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Reconstructing the history of heavy metal pollution in the southern Pennines from the sedimentary record of reservoirs: methods and preliminary results

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Abstract

Although the southern Pennine uplands have experienced industrially derived heavy metal pollution for almost two hundred years, an historical analysis of its depositional record has not yet been undertaken. The area has no natural lakes but has many reservoirs, and despite the potential for sediment disturbance due to fluctuating water levels, reservoir sediments can be used as a record of heavy metal pollution. A methodology for the selection of reservoirs with undisturbed sedimentary records, and the verification of sediment stratigraphy is proposed. Preliminary results of metal analysis from the Howden reservoir indicate trace metal contamination with Zn > Pb > Cr > Ni = Cu.

Key Words

Heavy metals, sediment, reservoirs, southern Pennines, methodology.

Introduction: the southern Pennines and potential use of reservoir sediment profiles

The southern Pennines (Figure 1) is a vitally important water supply region characterised by a high density of small reservoirs (Anderson *et al*. 1988). Potential water quality problems exist due to the emission of pollutants from urban-industrial areas such as Merseyside, Greater Manchester, Leeds and Bradford, Stoke and Sheffield since the 18th Century, and their deposition onto catchment soils and reservoirs in this region. Today, metal smelting, fossil fuel combustion and vehicular emissions are the main pollutants (Foster and Charlesworth 1996). Particular concern has been expressed over emissions of heavy metals from local industrial sources, which have been shown to be amongst the highest in the country (Environment Agency 1999). Consequently, both contemporary deposition, and the past accumulation of heavy metals in potentially erodible catchment soils and in reservoir sediments, could be problematic in this important water supply area.

In the absence of long-term instrumental records, lake and reservoir sediments can be utilised as archives of catchment or atmospheric inputs. Material eroded from the catchment, deposited from the atmosphere, and organic material produced within the water body itself, builds up over time (Petts and Foster 1985) and, under certain conditions, can provide a chronological record of inputs. The use of lake sediment profiles as an historical record is a well-established environmental monitoring technique (Mackereth 1966; Oldfield 1977; Engstrom and Wright 1984). Previous studies have shown that over 90% of heavy metals in aquatic systems are bound to sediments (Horowitz 1991; Calmano *et al.* 1993), and that, therefore, much of the metal input is retained in lake systems. Analysis of sediment profiles has allowed the determination of heavy metal loading in many regions with natural lakes (Foster *et al*. 1987; Johnson and Nicholls 1988; Williams 1991; Blais and Kalff 1993).

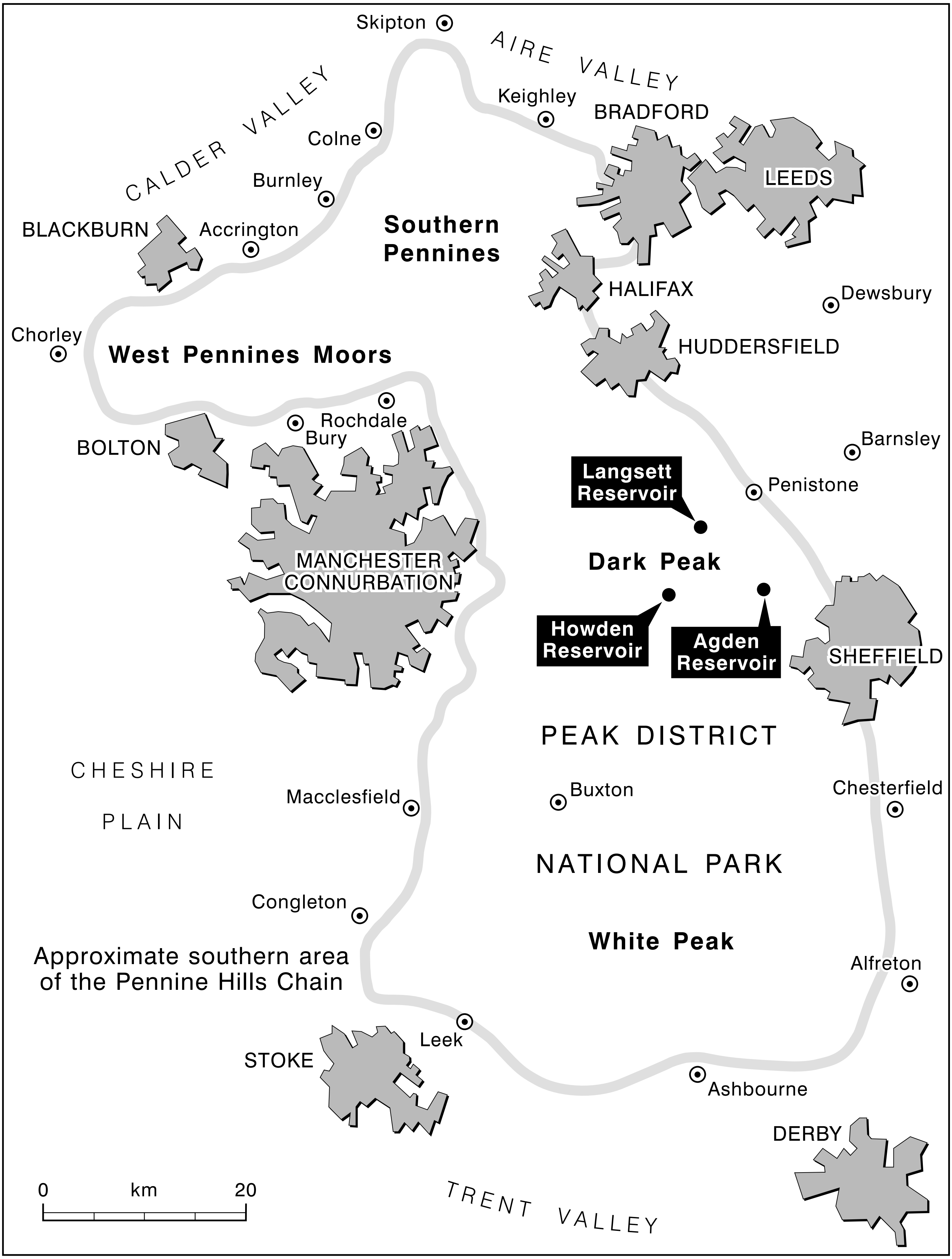

Figure 1: The southern Pennines.

For sediment profiles to reflect changing heavy metal inputs, the sediment must be undisturbed by bioturbation, wind stress or reworking caused by fluctuating water levels (Anderson *et al.* 1988). Further, metals must be unaffected by early diagenesis, that is, they must not migrate through the sediment in response to changing pH or redox conditions (Williams 1992). In addition, where levels of atmospheric heavy metal deposition are being considered, the sedimentation rate needs to be reasonably constant, as changes may dilute or concentrate the input of metals (Foster and Dearing 1987).

An assessment of sediment disturbance and metal mobility is therefore a prerequisite in any sediment profile study. This is particularly important for reservoir sediments, due to the greater probability of sediment disturbance from regular drawdown for water supply purposes. Drawdown can result in the exposure of marginal sediments, causing desiccation and cracking, followed by erosion and redeposition of sediments in the submerged part of the reservoir (Anderson *et al*. 1988). Scouring of channels through exposed sediments during low water levels may also result in sediment influx (Stott 1985). Despite these problems, previous studies have suggested that reservoir sediments may be a suitable source of historical depositional information (Stott 1985; Anderson *et al*. 1988; Foster and Walling 1994).

