FISKERTON, LINCOLNSHIRE
ANALYSIS OF THE MODERN IRON ANALOGUE SAMPLES BURIED FOR 30 MONTHS

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Summary

A project was initiated in December 2003 to investigate the deterioration of modern analogue samples buried in the vicinity of the Iron Age causeway at Fiskerton. The final sets of iron coupons were retrieved and analysed after 30 months burial. The results of X-ray diffraction analysis of the corrosion products on those 30 month coupons are reported here. The iron carbonate siderite was the dominant corrosion product at all soil horizons, and iron sulphides occurred in the lower waterlogged anoxic levels. Analysis of the previously recovered coupons and the calculations of the corrosion rates for all the burial periods are reported on elsewhere.

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Introduction

This study is part of a joint project to assess the deterioration of a range of modern test materials buried in the vicinity of the Iron Age causeway, in particular the effects of the deliberate rewatering of the field in 2004.

Modern materials serving as analogues for archaeological finds were buried for specific periods of time, recovered at intervals over several years, and then analysed to determine the extent and nature of deterioration. The materials tested were iron, copper, bone, antler and horn.

For the iron samples, the corrosion products were characterised by X-ray diffraction analysis (XRD). Results from the coupons recovered at 6, 12 and 18 months burial durations were reported previously (Fell 2005). This report presents the XRD results for the final group recovered, which have been buried for 30 months (Figure 1). Corrosion rates were calculated through weight loss per unit area, and are reported on elsewhere (Fell 2006).

F*igure 1. Inert plastic rods bearing iron coupons as recovered after 30 months burial. The iron coupons or bars of c. 50mm length are tied to the rods between the white spacers and are partly hidden in these images by soil that is in the recesses. Left: Rod 4 of Cluster 1 being pulled from the ground. Centre: upper part of Rod 4 of Cluster 1 (the north delph of the River Witham is visible in the background). Right: Rod 4 of Cluster 2 shown leaning against the fencing surrounding the groundwater monitoring point*

Soil and groundwater conditions

Other survey and monitoring projects have progressed at the same time as the burial experiments, including soil characterisation, groundwater monitoring and functional assessment (Last 2005). Of particular relevance to the burial studies is the groundwater monitoring, arranged and curated by JW and described previously (Williams 2005).

Although all these data are not yet fully available, relevant summaries are given here (Appendices 2–6), and syntheses for the earlier data are available (Last 2005; Fell and Williams 2004). Fuller results will be published as proceedings of a conference held in Lincoln in June 2006 (Williams in prep) and as proceedings of the international conference 'Preservation of Archaeological Remains In Situ' (PARIS3) held in Amsterdam in December 2006 (Williams et al in prep).

The principal variables in the soil and groundwater that have been considered in relation to the buried analogues are depths of burial, soil types, seasonal changes, and groundwater levels, pH, redox potential, chemistry and oxygen levels.

The analogue samples were placed in the ground at two locations, near the north delph of the River Witham at Cluster 1 monitoring point, and at 25 metres away to the north at Cluster 2 monitoring point. The soil types where analogues are buried are summarised in Figure 2 and Appendix 1, and they vary from degraded peat in the upper horizons to anoxic reedy silts in lower horizons (J Rackham pers comm). At Cluster 1, the upper soil horizons comprise shelly silts and degraded peat, with reedy silts (with clay components) dominating below 1.2 metres. There is a greater depth of peat at Cluster 2, and here the reedy silts start at around 1.5m below ground surface.

At Cluster 1, the analogue materials are particularly susceptible to changes in the water levels in the adjacent delph. For example, water levels are sometimes altered by flushing of the dykes, and very occasionally by clearance of the dykes. In October 2004, the water table was deliberately raised by the blocking of the land drainage ditches by the farmer towards the Countryside Stewardship Scheme. By mid-November, the water levels at Cluster 1 had raised slightly, to an average depth of 0.9m from the soil surface compared with previous levels of between 1.0m and 1.5m depth. Through 2006, the water levels remained in the region of 0.7m to 1.0m below ground level (Appendix 2).

The groundwater conditions at Cluster 2 could be expected to be less oxic than at Cluster 1, particularly in the lower levels where anoxic conditions should prevail. Through 2005, the water levels were around 0.3m to 0.6m depth from the surface and were more consistent than the previous levels which ranged from 0.7m to 1.6m depth (Appendix 3). During a comparatively dry period in the summer of 2006 however, the levels dropped for several months, to around 0.6m–0.9m.

The average pH values were slightly different at the two monitoring points (Table 1 and Appendix 4). At Cluster 1, the average readings were 6.5 – 6.7 before rewatering and 6.7 after rewatering. At Cluster 2, the average readings were 6.3 but the range was greater, particularly when the measurements of the upper

Cluster 1

Depth	
0.1m	
0.2m	
0.3m	
0.4m	
0.5m	
0.6m	
0.7m	
0.8m	
0.9m	
1.0m	
1.1m	C
1.2m	
1.3m	
1.4m	
1.5m	B
1.6m	
1.7m	A
1.8m	
1.9m	
2.0m	

Cluster 2

D

C

B

A

Ground surface

Support rod

Depth below ground (m)

Coupon No.

Depth below ground (m)	Coupon No.
0.56	8
0.77	7
0.98	6
1.19	5
1.32	4
1.45	3
1.58	2
1.61	1
1.93	

Iron
Spacer

Plough soil

Well preserved peat

Shelly silts
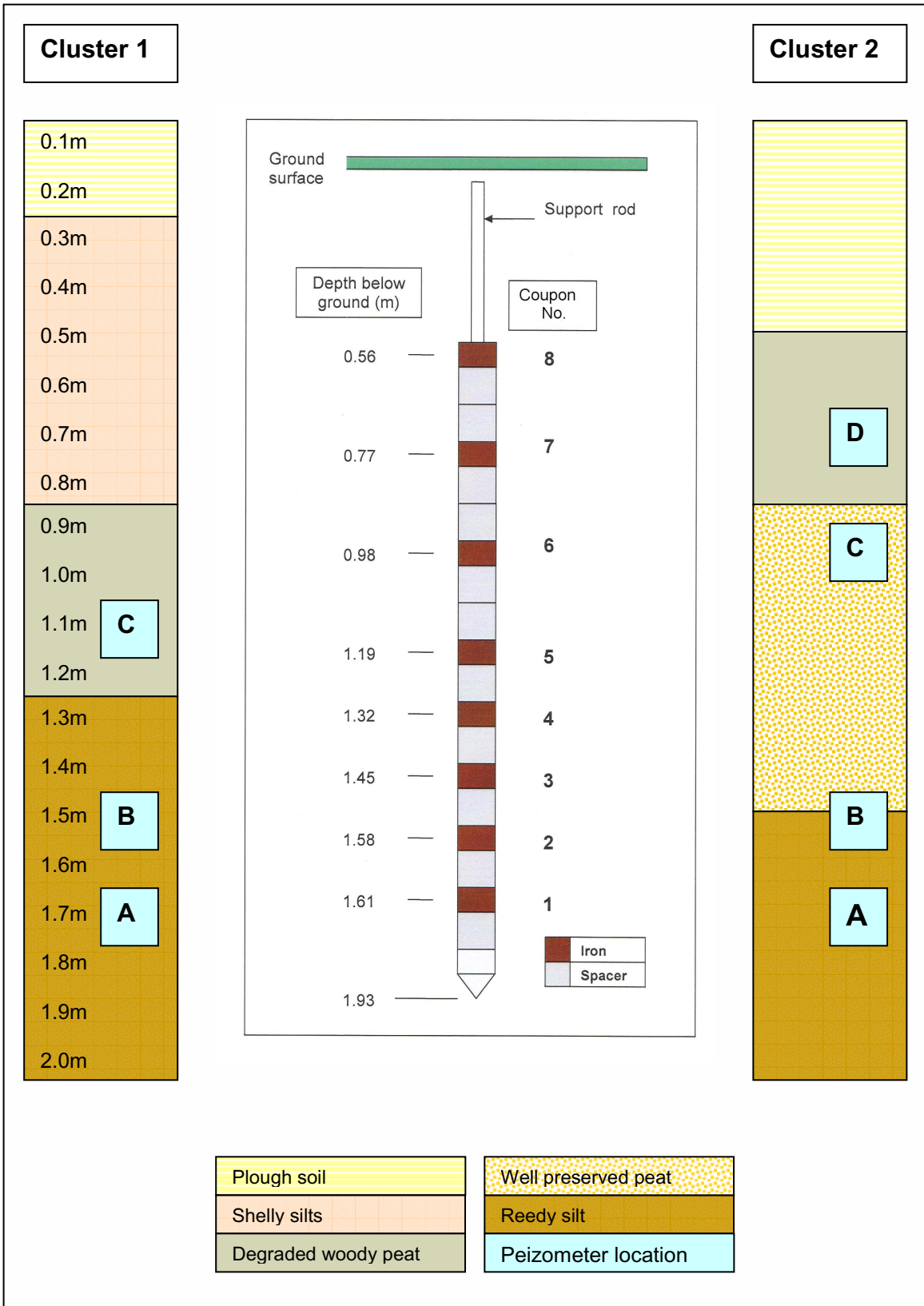
Reedy silt

Degraded woody peat

Peizometer location

Figure 2. Diagram of an installation rod (centre) bearing eight iron coupons showing their sequence, depths and approximate relationships to soil types and peizometers. Note that coupon 1 is lowest in the soil profile.

peizometers (C and D) are taken into account. The average vertical variation at both clusters is only slight. However, the lowest figures for the upper dipwells are 4.8 and 5.4.   Low pH results were recorded on occasions where de-watered soil was wetted again, replicating results that Caple and Dungworth (1998) reported for laboratory re-wetting experiments. After a few months of those levels becoming rewatered, pH measurements were similar to those in the lower peizometers.

