layer of the Upper North Grain, one of the small headwater streams flowing across the eroding peat, are in excess of 1,000 mg/kg (Rothwell et al., 2005) (Figure 4). A word of caution is necessary in the interpretation of these data. The high Pb concentrations are almost certainly a consequence of anthropocentric activities. In order to be certain, however, further work is required to set these Pb concentrations against natural background levels (Le Roux et al., 2010), perhaps by the deployment of isotope provenance techniques (Gulson et al., 1995). The aquatic Pb flux arriving via the feeder streams to the

Howden Reservoir is estimated at between 29.9 and 7.17 kg per year (Figure 5; Shotbolt et al., 2008). Given that there has been no mining activity and, further, that there are no reports of Pb mineralization in the upper catchment, the major contributor to this flux is almost certainly sourced from an anthropocentrically-derived atmospheric flux. It may be concluded, therefore, that catchment soils are currently acting as a sink for this Pb and that the reservoir is acting as a secondary store for Pb sourced from those same soils. It can be further estimated that 0.023 % of the catchment's Pb is mobilised by fluvial processes each year. Therefore *c.* 2.3% of the catchment soil Pb pool has been retained in the reservoir sediments over its 91 year lifespan (Shotbolt et al., 2008).

Figure 4. Down-core profiles of Pb concentration and the environmental magnetic parameters of χ (magnetic concentration) and SIRM / ARM (magnetic grain size) from Upper North Grain, a small headwater stream in the Derwent catchment. Dates for specific horizons are shown in two positions. Adapted from Rothwell et al. (2005).

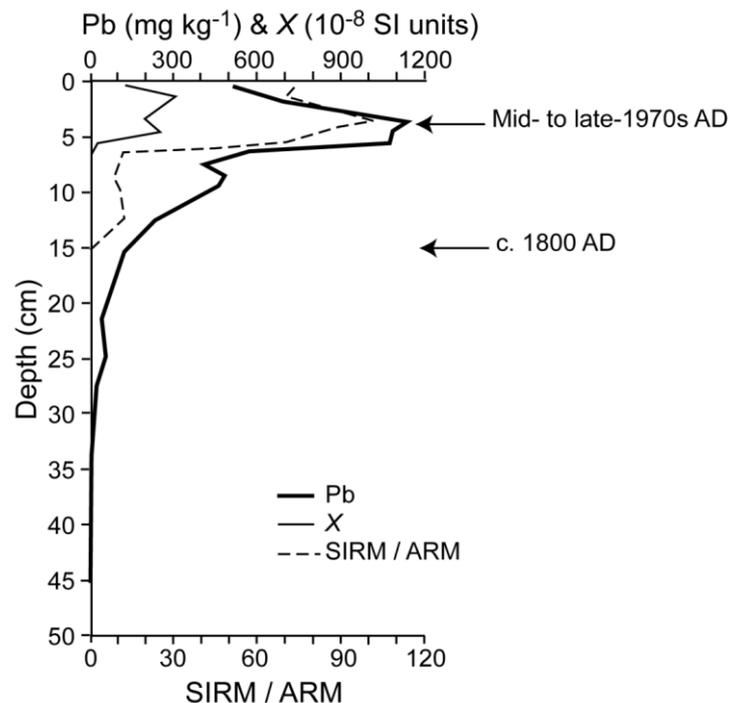
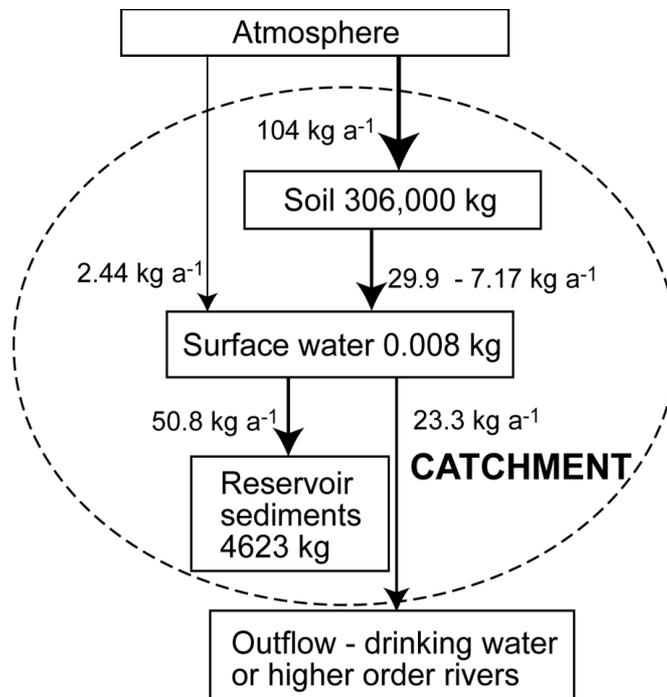