Anderson *et al*. (1988) assessed the potential of reservoir sediments in the southern Pennines for reconstructing water quality and atmospheric pollution. They concluded that although a detailed history of pollution from atmospheric sources could, in theory, be deduced from the analysis of reservoir sediments, the ability to do this in the southern Pennines would be severely limited by the availability of relatively undisturbed sediment. They suggest that regular drawdown has rarefied undisturbed stratigraphic records. Our study is an attempt to locate any reservoirs where sediment has remained undisturbed, and to use these sediment profiles to reconstruct heavy metal pollution histories. Reservoirs in a broad arc covering the uplands to the north and east of Manchester (Figure 1) are investigated. Specifically we aim to, establish criteria for selecting suitable sites; develop a methodology for identifying undisturbed sediment chronologies suitable for historical reconstruction (including determining the number of cores necessary to provide metal profiles representative of the reservoir), and assess metal mobility in the sediment profile.

Site selection: identification of reservoirs with suitable sedimentary records

Numerous factors prevent reservoir sediment from accurately representing the history of heavy metal inputs. The main factors include; reservoir management practices (particularly severe drawdown events and dredging), lifespan of the reservoir, rapid sedimentation rate, and significant catchment natural storage features and/or sediment control structures (residuum lodges, conduits and bywashes). The ideal reservoir, one to which these problems do not pertain, is unlikely to exist, but it is of primary importance to identify those reservoirs most likely to contain suitable stratigraphic sedimentary records prior to sample collection. This was undertaken using the selection criteria outlined as points 1 – 6 below.

To assess reservoir suitability, information was collated from reservoir managers (North West Water[1], Yorkshire Water[2], Severn Trent[3], and British Waterways[4]). Further data were obtained from previous work in the area, on reservoir sedimentation rates (Butcher *et al.* 1993), catchment sediment yield and delivery (Labadz *et al.* 1991), sedimentation rates and land use change (Stott 1985), atmospheric pollution reconstruction (Anderson *et al.* 1988), reservoir management in terms of sedimentation (White *et al.* 1996), and consolidation of old embank-ment dams (Tedd *et al.* 1997). Using this information the suitability of the 192 reservoirs in the region were then assessed against the following criteria:

1. *Sites should be headwater reservoirs.* This is to ensure the sediment record solely represents material eroding from, and falling onto, the catchment. Reservoirs that were downstream of other reservoirs were therefore discounted. Of the original 192 reservoirs considered, 73 were eliminated at this stage. Table 1 lists the resulting 119 headwater reservoirs in the study area.
2. *The reservoir should have been built prior to 1930 to ensure the sedimentary record incorporates the most intense period of metal deposition.* Industrialisation began in the north west in the 18th Century, and there is evidence of lead mining and smelting in the Pennines in Roman times (Raistrick 1973). However, the greatest heavy metal deposition has occurred during the 20th Century (Livett *et al.* 1979;

Anderson *et al.* 1988). For an investigation into the history of heavy metal pollution, only reservoirs which have accumulated sediment over much of this intensive industrial period will be of use. Therefore, the most recently built reservoirs (those constructed after 1930) were discounted. A longer record would be preferable, thereby encompassing the earlier period of industrialisation, e.g. Slaithwaite, Warland and Black Moss reservoirs are around two hundred years old. However, although these reservoirs potentially contain the longest sedimentary records, their greater age means there is a greater probability of sediment disturbance (Anderson *et al.* 1988).

3. *Sediment depth should not exceed one metre.* The maximum length of sediment which can be removed *in situ* using the Mackareth mini-corer (Mackareth 1969) which was used in this and many sediment-based studies (Foster *et al*. 1987; Rippley 1990; Hutchinson 1995) is one metre. Therefore, it is not possible to collect the whole record if there is more than one metre of sediment. Furthermore, high rates of sedimentation may result in dilution of the metal concentrations below instrumental detection limits of standard flame atomic absorption spectrometry used for metal analysis. Sediment depth can be inferred from capacity loss data, which was available for some reservoirs in the study area from work carried out by Labadz *et al.* (1991), Butcher *et al.* (1993) and White *et al.* (1996). A large loss of water holding capacity implies a significant depth of sediment, though the actual depth will also be dependent on the shape of the reservoir. Reservoirs where total capacity loss was greater than 20%, and sites where significant sediment infilling was documented, were discounted, given that this is indicative of sites where sediment depth is likely to be greater than one metre. In addition, small reservoirs with no obvious catchment inputs were also discounted as some sedimentation is necessary in order to obtain a core.
4. *Sediment should have remained relatively undisturbed since deposition.* Disturbance will result from reservoir management practices, particularly drawdown, drainage or dredging of sediment. Records of water levels and reservoir management have generally been maintained since 1931, but are not always obtainable. However, records of drawdown during 1995 (a drought year with marked water shortages in this area) were available for most reservoirs. Water levels in 1995 were expected to be consistently low, increasing the likelihood of sediment disturbance in many reservoirs. Initially, therefore, reservoirs in which water levels were drawn down to, or beyond 'dead water' levels (the normal maximum extraction level) in 1995 were discounted. Reservoirs where drainage or sediment removal by dredging or scour valve testing had occurred were also eliminated.
5. *There should be minimal sediment control structures and preferably no inputs of water from outside the catchment.* Sediment control structures such as residuum lodges and by-washes, and conduits that alter the effective catchment area of the reservoir, will complicate the amount and particle-size of catchment inputs (White *et al*. 1996). Catchments with these features were therefore also discounted. Sites with other significant natural or artificial sediment storing features in the catchment (i.e. water holding tanks, ponds, or small reservoirs) were also discounted.
6. *There should be no other factors that might adversely affect the sedimentary record.* In addition to the five criteria listed above, there may be other problems with sample sites, for example quarrying in the catchment or contamination incidents. These sites were also eliminated. Finally, sites where no catchment or reservoir management information at all was available were also discounted.

Reservoirs were eliminated when they failed to meet any of the aforementioned criteria (shaded cells in Table 1). Although some of sites eliminated may still be of some value for reconstructing pollution histories, this selection procedure has allowed the identification of thirteen sites with the greatest probability of having a usable sedimentary record (bold type in Table 1). These are Agden, Belmont, Broomhead, Howden, Langsett, Midhope, Mixenden, Roddlesworth, Snailsden, Sunnyhurst, Teggsnose, Trentabank, and Yateholme reservoirs. Howden, Agden and Langsett reservoirs were selected for this study because of their close proximity to each other (which implies that they have been largely affected by the same sources of atmospheric pollution), and their central location in the study area between Manchester and Sheffield (Figure 1).

Establishing the chronology of the sediment

To develop a suitable methodology for establishing an historical reconstruction of metal loadings from sediment profiles, the chronology of the sediment must be established and any disturbances identified. There are three stages involved in establishing core stratigraphy.

1. Core collection

One metre sediment cores were collected using a Mackareth mini-corer (Mackareth 1969). Between eight and ten cores were collected from each reservoir. Cores were taken from central, intermediate and marginal zones. A depth sensor was used to ensure core sites avoided former river channels. For the purposes of this paper, cores from Howden reservoir (Figure 2) are considered in detail and preliminary comparisons are made with cores from Agden and Langsett reservoirs.