Table 1. Summary of average pH and Eh values for October 2003 to October 2006 showing values per peizometer before and after rewatering of the field

Peizometer	pH	Redox potential (Eh)
Before rewatering (October 2003 to September 2004)		
Cluster 1 A	6.5 (6.09 – 6.83)	-39 (-100 – +49)
B	6.7 (6.05 – 8.61)	+12 (-63 – +81)
B*	6.5 (6.05 – 6.67)	+12 (-63 – +81)
A+B*	6.5 (6.05 – 6.83)	-13 (-100 – +149)
Cluster 2 A	6.7 (5.98 – 7.78)	-46 (-170 – +58)
B	6.3 (5.86 – 6.88)	+28 (-28 – +87)
C	5.5 (5.28 – 5.72)	+87 (+76 – +113)
D	—	—
A+B+C+D	6.3 (5.28 – 7.78)	+4 (-170 – +113)
After rewatering (October 2004 to October 2006)		
Cluster 1 A	6.7 (6.4 – 7.74)	-7 (-97 – +161)
B	6.7 (6.33–7.52)	-6 (-105 – +159)
A+B	6.7 (6.33 – 7.74)	-7 (-105 – +161)
Cluster 2 A	6.5 (6.23 – 6.9)	-30 (-195 – +170)
B	6.3 (5.86 – 6.97)	-36 (-218 – +89)
C	6.0 (4.82 – 6.64)	+19 (-66 – +90)
D	6.4 (5.24 – 6.81)	+33 (-40 – +129)
A+B+C+D	6.3 (4.82 – 6.97)	-12 (-218 – +170)

Bracketed figures show the range.   * Ignoring an anomaly in May 2004

Values for redox potential at Cluster 2 were more reducing with depth whereas readings for the two peizometers placed at Cluster 1 were close together, whilst a third installed higher up the sequence never received water and therefore no readings were taken (Table 1 and Appendix 5). Initially, redox measurements were collected using a probe, inserted into water, recovered using a hand bailer from the proximal boreholes located to the east (see Williams 2005, fig 2.1). This system provides good trend data, comparing at a gross scale the difference between the lower and upper levels on site, and this can be seen in the slight

difference in the average values between Cluster 2 A/B and C/D. The results would be more striking if the somewhat anomalous results were removed (such as 170mV in Cluster 2A). More recently, *in situ* redox probes have been installed, and initial results support the general indications that the deposits are more reducing with depth (Figure 3). In this case, the data from the *in situ* probes are more reducing than the water based system, and the results less variable.
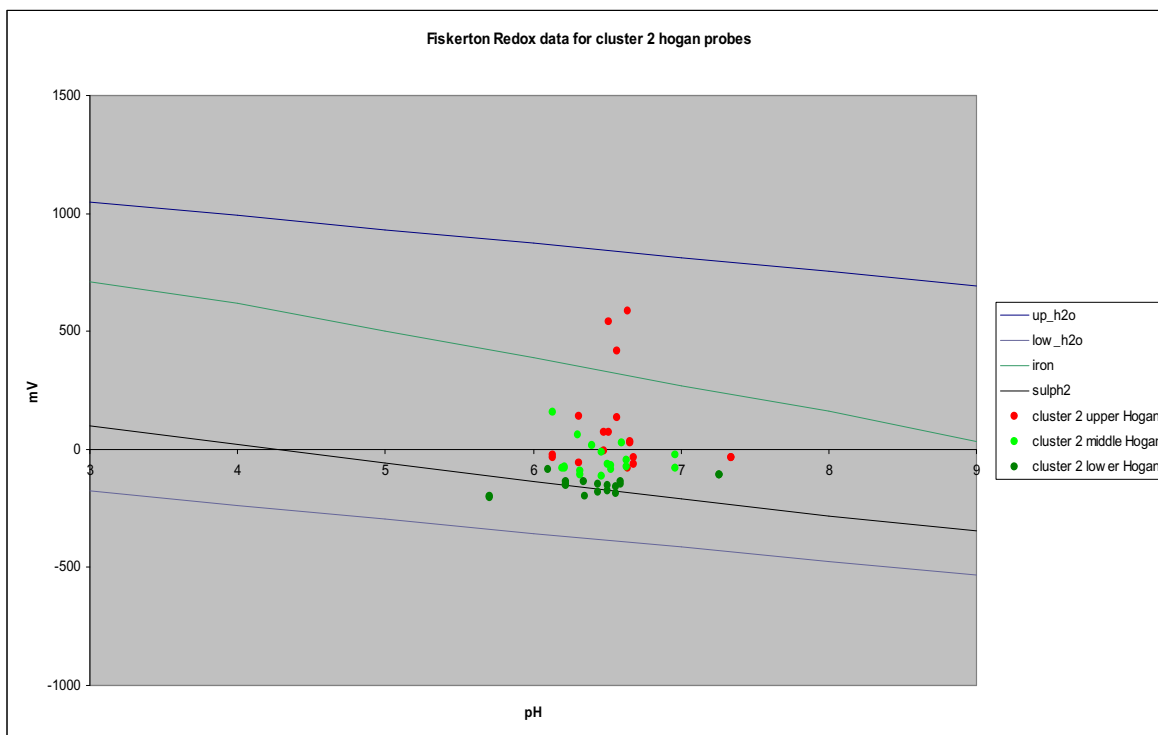

Figure 3. Measurements for the *in situ* redox probes at Cluster 2 during 2006, showing clear separation between the lower silts (dark green), the peat above (light green) and the degraded woody peat (red)

Chemical measurements for the period March 2004 to December 2006 show notably high sulphate and high calcium (Appendix 6). During this period, the sulphate concentration averaged 1023mg/l (range 656 – 1520 mg/l), which may be important for microbial activity. Its origin may be from prior saline conditions when the Witham was partially tidal during periods of its history (Field and Parker-Pearson 2003, 1), or the sulphate may have arisen through the use of soil fertilisers. Calcium, averaging 497mg/l (range 425 – 571mg/l), is also high, as expected in near-neutral soils (cf Bohn et al 2001, 37). Its presence may in part be due to limestone in the local geology and within the Iron Age causeway, as well as the shelly deposits in upper soil horizons (Field and Parker-Pearson 2003, 12). Other elements that are relatively high in concentration are iron and manganese; in low oxygenated soils, sulphate, iron and manganese are able to act as electron acceptors and may therefore be important for microbial activity (cf Bohn et al 2001).

Methodology

Recovery and preparation of the iron coupons
The methods employed to prepare and install the analogue materials are described in Fell et al (2005). The iron samples are small bars c. 50mm in length that are also referred to in this text as bars or coupons. These were mounted separately on a series of inert plastic installation rods designed to be inserted in the ground with the aid of an auger to minimise soil disturbance. In December 2003, the rods were inserted in the ground to depths up to 1.7 metres, correlating with known soil conditions. Figure 2 shows an installation rod bearing eight coupons of iron, and the approximate depth at which they were buried.

Twelve rods of analogue iron samples were prepared, each rod bearing eight iron coupons. Six rods were installed in the ground at the two monitoring points Cluster 1 and Cluster 2. One rod was recovered from both locations at 6 months (22 June 2004), 12 months (8 December 2004), 18 months (22 June 2005), and the final collection was at 30 months (25 June 2006).

In June 2006, it was decided to collect all the remaining six installation rods together, in part because the corrosion was unexpectedly rapid. These would be stored in various ways and some analysed later as part of a different experiment to test the effects of short-term storage conditions.

One rod from each cluster was analysed immediately by XRD to determine the corrosion products; these are the rods termed 'Cluster 1 Rod 4' and 'Cluster 2 Rod 4' in the original methodology statement, where dimensions and weight are given (Fell et al 2005, 13–21, table 4.1).

Storage of the bars
The rods were recovered from the ground on 25 June 2005 and wrapped in plasticized foil to attempt to maintain relatively cool conditions. They were transported to the laboratory in Portsmouth where they were refrigerated immediately at 4℃, less than 12 hours after recovery.

On the following day, the individual bars were detached from the rods, loose soil was removed, and their condition described (Appendix 1). The bars were then photographed in sets (eg Figs 4 and 7), allowed to dry out (Cluster 1 bars) or dried out with industrial methylated sprits spray (Cluster 2 bars), rephotographed, and sampled for XRD analysis. The latter samples were dry stored with desiccant until they could be analysed in the subsequent few days.