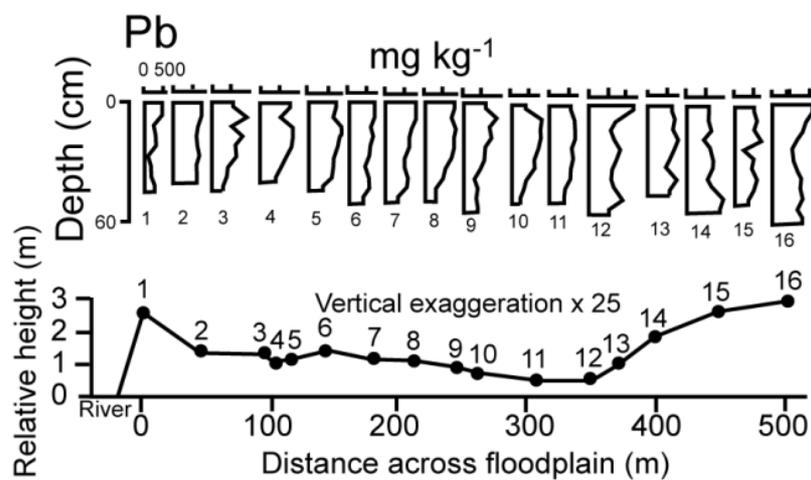
Figure 5. Mass balance model of Pb transport and storage for the Howden catchment in 2005. Adapted from Shotbolt et al. (2008).



In mining-affected river systems, Pb-bearing sediment has often been discharged passively as a waste product of the mining process (e.g., in the Tyne catchment, NE England, mainly during the late 18th and 19th centuries; cf., Macklin and Dowsett, 1989). Patterns in the Pb composition of floodplain sediments suggest that passive dispersal of Pb-contaminated sediment occurred in the Derwent catchment. For example, sediment-borne Pb concentrations in the River Ecclesbourne decrease downstream from the mining sites, probably as a consequence of dilution from uncontaminated sediment (Moriarty et al., 1982). This is not the case, however, with the Wye where, possibly as a function of additional mining-derived inputs, no clear downstream contamination dilution can be observed; by contrast, the burden increases downstream towards the Derwent confluence (Zhang, 2008). Sediment-borne Pb concentrations in fluvial soils downstream of the Mill Close Mine (the most productive of the

Derbyshire Orefield) are also elevated above background Pb concentrations (Bradley and Cox, 1990). These concentrations do not, however, show clear trends either vertically or horizontally with distance from the river channel (Figure 6; Bradley and Cox, 1990), suggesting long-lived, mining-related inputs of Pb to this area that may be continuing to the present day. For example, Bradley and Cox (1990) estimated that the supply of metals to the Mill Close reach of the Derwent is 360 kg Pb per year, which equates to a loading of 266 mg Pb per m² to the floodplain surface.

Figure 6. Transect across the Derwent floodplain at Mill Close, showing sediment-borne concentrations of Pb. Adapted from Bradley and Cox (1986).