2. Initial core assessment

A visual assessment was made for any discontinuities in the sediment. Volumetric magnetic susceptibility (κ) was logged at 2 cm intervals down the cores using a Bartington MS2C loop sensor. Magnetic susceptibility (κ) is a measure of the 'magnetisability' of a

Table 1: Headwater reservoirs in the southern Pennines; characteristics and data used to eliminate potentially problematic sites.

1 reservoir	grid ref	capacity (Ml)	2 age	3 sediment infill (% tot cap)	4 capacity at 1995 min.	5 A	 B	 C	6 other info
Agden	**425392**	**2859**	**1869**	**1.2**	**[23.22]**	**X**	**X**		
Arnfield	401397	975	1850	8.7	15.62 (S)	R	B		W
Ashworth Moor	382415	1591	1908	N	6.42	X	X		
Barbrook	427377	349	1910		93	X	X	X	U
Belmont	**367417**		**1827**			**X**	**X**		
Besom Hill	395408	21							B
Bilberry	410407	305	1845	88.52		X	X	X	B
Black Moss	403408	59	c1815	P		X	X	C*	
Blackmoorfoot	410412	3091	1876	7.44	[10.45] (T)	X	X	C	
Blackstone Edge	399418	808		P	4.29	X	X		
Bollinhurst	397383	384	1872		-10.98	R	B		W
Broadstone	419406		1859			R	B	C	
Broomhead	**426396**	**5191**	**1929**	**5.19**	**[19.77]**	**X**	**X**	**X**	
Brun Clough	401409		1848			X	B	C*	
Brushes Clough	395409	25	1859			R	B		B
Calf Hey	375422	606	1858		4.29	R	B		
Cant Clough	389430	1134	1876		0.93	R	B		
Carrbrook	391401					X	B		
Castleshaw Upper	399410	1087	1891		13.5	R	B		
Chew	403401	940	1914	33.4 (P)	7.01	X	X		
Churn Clough	378438	650	1892		-11	R	B		
Clough Bottom	384426	873	1897		-0.5	R	B		
Clowbridge	382428	1468	1866		1.08	R	B		
Coombs	403379	1484	1806			X	B	C	B
Cowm	388418	1084	1877			R	B		Q, F, U
Cowpe	384420	625	1911		10.1	R/E	B		
Cragg	384420	8		N		X	X	X	
Cranberry Dam	392420			N		X	X		
Crowhole	432374					X	X		W
Dean Clough	371434	1036			16.59		B		
Deanhead	403415	436	1840	3.48	[10.45] (D)	X	X	X	
Deer Hill	407411	736	1875	3.18	[10.45] (T)	X	B	C	
Delph	370415	2327	1921		19.77	R	B		

1 reservoir	grid ref	capacity (Ml)	2 age	3 sediment infill (% tot cap)	4 capacity at 1995 min.	5 A	B	C	6 other info
Diggle	402408	56	c1830		D		B	C	
Dingle	369414	361	1850	N	51.69	X	X	X	
Earnsdale	367422	456	1863		0	X	X		
Errwood	401375	4210	1967		-11.09				
Gaddings Dam	394422					X	X	C	
Godley	396395	278		N					
Gorple Upper	392431	1711	1934	3.04	[12.78]	X	X	C	
Gorpley	391422	598	1905	8.1	[12.77]	X	X	X	Q
Great Lodge	383418			N		X	X	X	
Green Withens	398416	1356	1924	1.56	[12.95] (T)	X	B	C	
Greenfield	402405	462	1897		-2.88	X	B		W
Guide	370425	396			-7.97	X	X		
Haigh Cote Dam	404429					X			
Hanging Lees	397413	95	1866		-11.76	R	B		
Heeley Dam	395423					X	X		
High Ridings	366410		1892	N					
Higher Chelburn	395418					X	X		
Higher Swineshaw	400399	770	1869		-1.59				
Hoddlesden	372423		1849			X	X		
Hollingworth Lake	393414	2620	1854	2.6	S	E	X		U
Holme Styes	414405	314	1840	0.76	[10.49] (T)	X	X	X	
Howden	**417393**	**8990**	**1912**		**19**	**X**	**X**	**X**	
Hurst	405393	168	1838			R	B		
Hurstwood	388431	1373	1925		-6.4	X	X		
Keighley Moor	398439	332	1846	4.46	[9.34]	R			
Kinder	405388	2341	1912	15 (P)	24.97				
Lamaload	397375	1909	1964		16.4				
Langsett	**420400**	**6400**	**1905**	**14.29**	**[16.08]**	**X**	**X**	**X**	
Leeming	**404434**	**550**	**1877**	**2.16**	**[13.22]**	**R**	**B**		
Leeshaw	**401435**	**600**	**1879**	**14.3**	**[13.22]**	**R**	**B**	**C**	
Light Hazzles	395419	318	1801		-10.64	X	X		B
LInacre (Upper)	432372	572	1964		68	X	X	X	Q
Lower Laithe	401436	1318	1926	6.24	[14.9]	R	B	X	
March Haigh	401412	240	1830s			X	X	C*	
Midhope	**422399**	**1859**	**1877**	**0.96**	**[16.08]**	**X**	**X**		
Mitchell’s House	379426	493			2.25 (D)				
Mixenden	**406428**	**478**	**1873**	**0.002**	**[1.89]**	**X**	**X**	**X**	
Naden Upper	385417	364	1846		-11	R	B		Q
Norman Hill	396413	220	1866		-11 (D)	R	B		
Ogden	406430	990	1858	3.4	[1.89] (D,T)	R	X	X	Q
Parsonage	370432	892			-3.24				W
Ramsden Clough	391421	473	1882	5.3	8.33 (D)				U, Q
Ramsley	428374	77	1880?	N	80.5 (D)	X	X	X	U
Readycon	398411	376	1883		-8.85	R	B		W
Redbrook	402409	165	1815			X	B	C	
Redmires Upper	425385	1500	1854	11.39	[27.17]	R	B	C	F
Riding Wood	411405	190	1878	19.06	[10.49]	X	B	X	
Rivelins Dams (Upper)	427387	223	1848	10.5	[59]	X	B	C	
Roddlesworth	**366422**	**606**			**26.75**	**X**	**X**		
Rooden	397411	1206	1901		-11.15	X	X	C	
Royd Moor	422405	822	1934	2.93	[13.08]	R	B	X	
Scout Moor	382419	217	1910		0.51	R		C	
Shuttleworth	381418					X	X		
Slaithwaite	403414	310	1797			X	X	X	
Snailsden	**413403**	**196**	**1899**	**15.88**	**[16.5]**	**X**	**X**	**X**	
Sparth		37	1807			X	X	C	