To enable corrosion rate calculations, the bars themselves were chemically stripped and weighed (Fell 2006). The remaining four installations rods of bars were stored at 4℃ within the original plasticized foil, as recovered from site. These will be analysed in various ways at a later date.

X-ray diffraction analysis

X-ray diffraction analysis will detect only crystalline phases and therefore amorphous components will not be determined. Nevertheless, it is a standard analytical method for determining minerals and corrosion products on archaeological artefacts, as well as numerous other applications.

Samples in the order of 1mg were ground in an agate mortar prior to analysis. X-ray diffraction data were collected on a Philips PW 1840 powder diffractometer using cobalt Kα radiation (wavelength Kα1 = 0.178896nm, Kα2 = 0.179285nm) incorporating a solid-state silicon detector. The running parameters were normally 40kV 40mA for X-ray generation. Data collection was between the angles 7 and 100°2θ, at step size 0.10° per step, time per step 5s, wi th a receiving slit width of 0.3mm.

A search-match computer programme was used to identify unknown components in the diffraction patterns by comparison with standards in the powder diffraction file (International Centre for Diffraction Data, ICDD). Initially powder diffraction files database version PDF-1 was employed; later, in 2006, version PDF-2 was used. Minerals named in this report, their formulae and their PDFs are shown in Table 2.

Table 2. *Corrosion products and other minerals detected by XRD*

Mineral name	Formula	Common name	PDF-1 no.
Goethite	α-FeOOH	Iron oxyhydroxide	29-0713
Magnetite	Fe_3O_4	Iron oxide	19-0629
Maghemite	γ-Fe_2O_3	Iron oxide	39-1346
Siderite	$FeCO_3$	Iron carbonate	29-0696
Lepidocrocite	γ-FeOOH	Iron oxyhydroxide	44-1415
Akaganéite	β-FeOOH	Iron oxyhydroxide	34-1266
Greigite	Fe_3S_4	Iron sulphide	16-0713
Mackinawite	$Fe_{1+x}S$	Iron sulphide	24-0073, 15-0037
Pyrite	FeS_2	Iron sulphide	42-1340
Vivianite	$Fe_3(PO_4)_2.8H_2O$	Iron phosphate	30-0662
Iron sulphide	FeS	Iron sulphide	23-1120
Calcite	$CaCO_3$	Calcium carbonate	05-0586
Quartz	SiO_2	Silicon dioxide	31-1233, 33-1161

Results

Cluster 1
The corroded coupons, as recovered and removed from their installation rod, are
shown in Figure 4.
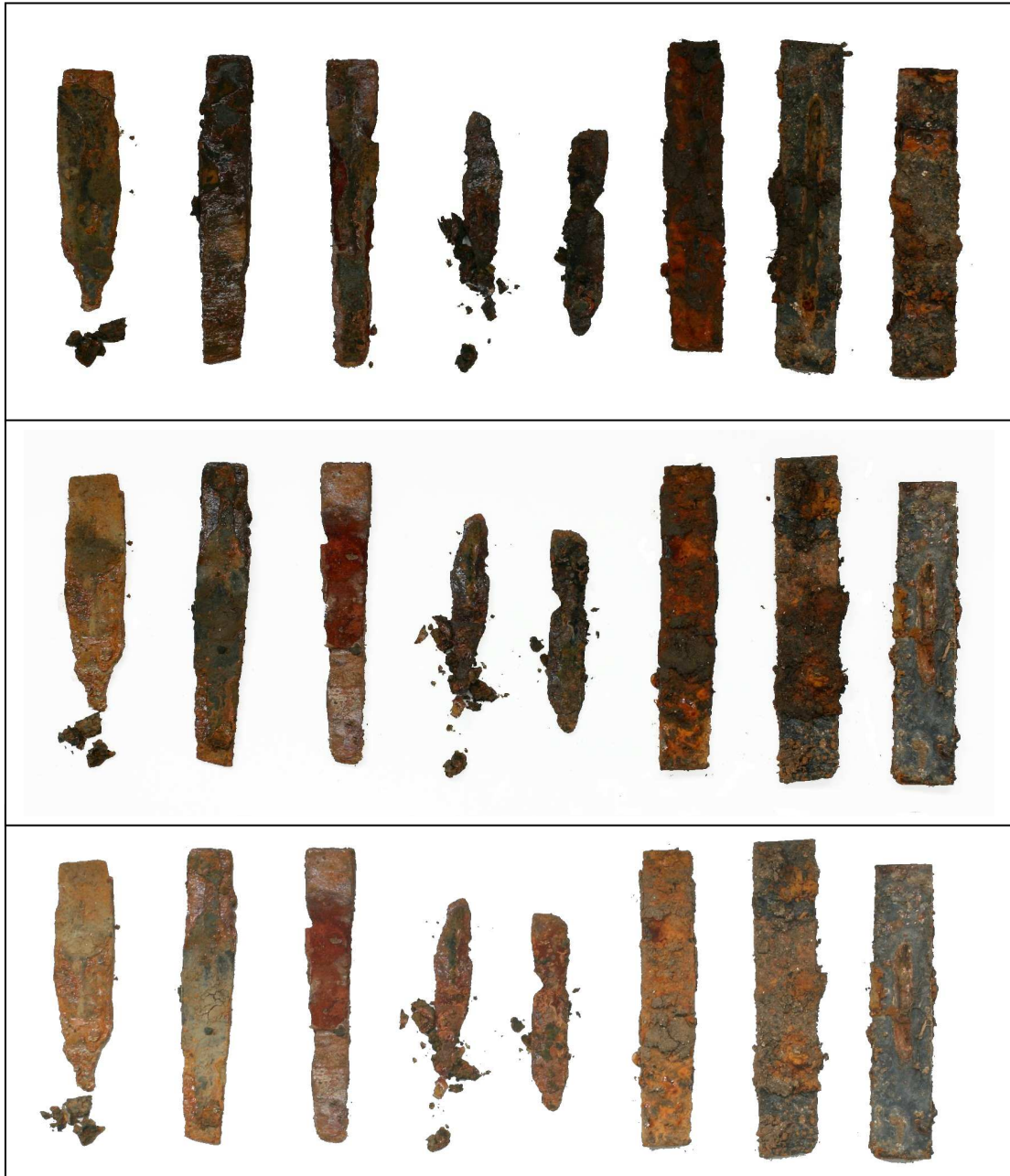
*Figure 4. Cluster **1** coupons as recovered showing the variability in condition and
colour. The top two rows show the two sides of the same eight bars, in sequence
with coupons 1 at the left, coupon 8 at the right. The coupons have been removed
from the installation rod and loose soil has been detached, but they have not yet
dried out. The lowest row shows one side of the coupons after drying out (for
comparison of colours only). Lengths of original coupons c. 50mm.*

The XRD results for the coupons from Cluster 1 are summarised in Table 3 and Figures 5 and 6. Coupons 1 to 5, buried deeper than 1.2 metres, yielded principally siderite, with small amounts of iron sulphides and iron oxides. The upper three coupons, Coupons 6 to 8, yielded mainly goethite and calcite.

Table 3. Cluster 1: summary of XRD results for coupons buried for 30 months

Bar	Depth mm	XRD no	Major	Minor	Trace
8	565	5411	Calcite Goethite	Quartz	
7	775	5410	Calcite Quartz	Goethite	
6	985	5413	Goethite Calcite	Siderite Quartz Maghemite*	
5	1195	5408	Siderite	-	
4	1325	5407	Siderite	Maghemite*	Quartz
3	1455	5406	Siderite	-	Quartz Maghemite*
2	1585	5405	Siderite	-	Quartz, Maghemite*
1	1615	5404	Siderite	-	Mackinawite Quartz

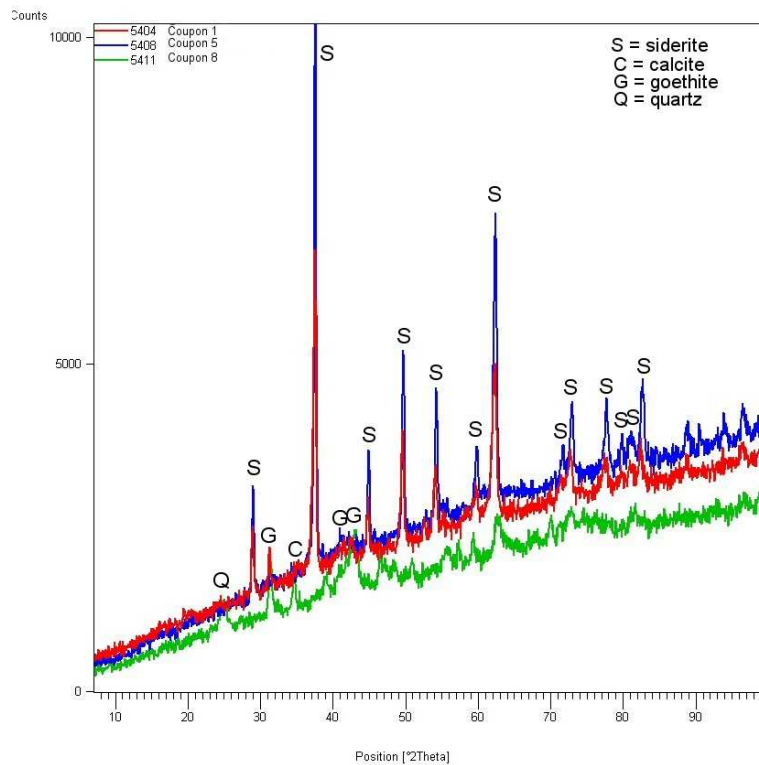* Magnetite or maghemite (cannot be distinguished by XRD)