A documented example of direct, catastrophic fluvial discharge of Pb-bearing materials to the Derwent is the Stoney Middleton tailings dam failure in January 2007 (the active dispersal pattern referred to in the Introduction). Approximately 113 tons of fine-grained mine tailings were released into Stoke Brook and the Derwent following heavy rainfall leading to the failure (Figure 7; Environ Liverpool, 2008; Worrall, 2009). Samples of

the deposited tailings taken immediately after the spill exceeded the Swedish contaminated soil guidelines for Pb (Table 1). Clean-up operations carried out in June 2008 revealed that a much larger spill had occurred in 1968, and that many of those tailings remained within the floodplain sediments (Worrall, 2009). This suggests that the impacts of the 2007 Stoney Middleton tailings dam failure served to add to historic contamination, just as with other failures elsewhere in the world (e.g., the 1996 Porco tailings dam spill in Bolivia, Macklin et al., 1996).

Figure 7. Mining-deposited sediment at Stoney Middleton village and in the Derwent channel following the Glebe Mine tailings dam failure. Used with permission.



Table 1. Contaminated land guideline values for lead for selected countries, and Pb concentrations in UK-wide soils and in Derwent catchment soils and tailings. Adapted from Rothwell et al. (2005).

Country	Contaminated land guideline	Pb (mg/kg)	Reference
UK	SGV: residential land	450	4
	SGV: allotment		4
	SGV: commercial / industrial land	750	4
Sweden	Guideline value: polluted soils (slightly serious – extremely serious)	<80 - >800	8
Netherlands	Target level: polluted soil /sediment	85	9
	Intervention value: polluted soil / sediment	530	9
Canada	CSoQGs: agricultural land	70	2
	CSoQGs: residential / parkland	140	2
	CSoQGs: commercial land	260	2
	CSoQGs: industrial land	600	2
Australia	SIL: residential land	300	7
	SIL: Parkland	600	7
	SIL: commercial / industrial land	1500	7
UK	Average soil values (range, <i>mean</i> , median)	3 – 16338 (74, 40)	6
Derwent	Darley Dale (range, <i>mean</i>)	130 – 1200 (620)	1
	Ambaston (range, <i>mean</i>)	340 – 1400 (1000)	5
	Winstar, garden soil (range, <i>geometric mean</i>)	2400 – 23000 (7100)	3
	Winstar, vegetable soil (range, <i>geometric mean</i>)	2200 – 22000 (9500)	3
	Stoney Middleton tailings repository (<i>mean</i>)	4600	10
	Stoney Middleton, ‘unaffected’ soil (<i>mean</i>)	1500	10
	Stoney Middleton, ‘affected’ soil (<i>mean</i>)	2000	10

Abbreviations: SGV: Soil Guideline Value; CSoQGs: Canadian Soil Quality Guidelines; SIL: Soil Intervention Level; nd: not determined. References: ¹Bradley and Cox, 1990; ²CCME, 2002; ³Cotter-Howells and Thornton, 1991; ⁴DEFRA, 2002; ⁵Hudson-Edwards et al., 2004; ⁶McGrath and Loveland, 1992; ⁷NEPC, 1999; ⁸SEPA, 2002; ⁹VROM, 2000; ¹⁰Wilding, 2007.

The geochemical evidence suggests that mining has provided much of the fluvially-transported Pb in the Derwent and Pb isotopic fingerprinting suggests that it may also be important on a wider regional scale. Lead isotopic data for sediments from the River Trent downstream of the Derwent confluence suggest both a mining- and industrially-derived source for Pb, in the latter case from a local power station and railway marshalling yard (Izquierdo et al., 2012). These data suggest that the Derwent catchment as a whole is a significant point source of contamination impacting on the Trent. The DVMWHS lies upstream of the Derwent-Trent confluence and downstream of middle and upper courses of the river; hence, any Derwent-borne Pb contamination of the Trent must also traverse the WHS and the site is therefore highly likely to be impacted by contaminated sediment. This conclusion is reinforced by sampling undertaken near the Derbyshire village of Ambaston, which lies downstream of the DVMWHS between the city of Derby and the Derwent-Trent confluence. Sediments here are highly contaminated with Pb (range: 340-1,400 mg/kg mean = 1,020 mg/kg; Hudson-Edwards et al., 2004). This contamination is likely to be derived principally from upstream mining and associated processing sources, but may be augmented by contaminants deriving from industrial sources in Derby.