1 reservoir	grid ref	capacity (Ml)	2 age	3 sediment infill (% tot cap)	4 capacity at 1995 min.	5 A	 B	 C	6 other info
Spring Mill	387417	604	1887		10.5	X	X		Q
Springs	369414	609	1830	N	2.55	X	X	X	
Strines	422390	2332	1871	17.6	[23.22] (D)	X	X	X	
Strinesdale Upper	395406	18	1832						B
Sunnyhurst	**367422**	**439**			**49.6**	**X**	**X**		**U**
Swellands	403409	183	c1821			X	X	C	
Swinden	388433	528	1864		0.66	R	X		
Swineshaw (upper)	404395	256	1865		17.83	R	B		
Teggsnose	**394371**	**111**	**1871**		**13**	**X**	**X**	**X**	
Thornton Moor	405433	795	1885	5.96	[34.9]	R	B	C	
Tittesworth	399359	6400	1963		15	X	X	X	
Toddbrook	400380	1288	1840			X	B	C	W, F
Trentabank	**396371**	**590**	**1929**		**2.97**	**X**	**X**		
Tunnel End				94.04	S				
Turton & Entwhistle	372417	3466	1836		13.69	X	X		W
Upper Coldwell	390436	190	1935		-17	X	X		
Upper Windleden	415401	806	1890	6.45	[6.5]	R	B	X	
Walshaw Dean Upper	396434	911	1907	7.5	[12.78]	X	B	X	
Wards	366416			P		X	X		
Warland	394420	1818	1801		10.11	X	X	C	
Warley Moor	403431	741	1872	3.92	[1.75] (T)	R	B		
Watergrove	390417	3270	1938		8.68	R	B		
Watersheddles	396438	867	1878	4.2	9.34x	R	B	X	
Wessenden Head	406407	341	1881	4.02	[10.45] (T)	X	X	C	
White Holme	396419	1682			1.05	X	X	C	
Widdop	393432	2880	1878	4.86	[12.78] (T)	R	B	C	
Withens Clough	398422	1330	1894	7.6	[3.2] (T)	R	B		
Woodhead	409399	5369	1876	8.7	-15.12	R	B		
Yarrow	362416	3252	1875		5.69	X	X		Q
Yatesholme	**411404**	**415**	**1878**	**0.22**	**[10.49]**	**X**	**X**	**X**	

Total number of reservoirs investigated = 192

Number of reservoirs remaining after stepwise elimination by criteria 1 to 6 (unshaded):

1	2	3	4	5A	5B	5C	6
119	113	97	65	43	34	27	13

Key:

Column 3 N = no apparent catchment; P = silted up with peat.

Column 4 Minimum net capacity at lowest 1995 drawdown as % of total capacity
[figures in brackets are Yorkshire Water reservoirs for which 1995 capacity values were only available for groups of reservoirs];
D = drained; S = sediment removed;
T = scour tests documented (possible sediment removal).

Column 5A E = water holding pond/tank/small reservoirs upstream;
R = residuum lodge; X = no residuum lodge.

Column 5B B = bywash channel; X = no bywash channels.

Column 5C C = conduits transporting water into or out of the catchment
(C* = conduits used in the past but no longer operational); X = no conduits.

Column 6 B = dam breached; F = contamination; Q = quarries or mining in the catchment;
U = unused for water supply at present; W = weir.

material (Dearing 1994). The magnetism is derived predominantly from primary and secondary minerals eroded from the catchment, and magnetic minerals deposited from the atmosphere, the majority of which are the product of industrial processes and vehicular emissions (Thompson and Oldfield 1986). The magnetic profile of an undisturbed sediment core will therefore reflect changes in the amount and type of magnetic inputs through time. Magnetic profiles vary across the reservoir, as particle size varies (Bradshaw and Thompson 1985) with coarse material being deposited rapidly in the upstream area of the reservoir, and finer material further into the reservoir (Anderson *et al*. 1988). Magnetic susceptibility profiles will also vary due to sediment focusing, as marginal sediments are resuspended and redeposited in more central areas (Thompson and Oldfield 1986) especially where frequent drawdown aids this process. Many studies have shown susceptibility profiles of central cores have a distinct 'signature' that is fairly consistent across this zone (Thompson *et al*. 1975). In contrast, frequently reworked marginal cores exhibit no such consistency. The similarity of central cores can be used to identify any anomalous or disturbed cores (Thompson and Oldfield 1986) and to identify cores suitable for further analysis (Oldfield *et al.* 1983).

Figure 3 shows magnetic susceptibility (κ) profiles from Howden cores. Profiles can be divided into two sets, cores 1 to 5 from central areas and cores 6 to 10 from reservoir margins (Figure 2). Marginal cores demonstrate relatively low susceptibility, with the exception of core 9, and core 10 at depth. Material deposited at the reservoir margins will consist of coarse, predominantly catchment, inputs and the low susceptibility reflects the magnetically impoverished nature of the Millstone Grit bedrock (Hutchinson 1995). Sediment will also have been frequently exposed during drawdown so removal of material will have effectively erased any temporal record in the marginal cores. Cores 1 to 5 are from deeper areas of the reservoir that are unlikely to have been exposed during drawdown. In contrast to the marginal cores, these cores show a definite 'magnetic signature,' with a peak in susceptibility occurring between 8 cm and 14 cm from the surface in all central cores. Exceptionally, cores 3 and 4 are similar. These are from the deepest zone of the reservoir, where the potential for serious disturbance to sediment chronology is limited to inwashing of material during drawdown. Such material, if identifiable, should not prohibit historical reconstruction. Their similarity suggests either sediment has remained undisturbed in this region of the reservoir, or that any disturbance has affected the whole of this deepest zone. These cores are considered the most suitable for further analysis. Analysis of cores from the other reservoirs also suggests that the best cores will come from the deepest zone, though this may not be the case for all southern Pennine reservoirs (Stott 1985).

Cores 3 and 4 were then extruded, cut into 1 cm sections and dried at 40°C for 48 hours. Water content and dry bulk density were determined (Rowell 1994) to allow identification of any changes in material, primarily the original soil surface where this was retained.

3. Chronology assessment

The 1 cm sections from cores 3 and 4 were homogenised and packed into 10 ml pots for single sample mass specific susceptibility measurement. A Bartington MS2B single sample dual frequency sensor was used to measure low (χ_{lf}) and high (χ_{hf}) frequency susceptibility (Dearing 1994). Frequency dependent susceptibility (χ_{fd}) was calculated from this, and used to detect the presence of ultrafine (*c.* 0.03 mm) magnetic minerals associated with soil processes (Dearing 1994). Changes in frequency dependent susceptibility may therefore indicate a change in sediment source from topsoil to subsoil or vice versa. All samples were measured from core 3 and alternate samples from core 4. The measurement of susceptibility on a dry mass basis rather than a wet volumetric basis, and on single samples rather than at intervals down the core, allows a more accurate and detailed analysis of the susceptibility profile. Organic matter was determined, as loss-on-ignition, after heating to 500°C for eight hours (Rowell 1994).