Figure 5. Selected XRD spectra for coupons 1, 5 and 8 buried at Cluster 1
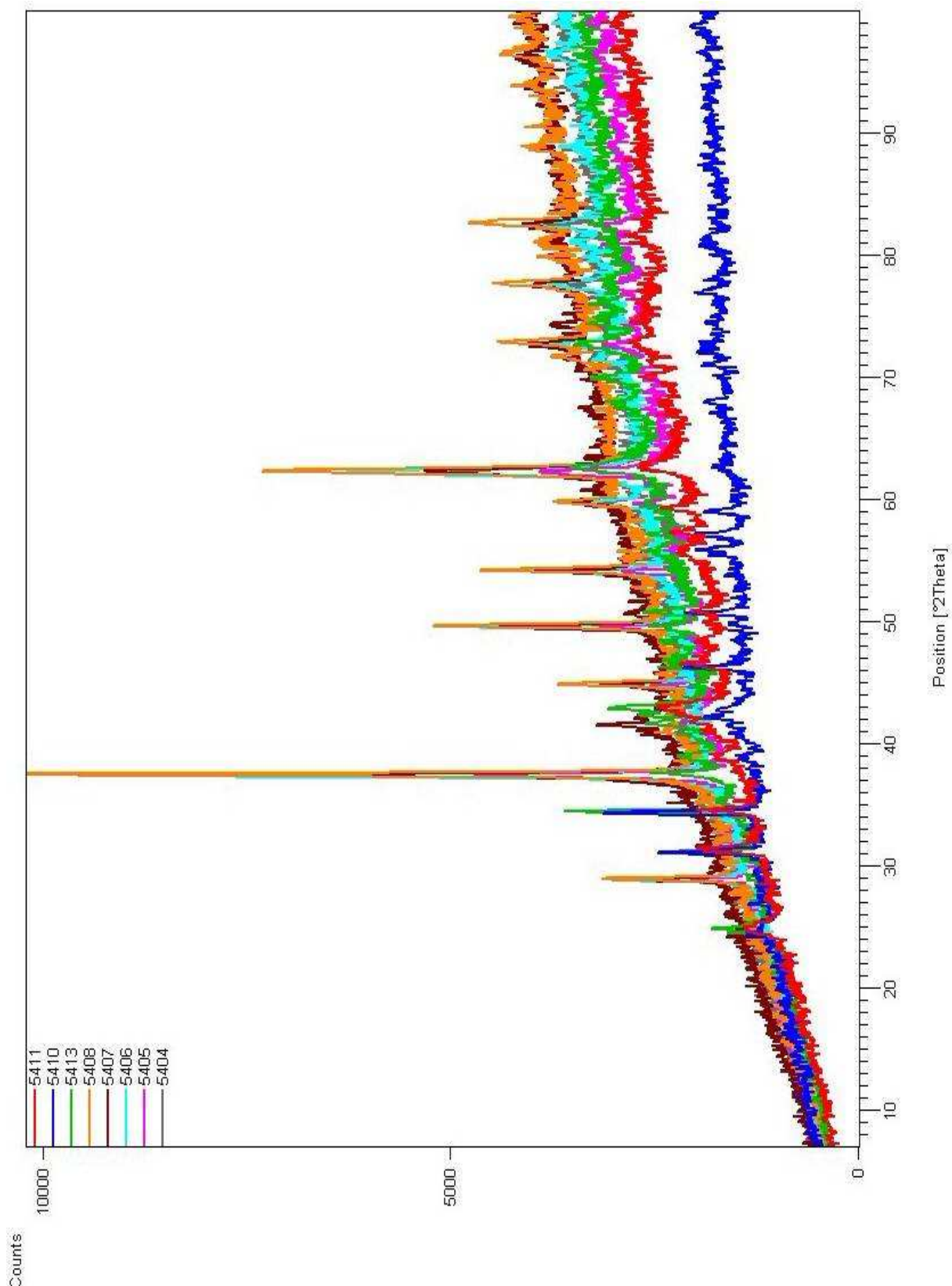
Figure 6. XRD spectra for the eight coupons buried for 30 months at Cluster 1

5411 = bar 8 (uppermost in soil profile); 5410 = bar 7; 5413 = bar 6; 5408 = bar 5;
5407 = bar 4; 5406 = bar 3; 5405 = bar 2; 5404 = bar 1 (lowest in soil profile)

Cluster 2

The corroded bars, as recovered and removed from their installation rod, are shown in Figure 7.

*Figure 7. Cluster **2** coupons as recovered showing the variability in condition and colour. The top two rows show the two sides of the same eight bars, in sequence with coupons 1 at the left, coupon 8 at the right. The coupons have been removed from the installation rod and loose soil has been detached, but they have not yet dried out. The lowest row shows one side of the coupons after being dried out (the sequence across the page is the same as in the upper two rows but their orientations are not necessarily the same). Lengths of original coupons c. 50mm.*

Results from coupons at Cluster 2 are summarised in Table 4 and Figures 8 and 9. All of these coupons yielded primarily siderite, with some mackinawite also in the lower five coupons, and a variety of other minor phases on the upper three coupons.

Table 4. Cluster 2: summary of XRD results for coupons buried for 30 months

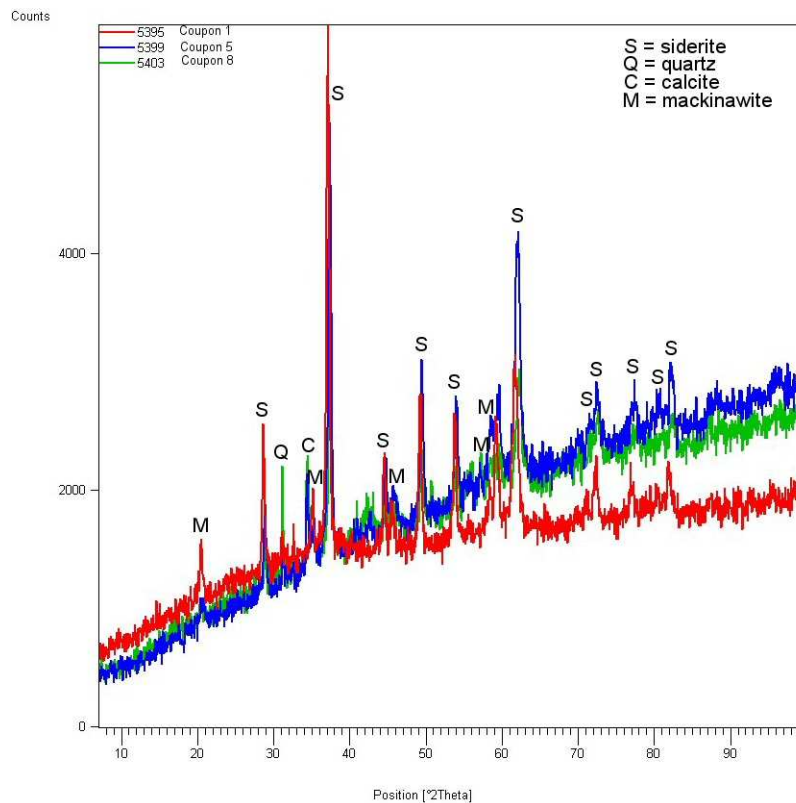| S	Depth mm	XRD no	Major	Minor	Trace
8	565	5403	Siderite	Calcite Quartz	
7	775	5401	Siderite	Calcite Quartz Lepidocrocite	
6	985	5400	Siderite	Greigite	Quartz
5	1195	5399	Siderite	Mackinawite Calcite	Clay constituents
4	1325	5398	Siderite	Mackinawite	-
3	1455	5397	Siderite	-	-
2	1585	5396	Siderite	Mackinawite	-
1	1615	5395	Siderite	Mackinawite	Quartz