3.3. Introduction of Pb into the Derwent catchment by aeolian processes

Aeolian transportation has been, and remains, an important contaminant vector for introducing Pb to the Derwent catchment. The upper Derwent, in particular, although not subject to mining input, is nevertheless significantly impacted upon by wind-transported, fine-grained Pb contamination from extra-catchment sources (Rothwell et al., 2005; Moors For The Future, 2015). Reference has already been made to the high Pb concentration of the Upper North Grain sediment profile (Rothwell et al., 2005). Emphasising the extent of this

input, Shotbolt et al. (2008) estimated the atmospheric Pb flux input into the Howden reservoir catchment to be *c.* 104 kg per year (Figure 5). The Manchester conurbation to the west provided, and to some extent still provides, the bulk of the aeolian Pb contamination to the Derwent as a function of the prevailing westerly winds (Shotbolt et al., 2008).

Ore smelting is a process which adds to the aeolian contaminant load (e.g., Outridge et al., 2011; Patterson and Settle, 1987). Historically, numerous Pb smelters were sited in and around the Derbyshire Orefield, and these probably supplied a significant proportion of the catchment's Pb load. Furthermore, although some of the smelting sites were located on Millstone Grit on the fringes of the Derwent catchment (e.g., Stone Edge), these also supplied considerable quantities of aeolian-borne Pb. At Stone Edge, for example, soil Pb concentrations remain at *c.* 500 mg/kg at 700 m in a north westerly direction from the centre of the site, where concentrations reach > 30,000 mg/kg (3 wt. %; Merry, 1988).

Smelter airborne particulate Pb transfer to the Derwent continued into the 20th century and is ongoing. The H.J. Enthoven and Sons secondary Pb smelter at Darley Dale near Matlock (on the site of the former Mill Close mine) is the largest capacity single-site Pb producer in Europe, with a production of *c.* 80,000 tons of Pb products per year. The plant is a recycling enterprise, with the Pb input stream comprising principally of spent car batteries (Enthoven and Sons, 2014). The concentration of soil-borne Pb declines from *c.* 2,000-8,000 mg/kg in and around the smelter, to 443-787 mg/kg in sites down-wind at Darley Dale, Birchover and Upper Matlock (Lageard et al., 2008). These Pb concentrations are higher than those of soils not impacted by smelting (70-196 mg/kg Pb). In 1982, the Pb concentration in the air around the plant was *c.* 1.7 $\mu\text{g m}^{-3}$, but this had fallen to 0.2-0.4 $\mu\text{g m}^{-3}$ by 1998 as a result of improved practice (Lageard et al., 2008). However, even the latter range exceeds the

Environmental Protection Agency's rolling three month average Pb 'not to be exceeded' concentration limit in air of $0.15 \mu\text{g m}^{-3}$ (EPA, 2008).

3.4. Introduction of Pb into the Derwent Catchment by chemical remobilisation processes

Many current and historic mining sites world-wide are affected by acid mine drainage (AMD), which is caused by the formation of acid- and metal-bearing solutions as a result of the oxidation of iron sulphide minerals in mine wastes (Nordstrom, 2011). However, the potential for the formation of AMD in the Derwent catchment is low. This is due to two principal factors in the catchment's mineralogical profile: the comparatively low abundance of acid-evolving iron sulphide minerals and the underlying limestone rocks, which buffer and thus forestall acidity development. Although soils developed on the upper Derwent's Millstone Grit are acidic, their soil Pb concentrations are lower than those developed on limestone, and therefore the potential for large-scale acidity-related chemical remobilisation of Pb is low.