Figure 4 shows detailed susceptibility profiles of cores 3 and 4, and a core collected from the central zone of Howden reservoir in 1987 (Hutchinson 1995). The low frequency susceptibility profiles of all three cores are similar (Figure 4). An additional accumulation of sediment appears to be the only major difference between cores collected in 1987 and 1998, despite major fluctuations in water levels in this time. This indicates that there has been no major physical disturbance to chronology affecting the pre-1987 sediment. The three cores were all collected from

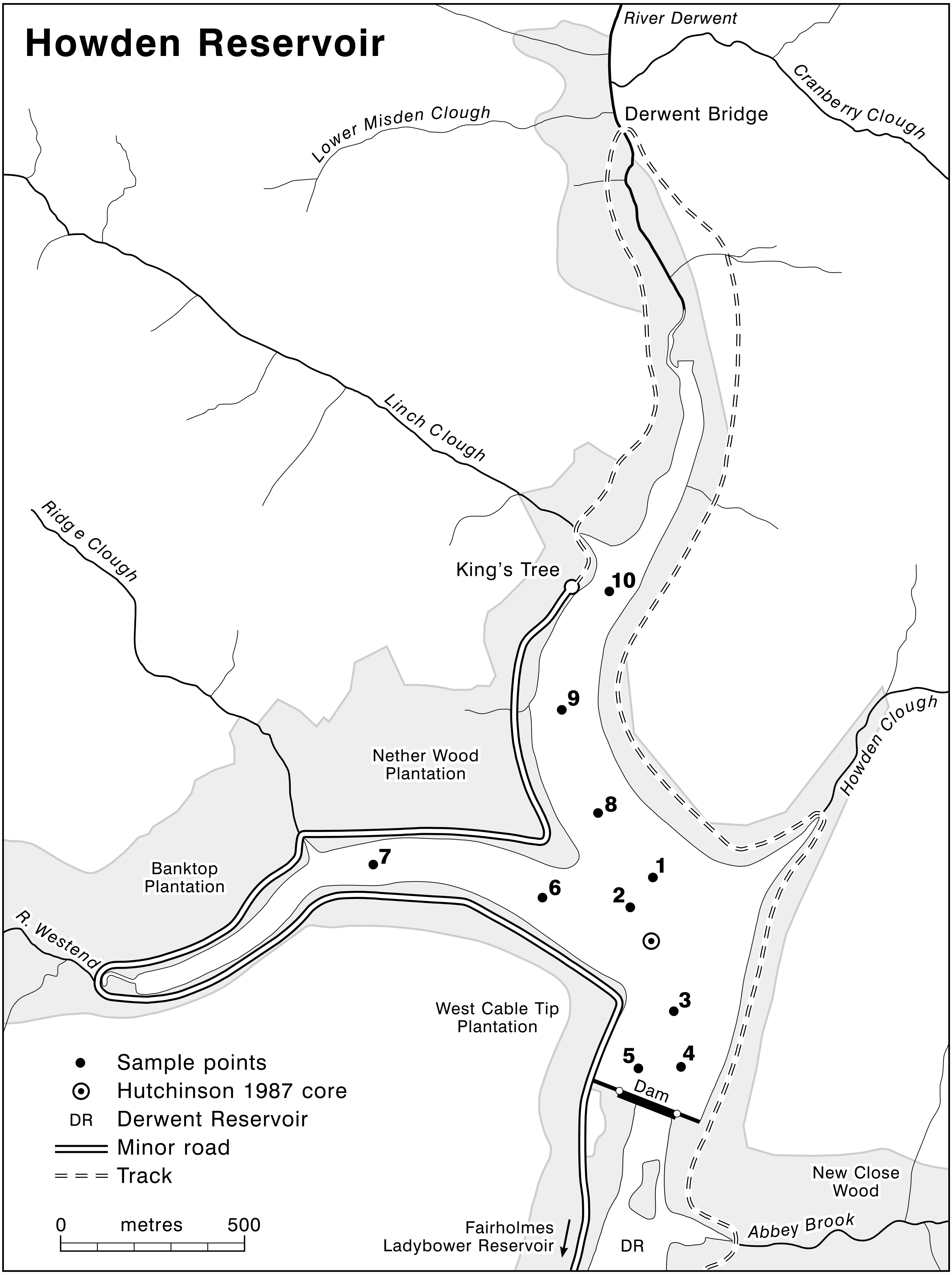

Figure 2: Howden reservoir sample sites.

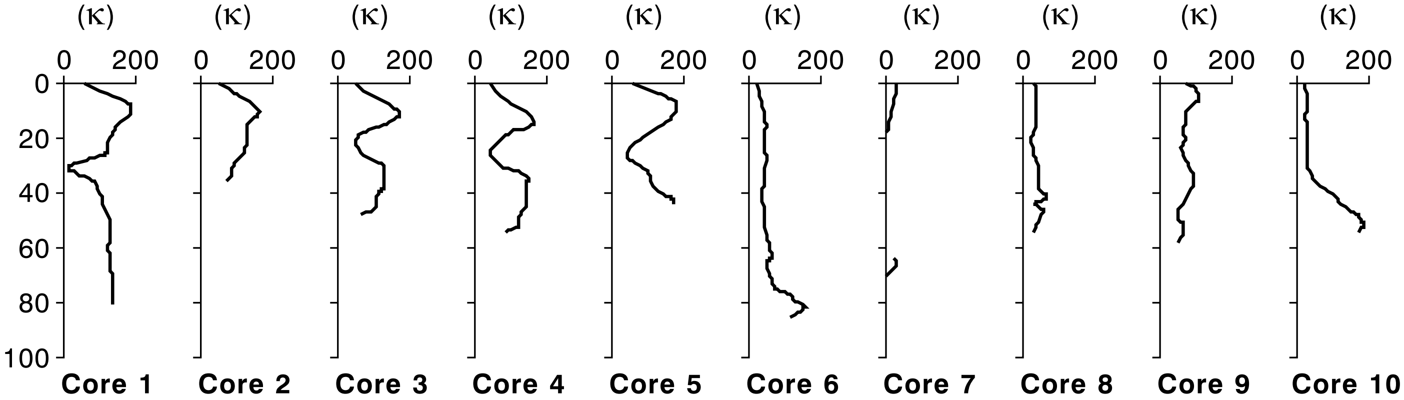

Figure 3: Volumetric susceptibility (κ) profiles of cores from Howden reservoir.

different areas within the deepest zone of Howden reservoir (Figure 2). The similarity of low frequency profiles suggests that, in Howden at least, it is possible for one core to be representative of deposition within this zone.

Each profile shows two peaks divided by a zone of consistently low susceptibility (zone A). Comparison of core 3 and the 1987 core (susceptibility of core 4 was measured every 2 cm, so the precise location of peaks cannot be established) show similar sediment accumulation below the lower peak (Table 2). However, the depth of zone A is almost 50 % greater in the 1998 core, and accumulation from the first peak to the surface is 20 % greater in 1998. The latter can be explained by post 1987 accumulation. Based on accumulation rates before zone A, this suggests an additional accumulation of 2.48 cm (0.23 cm yr^{-1}). However, the difference in the depth of zone A requires a different explanation.

Hutchinson (1995) suggested this low susceptibility zone was caused by an inwash of material during a period of extreme drawdown. Low water levels would allow material eroded from the catchment and exposed marginal sediments to be transported to, and deposited in, the deepest zone of the reservoir. Site 3, being further down the reservoir, may have received a larger inwash of sediment, explaining the greater depth of zone A at this location.

The mean organic matter content in zone A is 32.3% compared to 23.2% in the sediment above and below (Figure 4). Water content and bulk density increase and decrease respectively in zone A compared to surrounding sediment (Figure 4). χ_{fd} results from the 1987 core (Hutchinson 1995) suggest a change in source material to one depleted in ultrafine minerals, possibly subsoil. However, this cannot be deduced from data from the present study.