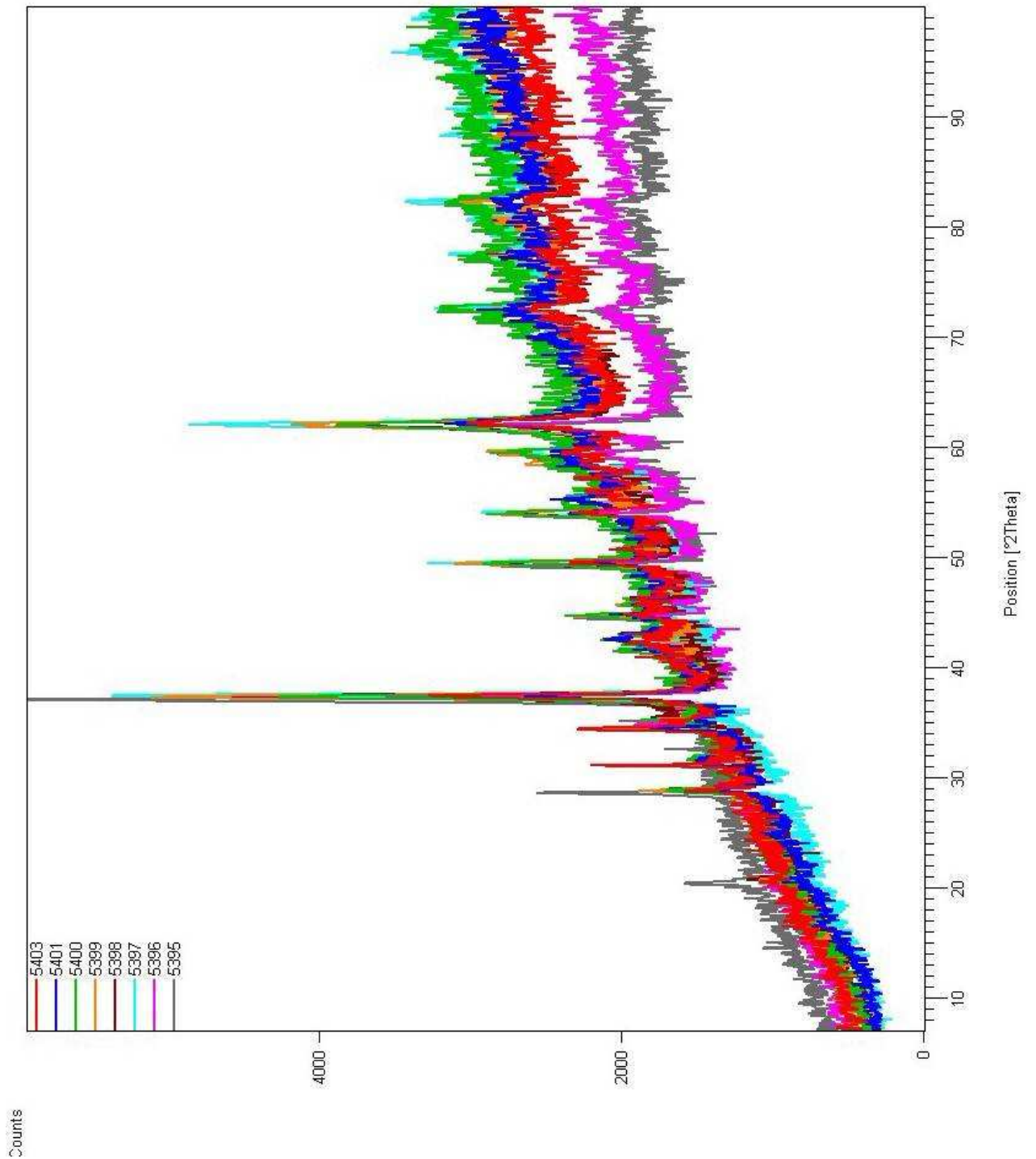Figure 8. Selected XRD spectra for coupons 1, 5 and 8 buried at Cluster 2

Figure 9. XRD spectra for the eight coupons buried for 30 months at Cluster 2

5403 = bar 8 (uppermost in soil profile); 5401 = bar 7; 5400 = bar 6; 5399 = bar 5;
5398 = bar 4; 5397 = bar 3; 5396 = bar 2; 5395 = bar 1 (lowest in soil profile)

Discussion

Corrosion products

From previous analyses (Fell 2005), corrosion products determined on the coupons buried for six months were principally iron oxyhydroxides and oxides – goethite, magnetite and maghemite (Table 5). The presence of these oxidised species may in part be related to the presence of oxygen surrounding the coupons at the time of burial, as well as a lower water table prior to the rewatering of the field. However, analyses of the subsequent coupons, recovered at 12, 18 and now 30 months, showed that the commonest corrosion products found on those from the lower waterlogged and partly waterlogged levels were siderite, and iron sulphides such as mackinawite, greigite and pyrite. Iron sulphides and siderite were also found on the archaeological iron artefacts recovered during excavations in 1981 and 2001 (Fell and Ward 1998; Fell and Williams 2004). Together, these results suggest that the lower coupons are largely in anoxic conditions, which is supported by the measurements of the groundwater levels and redox potentials. Usually associated with anoxic microbial reactions is the presence of hydrogen sulphide, which was very obviously present at the time that the analogues were extracted from the ground.

Table 5. Summary of the main corrosion products identified at 6, 12, 18 and 30 months

S	Depth (m)	Corrosion products and water levels			
		6 months	12 months	18 months	30 months
Cluster 1					
8	0.56	●	●	●	●
7	0.77	●	●	●	● [shaded]
6	0.98	● — [shaded]	● — [shaded]	● — [shaded]	● — [shaded]
5	1.19	● [shaded]	●	● ■ ▲ [shaded]	■
4	1.32	●	●	■ ▲	■
3	1.45			■ ▲	■
2	1.58		▲	■ ▲	■
1	1.61	▲	●	■ ▲	■
Cluster 2					
8	0.56	●	● — [shaded]	● ■ — [shaded]	■ ▲ — [shaded]
7	0.77	● [shaded]	● ■	● ■ [shaded]	■ ▲ [shaded]
6	0.98	●	● ■	● ■ ▲ [shaded]	■
5	1.19	● — [shaded]	● ■	■ [shaded]	■ ▲
4	1.32	● ▲	■	■	■ ▲
3	1.45	● ▲	■ ▲	■	■
2	1.58	● ▲	■ ▲	■ ▲	■
1	1.61	●	■	■ ▲	■ ▲

● iron oxides; ■ iron carbonate; ▲ iron sulphides; — water level at recovery

[shaded] range of water levels since burial

14

The apparent dominance of siderite may conceal the true range of corrosion products. The analytical technique employed, XRD, does not have 100 per cent sensitivity and so minor phases are sometimes not detected. Furthermore, XRD only detects crystalline phases whereas some iron sulphides are known to be amorphous (cf Vaughan and Lennie 1991). The black appearance of many of the corroded coupons upon recovery (see Figs 4 and 7) certainly suggested that sulphides were present, and yet these were not always detected, perhaps because they were not crystalline.

Corrosion mechanisms
The presence of the individual corrosion products, principally iron oxides, iron sulphides and iron carbonate, can be explained by several corrosion mechanisms.

The commonest corrosion products from the oxidation of iron in aerobic environments are the oxides goethite and magnetite (Cornell and Schwertmann 2003). In anaerobic conditions, however, iron sulphides will form instead, as a consequence of bacterial activity whereby sulphate-reducing bacteria produce hydrogen sulphide from groundwater sulphate. At the same time, fermentative processes can reduce available organic matter in the soil to provide energy, and the by-products can include bicarbonate and carbonate. If free Fe^{2+} ions are available, and the local pH and other conditions are suitable, iron carbonate may precipitate. Siderite and the iron sulphide mackinawite are the primary products of anaerobic microbial corrosion (Tiller 1982, 139). Calcium carbonate is commonly formed during biogenic degradation of organic matter, and thus is often associated with sulphide production, although its origin may of course be geological.

At Fiskerton, the groundwater monitoring data suggests that there are a number of parameters that might have affected the corrosion processes. Principally, these are the high levels of sulphate and calcium, the slightly acidic pH and the slightly reducing redox potential. Furthermore, the lowest coupons were placed in reedy silts with clay components that are conducive to anoxic conditions. From the above pathways it seems likely that both the calcite and siderite found on the archaeological artefacts and on the modern iron at Fiskerton are most probably the by-products of the microbial metabolic pathway in which Fe^{2+} is continually precipitated as iron sulphide via sulphide production by sulphate-reducing bacteria.

Stability of siderite
The presence of siderite on the iron artefacts and on the analogues at Fiskerton is particularly interesting because it also occurs as a major corrosion product on archaeological ironwork at Nydam Mose in Denmark (Matthiesen et al 2003; Matthiesen et al 2004), as well as on archaeological artefacts in more oxygenated situations (Neff et al 2005) and in wet calcareous soils in laboratory tests (Angelini et al 1998). It has also been reported in mires, marine and in other locations where it forms through the biological reduction of available iron oxides (eg Pye et al 1990), although it can form as scales in other non-biological ways (Sontheimer et al 1981). At Fiskerton, its formation need not necessarily be through the same pathway as at Nydam Mose (where iron sulphides are absent) because the ground

water and soil conditions are different, although both sites have groundwater in the near neutral pH range.

Siderite is known to confer stability to iron through its passivating properties (Sontheimer et al 1981; Tiller 1982; Matthiesen et al 2003). Its presence may therefore be beneficial to the ironwork at Fiskerton, as has been suggested for artefacts and analogues at other archaeological sites (Matthiesen et al 2004).

Although the pH values recorded at Fiskerton were on average very slightly acidic, siderite would still be able to exist if all other conditions are favourable. The critical pH limit for the dissolution of siderite has been calculated to be 6.2 (Matthiesen et al 2003, 189), which is slightly lower than the pH values determined at Fiskerton. Furthermore, within an active population of bacteria, the local pH and other conditions can be rather different from the bulk groundwater.