Mineralogical analysis of soils from Winster village (Figure 3) has demonstrated, however, that chemical remobilisation of Pb has occurred in the Derwent catchment. The Pb in these soils is partitioned into a very stable (i.e., insoluble) Pb-phosphate mineral known as pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$; Cotter-Howells and Thornton, 1991), which has replaced the original Pb ore mineral galena (lead sulphide, PbS). Most of the Pb in the Derwent, however, occurs as galena (Mindat, 2015), which is less stable than pyromorphite (Scheckel et al., 2005), suggesting that potentially this Pb may be chemically more mobile than that at Winster.

It is possible that chemical remobilisation of Pb has occurred elsewhere within the Derwent, but to date this has not been studied or quantified. Floodplain environments are

subjected to regular changes in water table levels and inputs of organic matter, both of which can result impact on the mobility of metals such as Pb due to reduction-oxidation (redox) reactions (Ho et al., 2013; Shahid et al., 2012). In the case of oxidation reactions primary Pb-bearing minerals break down (e.g., galena, PbS), releasing Pb ions to solution, where they may be completely or partially taken up by the formation of secondary minerals (e.g., anglesite, PbSO₄, and cerussite, PbCO₃; Hudson-Edwards et al., 1996) or sorbed to the surface of Fe oxides (e.g., Pb-bearing goethite, FeOOH). Any ions which are not taken up *in situ* may go on to contaminate reaches of the catchment farther downstream. Reduction reactions favour the precipitation of Pb-bearing sulphides (Johnson and Hallberg, 2005). The balance between oxidation and reduction, and the ensuing impact on the mobility of Pb, is dependent on the position of the water table and, therefore, on the extent of flooding or desiccation.

4. Interactions between Heritage and Catchment Pb Contamination

It is clear that archaeological remains associated with historic metal mining, issues of pollution and contemporary environmental management are intimately linked (Howard et al., 2015). Within the boundaries of the mining landscapes themselves, the management issues that need to be addressed are relatively easily identifiable (Kincey et al., 2014), as are the stakeholder groups. However, beyond the limits of industrial activity the potential impacts of such pollution are perhaps less well considered.

In the Derwent catchment, many of the archaeological remains and historic buildings of the DVMWHS are situated downstream of the direct mining area, although some lead mining and smelting occurred within the area now demarcated as the World Heritage Site (Crossley and Kiernan, 1992; Rieuwerts, 2010). Therefore, although the UNESCO

inscription is not related to this extractive industry, the sediments contaminated with potentially toxic Pb moving through the valley floor corridor have the potential to impact on these internationally important monuments, both directly and indirectly. Direct impacts to the WHS might include (1) changing geomorphological character of the river and increased lateral erosion of the floodplain, particularly in response to changing flood frequency and magnitude, a process that was observed on the rivers of the northern Pennines during the Little Ice Age (Macklin, 1997); (2) build-up of contaminated sediments against building fabrics and historic water management structures such as weirs; (3) the remobilisation of contaminated sediments through weirs and other riverside structures during flood events, posing a risk to human health during clean-up activities; (4) risks posed to human health from areas of bare sediment that might be accessible to WHS visitors. The latter hazard is perhaps the major concern as there is a plethora of evidence going back over many years of the risks posed by Pb inhalation, particularly to the young (e.g., Centers For Disease Control and Prevention, 1997). Indirect effects of remobilization might include changes in the chemistry of the environment and changes in pH conditions that might contribute to the decay of building fabrics. It is important, therefore, to the long-term environmental health of both the DVMWHS and the wider catchment, that Pb stored within the sediment (peat) and water reservoirs of the upper catchment are not mobilized downstream. Upper catchment land managers should be aware of contamination risk onto the middle and lower courses. What must be avoided is a situation where the upper course becomes the source, rather than the store, for Pb, and thereby poses a serious threat to the conservation of heritage assets. Similarly, it is important that the sediments of the middle and lower courses remain *in situ*. Therefore the likely ongoing evolution of contaminant hotspots in the middle and lower courses should be assessed, particularly in the light of climate change and the effect this

might have on the Derwent floodplain. In the absence of such assessment, it is possible that the DVMWHS may be adversely affected by liberated pulses of contaminated sediment (c.f., Dennis et al., 2003).