Caesium-137 dating on the 1987 core, indicates this whole zone was deposited between 1954 and 1963 (Hutchinson 1995). During this period there was only one significant drawdown event in 1959. Water levels reached 17.98 m BTWL (Below Top Water Level) on the 16th of November 1959, the lowest level ever recorded at Howden reservoir [5]. The dry summer of 1959 was followed by severe storms in October. At Howden Dam, a 46.5 mm rainfall event on October 26th was the first significant rainfall recorded since July, and was accompanied by gale force winds (British Rainfall 1959). This occurred when the water level was 16.1 m BTWL.

Although there have been comparable drawdowns and larger rainfall events since, the conjunction of both is exceptional in Howden's history. For example, the water level was drawn down to 16.75 m BTWL in 1995, but the maximum daily rainfall over the drawdown period was only 21.5 mm [6]. It is plausible that the combination of heavy rainfall and strong wind, on exposed sediment and dry soils, resulted in the removal of a large amount of material from the catchment and from reservoir margins, and its redeposition in the deepest zone of the reservoir.

Zone A is very clearly defined in all deep water cores, and easily identifiable by single sample susceptibility and organic matter content. Therefore, sediment cores from Howden reservoir remain valuable as an historical record, as sediment throughout the rest of the core is undisturbed. In fact, this zone provides an easily obtained date for the sediment profile.

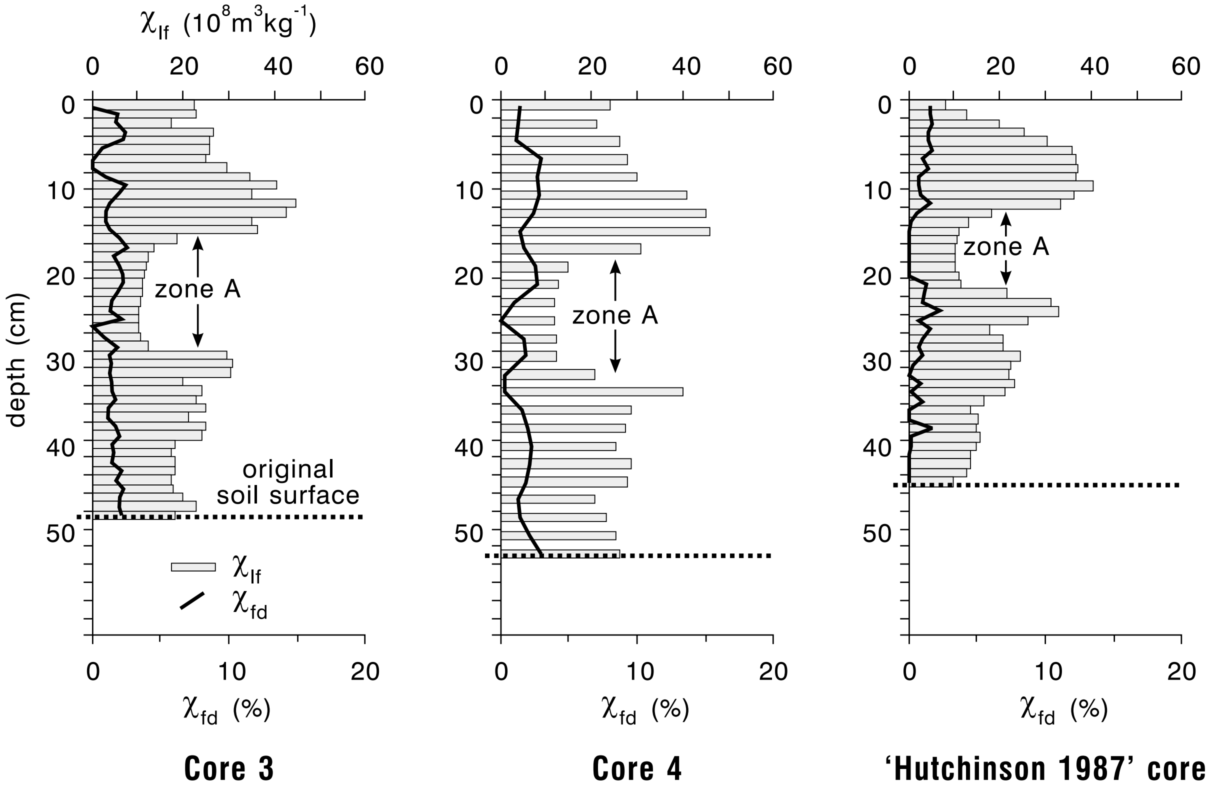

Figure 4: Low frequency (χ_{lf}) and frequency dependent (χ_{fd}) susceptibility profiles of central cores from Howden reservoir.

Susceptibility profiles from Langsett and Agden reservoirs do not have a similar low susceptibility zone (Figure 5). Water level records from Langsett reservoir show that although the reservoir is of a similar depth, it was only drawn down to 11.2 m BTWL in October 1959, and received less rainfall (35.8 mm). This does not appear to have caused significant inwash. Langsett and Agden susceptibility profiles are very similar, and show no obvious disruptions to sediment chronology. In addition, the sediment profiles are comparable to those from Howden reservoir if allowance is made for the low susceptibility inwash zone. This similarity between reservoirs is remarkable given differences in reservoir and catchment size, and the potential for sediment disturbance through drawdown, particularly in recent drought years. This strongly suggests that sediment has not been disturbed in Langsett and Agden reservoirs, and only in 1959 in Howden reservoir. It appears that only an unusual combination of events will disrupt sediment stratigraphy in the deepest zone of these reservoirs, and that the sediment profiles in all three reservoirs will be valuable historical records of heavy metal deposition.

Table 2: Sediment accumulation in central cores from Howden reservoir.

	Core 3 – 1998	'Hutchinson 1987' core
Base of core to lower χ_{lf} peak	17.5 cm	18.5 cm
Upper χ_{lf} peak to surface	11.5 cm	9.5 cm
Sediment accumulation in zone of low susceptibility	12.5 cm	8.5 cm

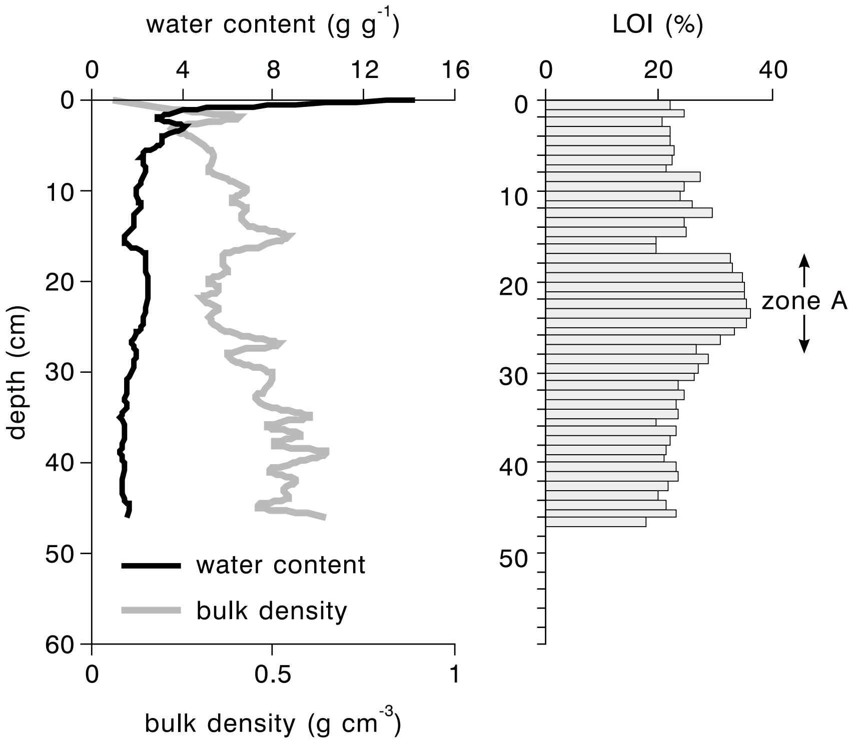

Figure 5: Water content, bulk density and loss-on-ignition profiles of Core 3, Howden reservoir.