Corrosion rates
The corrosion rates of the analogue iron samples increased dramatically over the 30 month period of the study except for those that were in drained, partly or fully oxygenated peat (Fell 2006). Characterisation of the corrosion products suggest that anaerobic microbial activity was dominant near to and below the water table, producing iron sulphides and carbonate. Although these products can be protective under certain conditions, if the protective corrosion film is broken, microbial corrosion can be very rapid.

The severe corrosion rates demonstrated on the experimental coupons at both Cluster 1 and Cluster 2 locations are unexpected and difficult to explain given that the principal corrosion product identified is the non-aggressive siderite. The severest and most erratic corrosion occurred on the coupons that were close to or below the water table levels. Presumably, therefore, the sulphide layers that were formed were not protective, or had been disrupted and were then no longer protective. On balance, the absence of protective films on the coupons, for whatever reason, seems the most plausible explanation for the aggressive corrosion.

During study of the archaeological artefacts from the 1981 excavation, it was clear that the better preserved artefacts were those that were buried in the lowest levels of the site, well below the variations in water table. However, of course, we do not know how many artefacts from any of the archaeological levels have totally corroded away. Conceivably the present water levels are insufficient to protect the clean surfaces of the modern experimental iron that has not had chance to develop well-formed corrosion layers. However, this need not necessarily be a concern for any archaeological iron artefacts that still survive in the ground, providing they have intact and protective corrosion layers.

The impact of rewatering
The parameters that seem to have most altered since the rewatering of the field are the raising of the water table and the associated changes in the oxygen levels within the soil profile. During the period monitored, the pH and redox potentials have not altered significantly, but sulphate levels have almost halved. These

factors do not explain the rapid corrosion rates on the analogue iron near the water table and add nothing further to the possible causes discussed earlier.

Conclusions

The corrosion products determined on both the archaeological iron and the analogues suggest that the re-watering of the site may be beneficial to the archaeological iron due to the presence of siderite and the continuation or re-introduction of anoxic waterlogged conditions. The predominance of siderite is significant because it is considered to confer stability to artefacts through its passivating properties. However, measurements of corrosion rates showed that (clean) modern analogue iron placed within the zones of fluctuating water tables had corroded rapidly despite forming potentially stable corrosion products. This may be because non-protective corrosion films had formed upon the recently buried modern iron, whereas the surviving archaeological iron was deposited in the Iron Age in more benign circumstances.

Acknowledgements

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Appendix 1. Condition of the iron bars as recovered, showing also burial depths and soil types

| Bar	Depth mm	Buried in soil type*	Condition of the bars #
Cluster 1			
8	565	Shelly silts	Oxidised. Orange deposits
7	775		Oxidised. Orange deposits
6	985	Degraded peat	Oxidised. Orange deposits
5	1195		Most has corroded away. Black. Some orange staining on the plastic rod
4	1325		As bar 5
3	1455		Not quite as corroded as Bars 4 & 5
2	1585	Reedy silts	All black. Less corroded than those above
1	1615		Black. Corroded away on the upper tie.
Cluster 2			
Generally these are less orange than those at Cluster 2			
8	565	Degraded woody	Little or no orange deposits
7	775	peat with wood	Little or no orange deposits (as Bar 8)
6	985		Little or no orange deposits (as Bar 8)
5	1195	Reasonably well	Black
4	1325	preserved peat	Black. Now very short, ?corroded away
3	1455		Black and robust
2	1585	Reedy silts	Black and robust (as Bar 3)
1	1615		Black and robust (as Bar 3)