In the context of heritage management, middle and lower course hotspot management potentially introduces an element of tension. Although the hotspots need to be assessed and perhaps remediated, they are historic assets in their own right and so remediation interventions should aim to be sympathetic to these structures and monuments. For example, spoil heaps, adits, mine processing floors, smelter sites and drainage soughs represent historic mining and industrial assets (Table 2). Moreover, many of these sites are contaminated with Pb, while others are populated by rare metallophyte (metal-loving) vegetation, which introduces the further aspect of 'nature conservation' into the overall management scheme (e.g. a species of liver wort found at the Stone Edge smelter; Barnatt and Penny, 2004; <http://www.derbyshirewildlifetrust.org.uk>).

Historic metal mining remains may become important drivers for sustainable regional development, ecotourism and geoconservation activities. At Potosí, Bolivia, for example, indigenous Quechua guide tourists in and around the past and current mining sites of the Cerro Rico, deriving from this a significant source of income (Pretes, 2002). In the UK context, the historic mining landscapes of Cornwall and west Devon, which also has WHS status, are considered to be key elements of the regional development plan (Landorf, 2009). Such approaches are demanding of detailed planning and analysis, not least in terms of ongoing consultations with local stakeholders (Landorf, 2009) and awareness of contaminant risk (Strosnider et al., 2011). For Cornwall this risk is highlighted by the high levels of arsenic (maximum of 6.7 wt. %), as found *in situ* in the building fabrics of the Poldice and

Table 2. Relationships between potential contamination of mining heritage assets and their management.

Mining heritage asset	Expected type and level of contamination	Mitigation and management	Heritage tension
Mining and processing sites	High if not actively managed	Active management required to forestall and possibly reduce contamination	Sites often lie outside of agricultural and urban use. They form recreational resources and natural refuges for native plants and animals
Underground passageways	Moderate, but potentially serious	Changes in water table levels may release contaminants as a function of redox changes and dissolution. Effects of former mine flooding and drying should be monitored	Tension is minimal as mitigation efforts should be aimed at maintaining the status quo for open passages. Public access should be controlled if sensitive mineralogical and/or heritage assets (e.g., water wheels) are present
Adit	Generally high	Block features or put filter systems in place	Integrity is potentially at risk as systems may be part of more extensive water management systems
Spoil heap	High	Capable of management if threat from erosion can be minimised. Capping and introducing vegetation cover are effective.	Revegetation and capping may obscure the spoil heap. Reprocessing of waste heaps to extract remaining metal may destroy heritage asset.
Tailings dams and associated impoundments	High	Historic tailings dams may fracture, releasing their contents to river basins. Natural mineral cementation reduces this risk	Tailings dams are a relatively recent innovation, so heritage tension is low
Drainage soughs	Generally low	Many soughs form a key element of catchment drainage and water supply infrastructure, and hence require management.	Modern maintenance and modification may impinge on preservation of historic assets.
Extant or collapsed smelter chimneys, bellows, etc.	Very high, particularly on internal surfaces	Awareness of contamination risk required by those responsible for site management	Possibility of public access restrictions at or around the site
Processing / smelting floor	Generally high	Monitoring of groundwater required to see if chemical remobilisation is occurring. Measures should be taken to prevent physical weathering.	Metallophytes may be present. The tensions are the same as those for mining and processing sites and spoil heaps
Mining-site pools, lakes and other water bodies	Generally high	Isolation from surrounding water courses through direct and indirect groundwater connections should be a priority	Drainage impinges on the integrity of the remains Recreational public access should be subject to monitoring and control

adjacent Wheal Busy arsenic works, which are both open to the public (Potts et al., 2002; Cornish-mining.org, 2015).