Metal mobility

The final aim of this study was a preliminary investigation of variations in metal concentrations in representative sediment profiles to determine whether metal mobility might prevent the historical record of metal deposition being retained. As the physical stability of the sediment has been established, it is the chemical stability that must be verified. Complex physical and biogeochemical processes influence the distribution and mobility of trace elements in aquatic systems (Murray 1987). Some authors have found mobilisation of heavy metals to be important (Williams 1992; Calmano *et al*. 1993; Song and Muller 1995). Equally, some have found no significant mobilisation of metals (Cornwall 1986; Flower *et al*. 1997). However, the assumption that all metals are immobile in the sediment may lead to erroneous conclusions about the timing and magnitude of metal inputs (Williams 1992).

Analysis of metal concentrations in cores 3 and 4 of Howden reservoir (Figure 2) was conducted using a partial digest adapted from a standard Ministry of Agriculture, Fisheries and Food method developed for estuarine samples (Jones and Laslett 1994). Samples were digested for nine hours using 9:1, HNO_3:HCl. Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn) were analysed using a flame atomic absorption spectrometer (Parkinson *et al*. 1989).

Profiles of Cr, Cu, Fe, Mn, Ni, Pb and Zn from Howden reservoir, core 3, are shown in Figure 7 (concentrations of Cd and Co were below detection limits for AAS analysis). Profiles from core 4 are largely similar. Ni, Cu, Pb and Zn have previously been measured in cores from Watersheddles reservoir, approximately 60 km north of Howden by Anderson *et al.* (1988). Comparison suggests that metal loadings to Watersheddles and Howden reservoir are similar: Ni and Cu concentrations are generally low (below 50 mg g^{-1}) though well above background levels (Anderson *et al*. 1988); and Zn and Pb concentrations are higher (up to 200 mg g^{-1}) for both reservoirs, though at Howden surface concentrations of 232 mg Cu g^{-1} and 344 mg Zn g^{-1} were found. No southern Pennine reservoir sediment profiles have been analysed for the other metals, but in this study Mn concentrations were generally between 150 and 200 mg g^{-1} increasing through the upper 6 cm to surface concentrations of 1244 mg g^{-1}. Cr concentrations were between 40 and 80 mg g^{-1}. Fe concentrations vary between about 20 to 50 mg g^{-1}, though reach 69 mg g^{-1} at the surface.

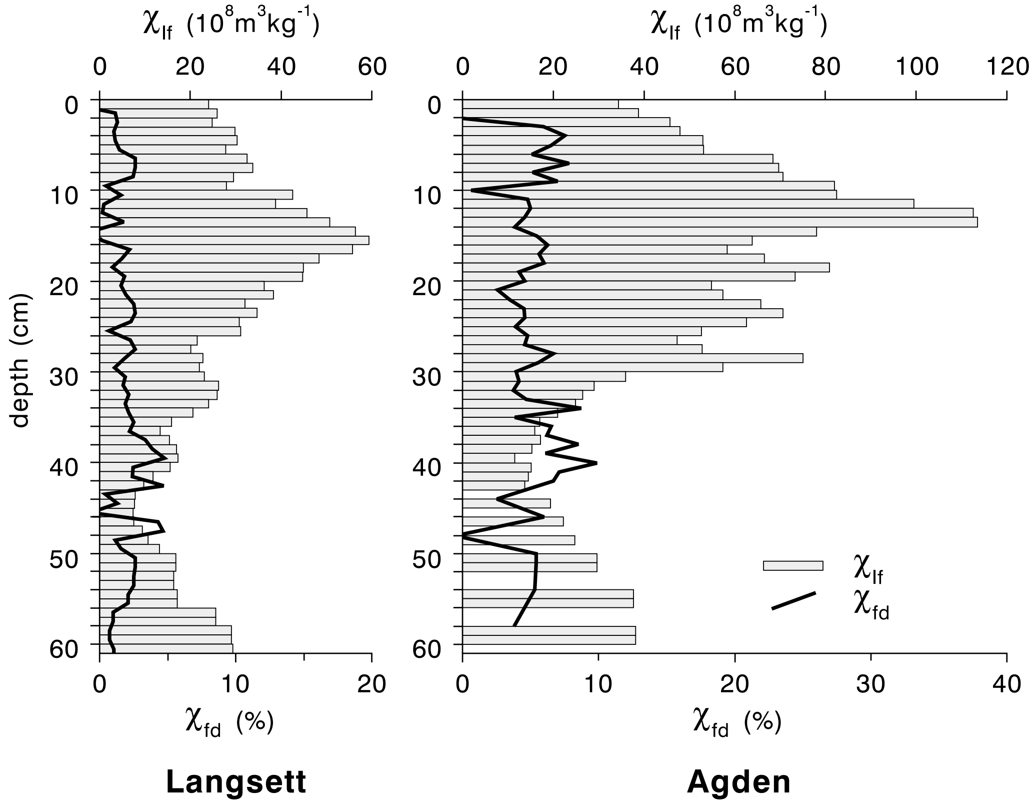

Figure 6: Low frequency (χ_{lf}) and frequency dependent (χ_{fd}) susceptibility profiles of central cores from Langsett and Agden reservoirs.

Mobilisation of metals is largely dependent on the pH and redox conditions in the sediment column (Calmano *et al*. 1993). In anoxic sediments, early diagenesis reduces Mn and Fe oxides to soluble Mn^{2+} and Fe^{2+} (Song and Muller 1999). These diffuse through the profile in response to concentration gradients, re-precipitating as oxides under aerobic conditions in the upper layers of sediment, or in the water column. The manganese profile of core 3 (Figure 7) closely mirrors the water content profile of this core (Figure 5), suggesting significant manganese mobilisation into the porewater, and diffusion through the core. Iron is generally less easily reduced than manganese (Song and Muller 1999). Fe concentrations are only slightly raised at the surface, suggesting minimal reduction of Fe oxides.

Heavy metals bound to Mn and Fe oxides, will be released by their reduction to Mn^{2+} and Fe^{2+} (Shaw 1990). Unless immobilised by adsorption onto organic matter, clay particles, or precipitation as metal sulphides, these metals will also diffuse through the core. Oxidative precipitation of these metals in the surface sediment (Williams 1992) or their release to the water column may result (Salomons and Forstner 1984; Petersen *et al*. 1995). Peaks in surface concentrations of Cu and Zn may therefor indicate co-cycling with Mn and Fe oxides (Song and Muller 1995).