* Information from James Rackham

\# Condition of the bars as removed from the installation rods in the laboratory on 26.6.2006, one day after recovery
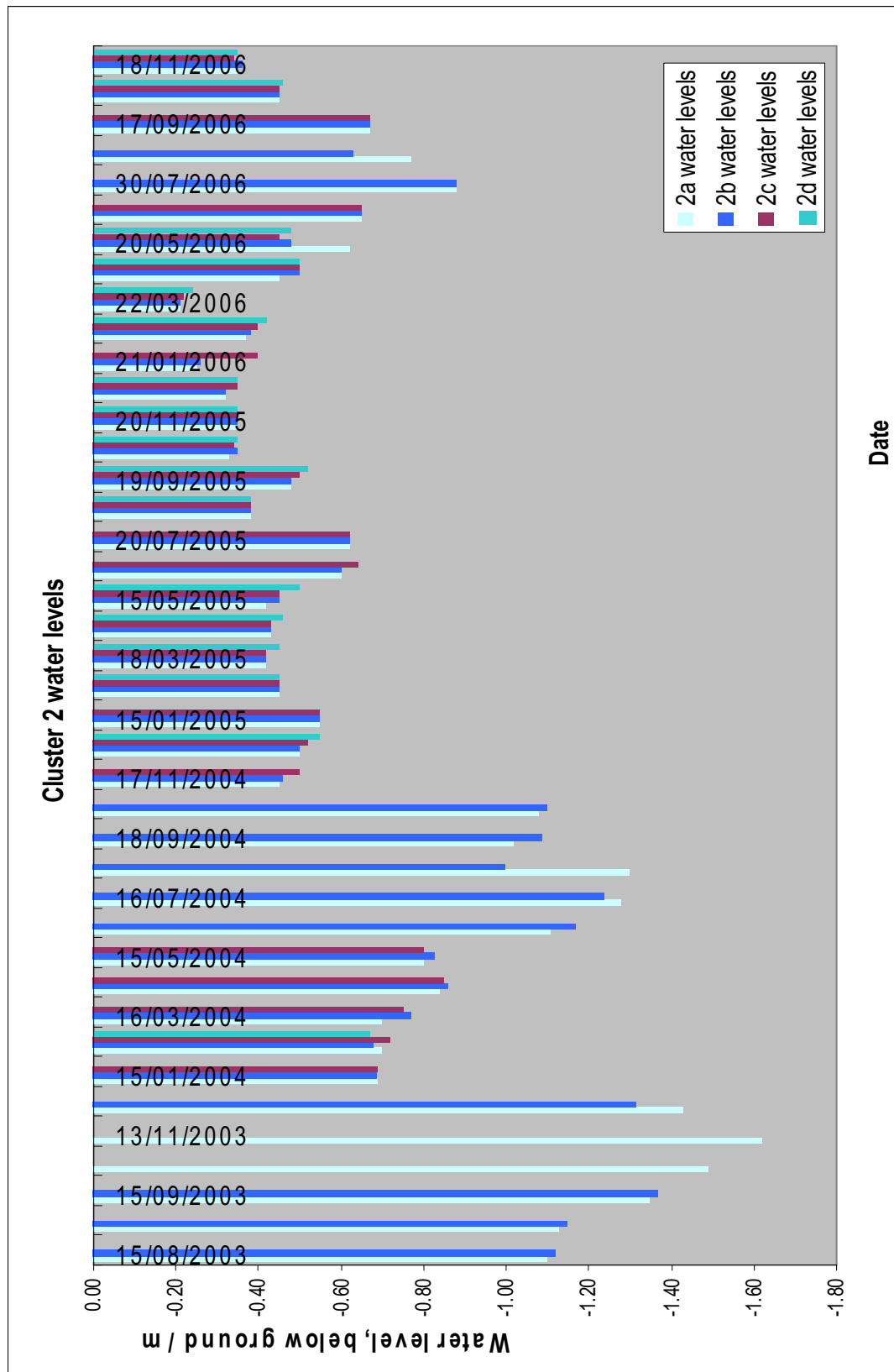
Appendix 2. Water levels at Cluster 1 for August 2003 to November 2006
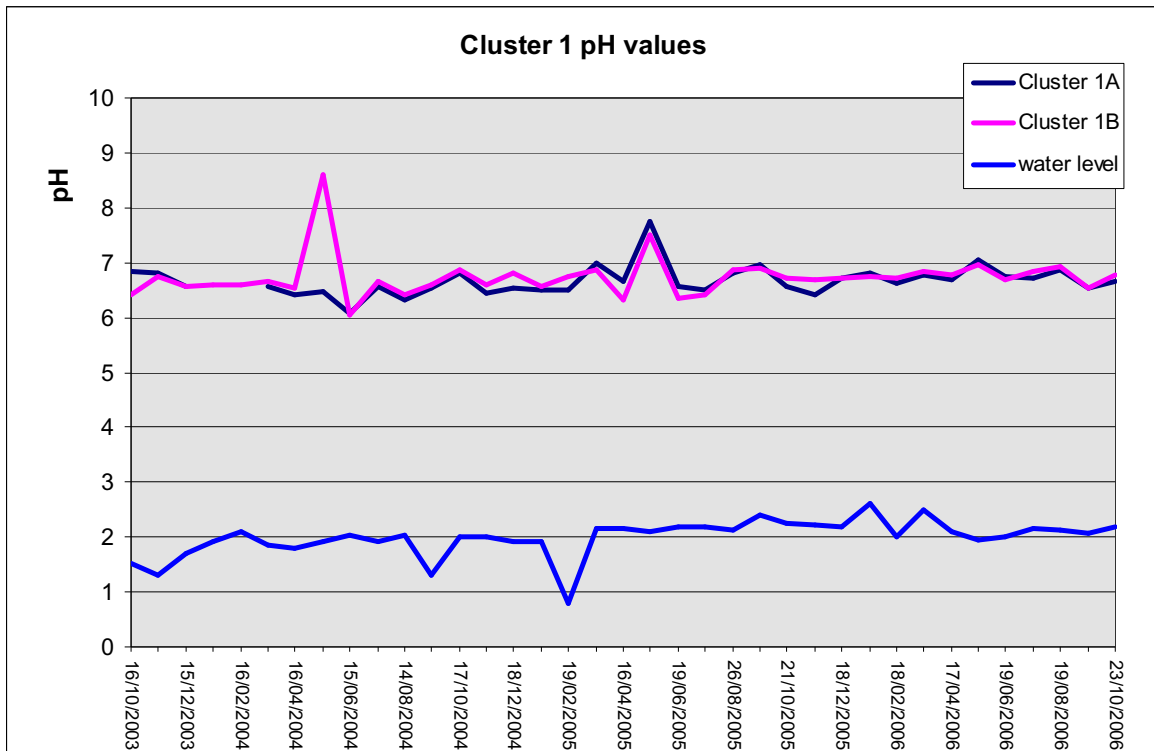
(measured as depths below ground surface)
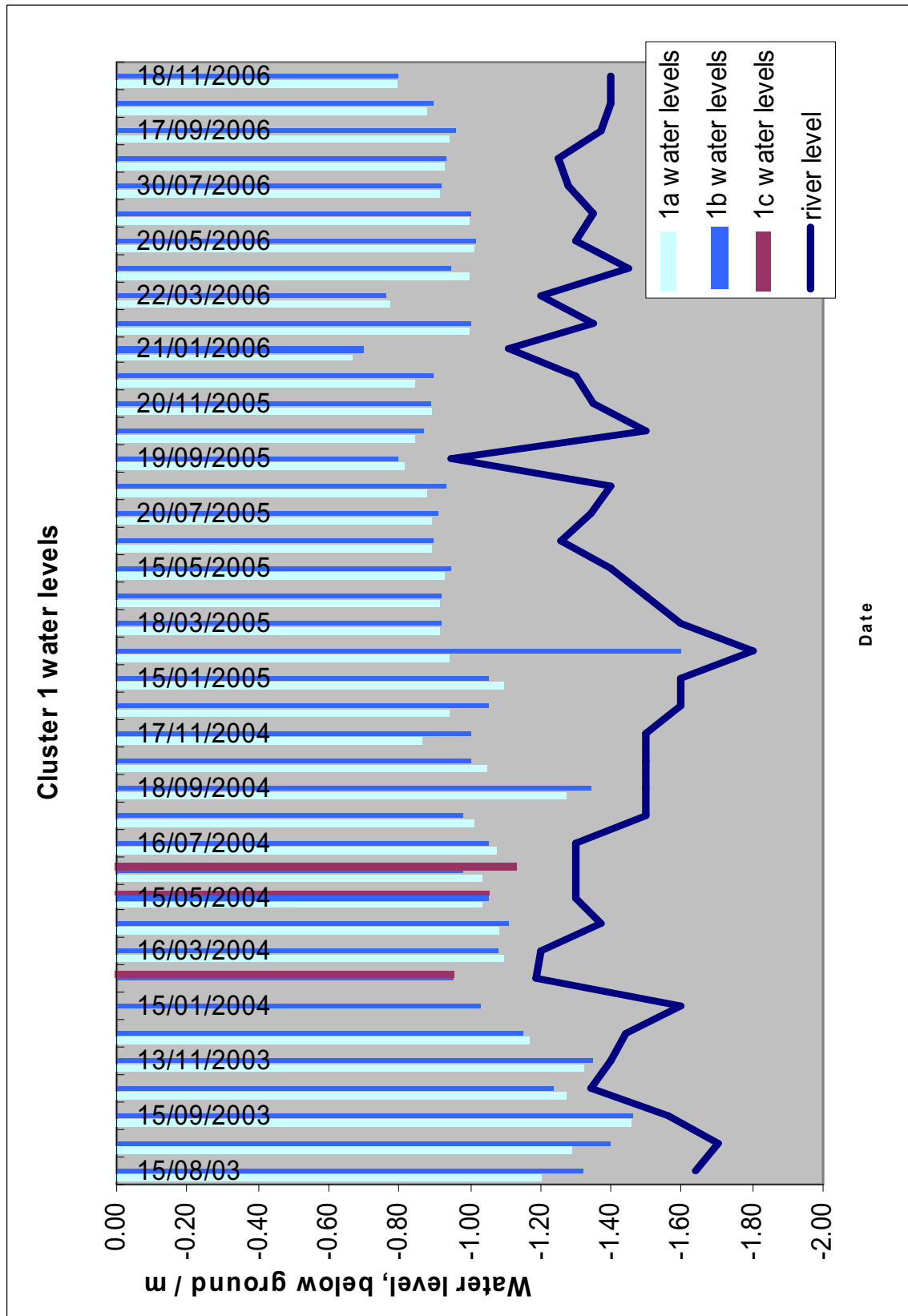
Appendix 3. Water levels at Cluster 2 for August 2003 to November 2006
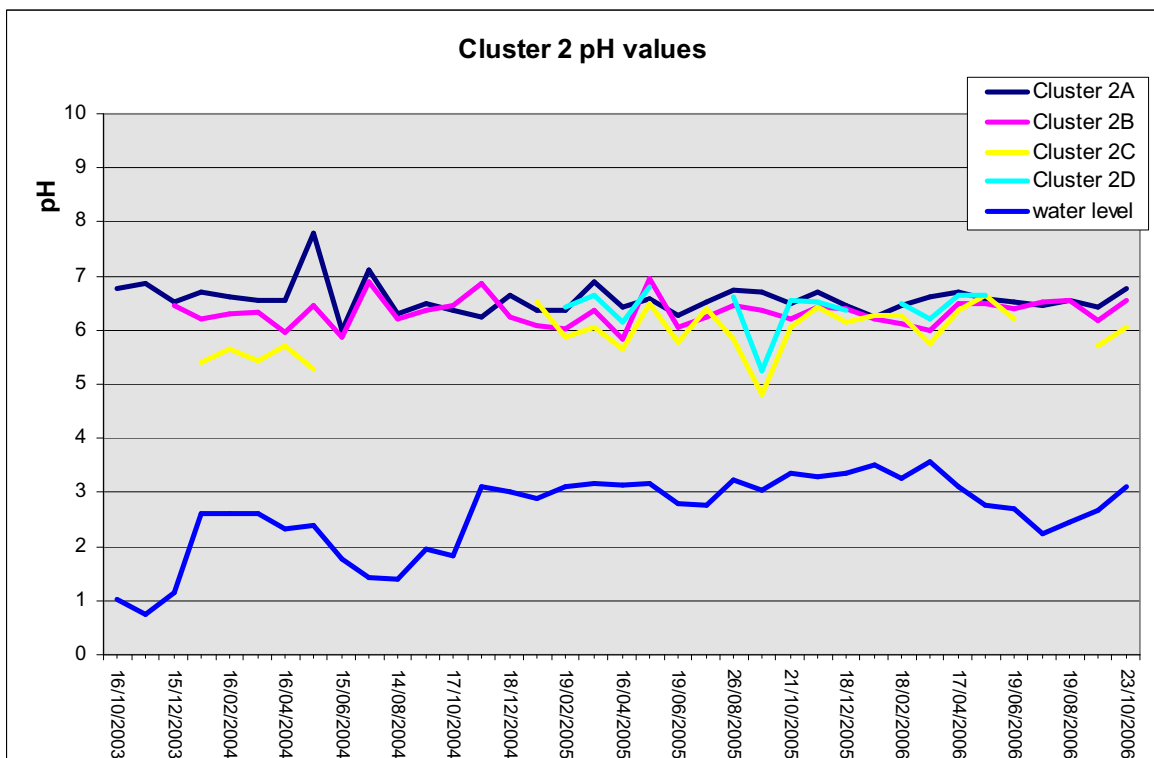
(measured as depths below ground surface