It is also pertinent to note that the Derwent in particular furnishes an example where remobilisation of metals from historic mining assets might impact on an important off-site heritage asset, in this case the textile mills and associated structures of the DVMWHS. This emphasizes the point that those responsible for landscape management should routinely approach system inheritance issues in broad (or holistic) terms. To this end, there is also an increasing impetus to view catchments as a whole in the context of water quality. This approach is exemplified by the Water Framework Directive (European Commission, 2015), which encompasses surface water, groundwater, the welfare of aquatic ecosystems and the sustainable development of all water bodies (Borja et al., 2006; Younger and Wolkersdorfer, 2004). Similarly, the development of Ecosystem Service Approaches, whereby the environment is conserved with the focused aim of benefiting humanity rather than as an abstract 'green' ideal for its own sake, dictates a wide field of view (Armsworth et al., 2007; Seppelt et al., 2011).

The Derwent catchment therefore provides material for a generic case study, permitting study of the interplay of diverse environmental and cultural variables. Such an integrated analysis demands input from many disciplines, including archaeology, history, ecology, mineralogy, geochemistry, geomorphology and geoconservation. This enables a holistic approach that from the geological perspective could provide a template for other studies of landscapes exemplifying the transition from Holocene to Anthropocene (Jordan and Prosser, 2014).

5. Conclusions

The Derbyshire Derwent catchment contains areas of high background metal soil concentrations, in particular Pb. In terms of the overall contaminant burden, however, metal mining and aeolian input into the basin significantly augment background soil concentrations to levels which often exceed regulatory limits. Mining here has had a long history, stretching back possibly into later prehistory on the basis of evidence from elsewhere in Derbyshire and the Peak District (Barnatt et al., 2013; Barnatt and Smith 2004;. Mill Close, the last major operating Pb/Zn mine in the catchment, closed in 1939, and there is a historic mining and smelting legacy of several millennia to be found in and around the valley. Moreover, aeolian contamination of the catchment, particularly by Pb, is an issue of ongoing concern, because of both continued input into the upper basin and the operation of the Mill Close smelter.

The contamination pattern of any catchment, and the Derwent is by no means an exception, is likely to be mobile rather than fixed. Moreover, climate change will impact on and most likely exacerbate contaminant mobility (Foulds et al., 2014). Hence, the DVMWHS, which lies in the middle and lower course of the catchment, is likely to be at increased risk from contaminants sourced from upstream. Yet there exists an incipient tension between the management of the risks posed by remobilization of catchment contamination to the DVMWHS and that of the preservation of the upstream historic mining assets. A sensitive, balanced and informed approach is therefore called for.

The bulk of contaminant distribution data were collected from the Derwent catchment mainly during the 1970s and early 1980s. As there has undoubtedly been considerable remobilisation of sediment since that time, contemporary sampling would be beneficial to assess accurately the risk of metal contamination. The likely extent of future contaminated sediment input into the DVMWHS should be established. The potential for ongoing water-

sediment interaction and the possibility of aqueous remobilisation of metals and their likely further deposition in secondary hosts should also be ascertained. Such a catchment-specific study is necessary if the threat to the DVMWHS is to be quantified and landscape-sensitive mitigation practices are to be implemented.

Acknowledgements

This research on which this paper is based stems from a Historic England funded project focused upon ‘*Better disaster planning and building in resilience for heritage*’ (NHPP 2C1, 6193, 6194, 6195). The project team is grateful to a number of individuals and organisations who provided support, information and encouragement throughout the life of the project. At Historic England, Kath Buxton, Jen Heathcote and Neil Redfern provided significant advice during the initial stages of project development, whilst Paddy O’Hara and Tim Allen (members of the Core Management Team) provided advice once the project was initiated. At Derbyshire County Council, Mark Suggitt (Director, DVMWHS) and Dr Dave Barrett (County Archaeologist) formed additional members of the CMT and provided additional logistical and data support. Valuable input was also provided by Steering Group members Rachael Hall (National Trust), Anna Harrison (British Geological Survey), Steve Kemp (Environment Agency), Tania Pells (DerwentWISE Partnership), Hannah Rigden (Natural England) and Ken Smith (Peak District National Park Authority). The librarians at Imperial College Library were also very helpful in sourcing previously unpublished data. We are grateful to Seth Scafe-Smith for his useful initial reading of the manuscript. Tim Mighall (University of Aberdeen) and an anonymous reviewer each provided valuable comments which considerably improved the text.

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