Metal mobilisation is also influenced by pH, which is lowered during the oxidation of organic matter (Calmano *et al*. 1993). Zn, for example, will be solubilised where pH < 5 (Bowen 1979); conditions typical in an anoxic sediment. In contrast, Forstner (1991) found Cu was not remobilised to any significant extent at pH 4.4. Surface peaks of Zn may, therefore, be caused by its release into the porewater due to low pH.

On the basis of the analysis presented here, it appears, besides Fe and Mn, there is some mobilisation of Cu and Zn associated with early diagenesis. However, low dry sediment weight means the surface peaks of Cu and Zn actually represent only a small mass of metals, and effects are limited to the upper centimetre of the sediment. Whether this could present a water quality problem, or whether this is sufficient to affect interpretation of the historical record for these metals requires further investigation for Pennine reservoirs. Future work is aimed at examining these effects further using sequential

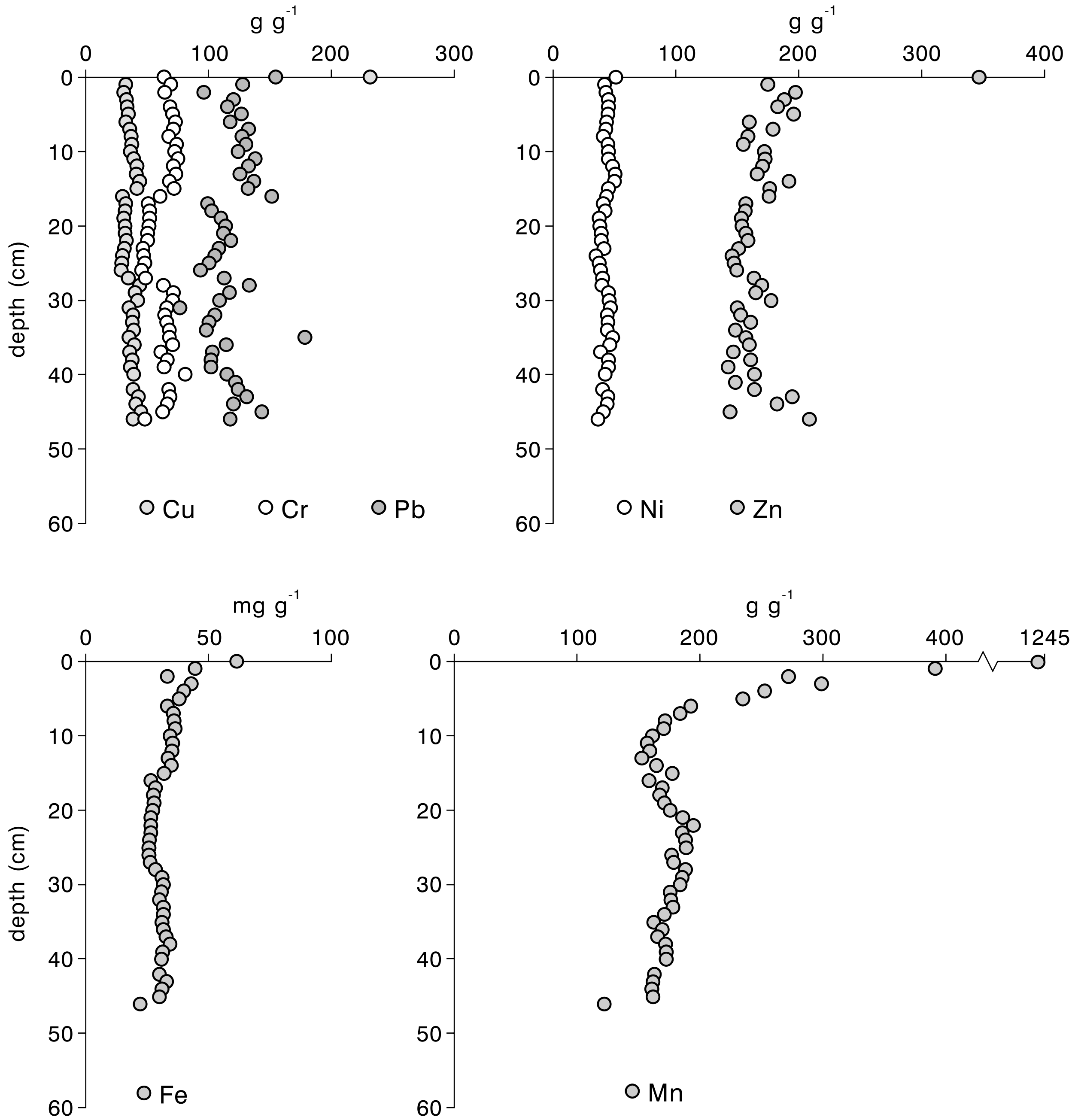

Figure 7: Heavy metal profiles of core 3, Howden reservoir.

extraction techniques (Tessier *et al.* 1977) to determine metal speciation and porewater analysis (Song and Muller 1999).

Conclusions

Reservoir sediment profiles in the southern Pennines represent a valuable record of certain heavy metal inputs onto this area. Although Anderson *et al.* (1988) suggested undisturbed records would be rare, this study has identified suitable reservoirs theoretically, and then verified their suitability through the analysis of sediment cores collected from the reservoirs.

Sediment chronology can be demonstrated by magnetic susceptibility measurements, which identifies any disturbance to the sediment. Deepwater sediments from Langsett and Agden reservoirs are shown to have remained undisturbed, and therefore have continuous stratigraphic profiles. Howden reservoir shows disturbance in the form of a clearly defined zone of low susceptibility, more organic sediment. This zone is attributable to inwash during an intense storm event in 1959 following a period of drought and reservoir drawdown. It is easily identifiable and therefore should not prohibit the rest of the core being used as a chronological record of inputs.

Both magnetic susceptibility and metal profiles of cores collected from across the deepwater zone are similar in the reservoirs studied. It is therefore also concluded that the analysis of one core can be representative of the whole deepwater zone. The replicability of cores must, however, be verified by susceptibility measurements of multiple cores from this zone.

Preliminary metal analysis of Howden sediment, shows high metal loadings of lead and zinc (up to 200 mg g^{-1}), and of chromium (40 to 80 mg g^{-1}), and high surface peaks of Cu (232 mg g^{-1}), Zn (344 mg g^{-1}), and Mn (1244 mg g^{-1}). Whether mobilisation is occurring on a scale that will detrimentally affect the sedimentary records value as a temporal record of inputs will be considered in future work. Pb, Cr and Ni profiles, at least, appear unaffected, and represent an historical record of inputs.

Notes

1. North West Water Ltd, Lingley Mere, Great Sankey, Warrington, WA5 3LP.
2. Yorkshire Water plc, Western House, Halifax Road, Bradford, BD6 2LZ.
3. Severn Trent Water Ltd, Avon House, St Martins Road, Coventry, CV3 6PR.
4. British Waterways, Pennine and Potteries Waterways Division, Church Lane, Marple, SK6 3BN.
5. Water level records for Howden reservoir: Severn Trent Water archives, Avon House, St Martins Road, Coventry, CV3 6PR.
6. Meteorological Office records, register of rainfall: The National Meteorological Archive, The Scott Building, Sterling Centre, Eastern Road, Bracknell, RG12 2PW.

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