Appendix 4. Groundwater pH values for Cluster 1 (upper) and Cluster 2 (lower) for October 2003 to October 2006
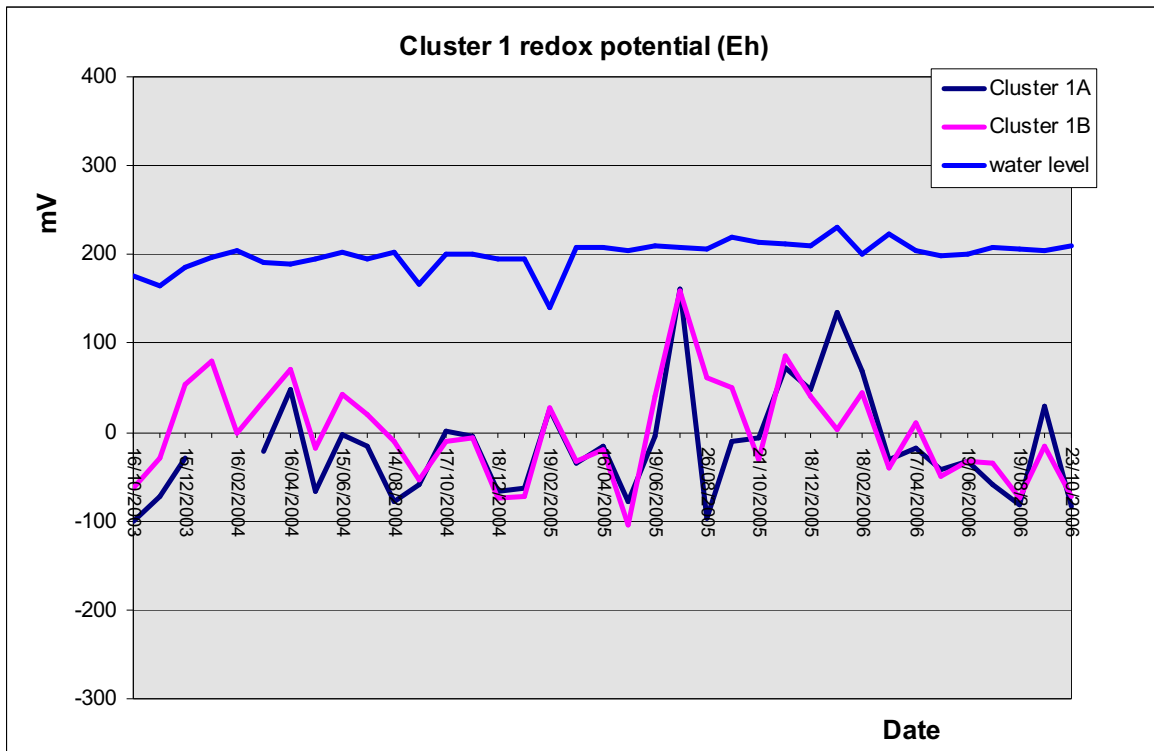

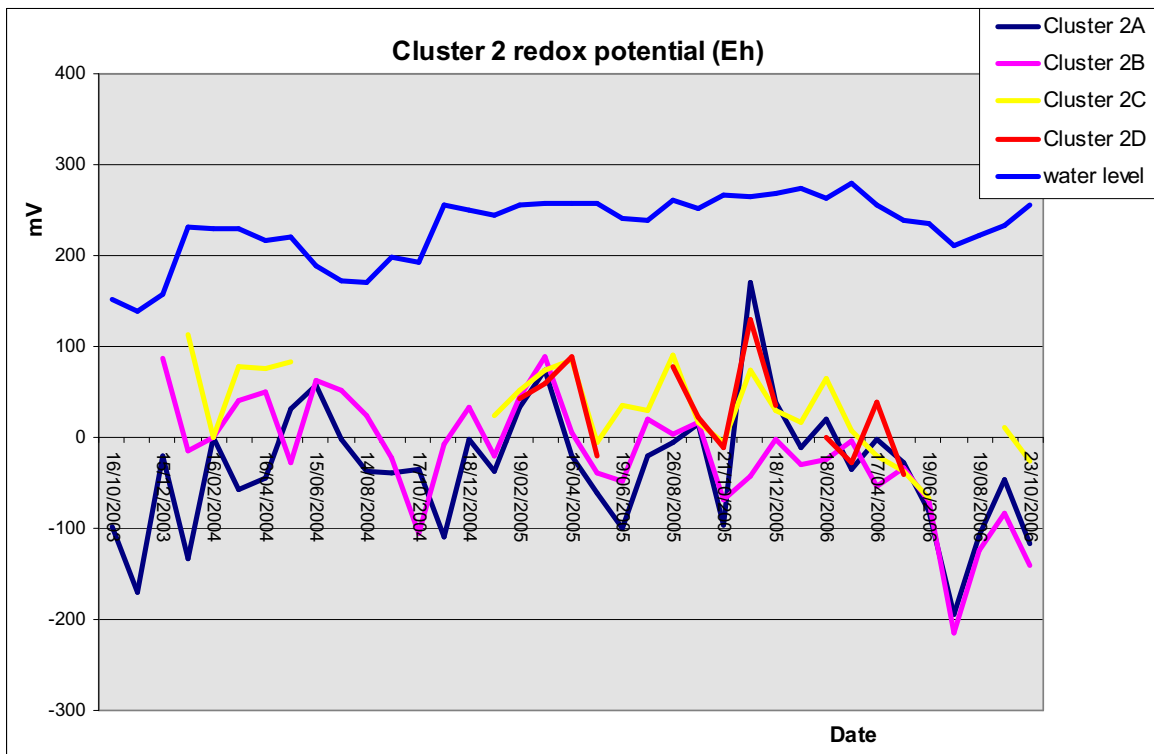Water level values shown in metres below ground surface

Water level values shown in metres below ground surface

Appendix 5. Groundwater redox potentials for Cluster 1 (upper) and Cluster 2 (lower) for October 2003 to October 2006


Water level values shown in metres below ground surface

Water level values shown in metres below ground surface

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Appendix 6. Selected groundwater data for Cluster 2 peizometer B for March 2004 to December 2006 [△]

	Min	Max	Average
pH*	5.8	7.0	6.3
Redox potential*	-215	+89	-19
Temperature (°C)*	5.2	20.7	12.0
Conductivity (mS/cm)*	1.78	2.66	2.34
Sulphate (SO$_4$ mg/l)	656	1520	1023
Calcium (Ca mg/l)	425	571	497
Chloride (Cl mg/l)	34	75	57
ortho-Phosphate (as P mg/l)	<0.02	1.9	0.14
Sulphide (S mg/l)	<0.01	1.8	0.2
Silicate (SiO$_2$ mg/l)	17.7	33.9	28
Iron (Fe mg/l)	9.4	44	22
Manganese (Mn mg/l)	2.8	4.5	3.4
Copper (Cu mg/l)	0.008	0.04	0.02
Nitrite (as N mg/l)	0.004	0.3	0.05
Nitrogen, total (as N mg/l)	8.1	27.5	13.2

[△] Excluding anomalous chemical data for Jan 2005

* Data to November 2006

25
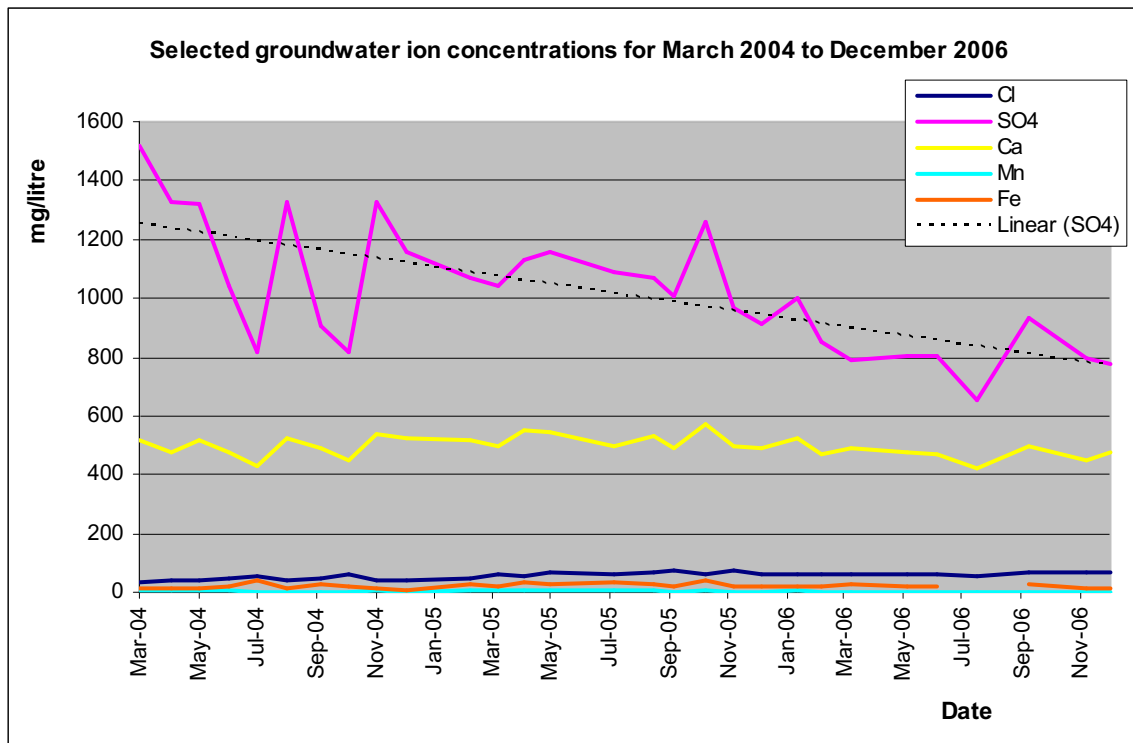
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