Chapter 4 Research methodology

4.1 Introduction

This chapter provides details of field and interpretive methods together with the rationale applied in their selection to address the research aim and objectives, that is: to determine the provenance, depositional environments and age of the sediments of the Gordano Valley, by identifying their aerial extent, surface morphology and geometries, establishing their stratigraphy and ages, interpreting their depositional environments and placing these within the context of reconstructions of regional Pleistocene palaeoenvironments.

In order to ensure collection of datasets that were valid, representative, rigorous and replicable, clearly defined and consistently applied procedural rules were adopted at the outset of data collection; validity and representativeness of datasets was ensured through careful design of the field sampling strategy and selection of study and sample sites. Rigour was ensured by accurate recording of the sediments present, careful collection and recording of observations and measurements, whilst replicability was ensured by the correct calibration and set-up of equipment. Wherever possible, conventional protocols were used in laboratory analyses; where this has not been possible the protocols used and rationale for their use is set out in the relevant section. A summary of field work and laboratory health and safety and ethical considerations is provided in Appendix V. Figure 4.1 shows key areas within the Gordano Valley with respect to this study.

4.2 Pilot study (core GV)

Since there are no exposures of minerogenic sediments available on the valley floor, a pilot study utilising a sediment core was necessary to establish the characteristics, thickness and fossil content of the sediments and to identify the most appropriate analytical procedures suitable for use in this research; results are discussed in the relevant sections. A core (core GV) of valley floor minerogenic sediments was retrieved from near the southern end of Weston Drove (N 51° 27.487’, W 002° 47.500’, Figure 4.11). Minerogenic sediments were reported by Jefferies *et al.* (1968) to be thicker in this region of the valley,

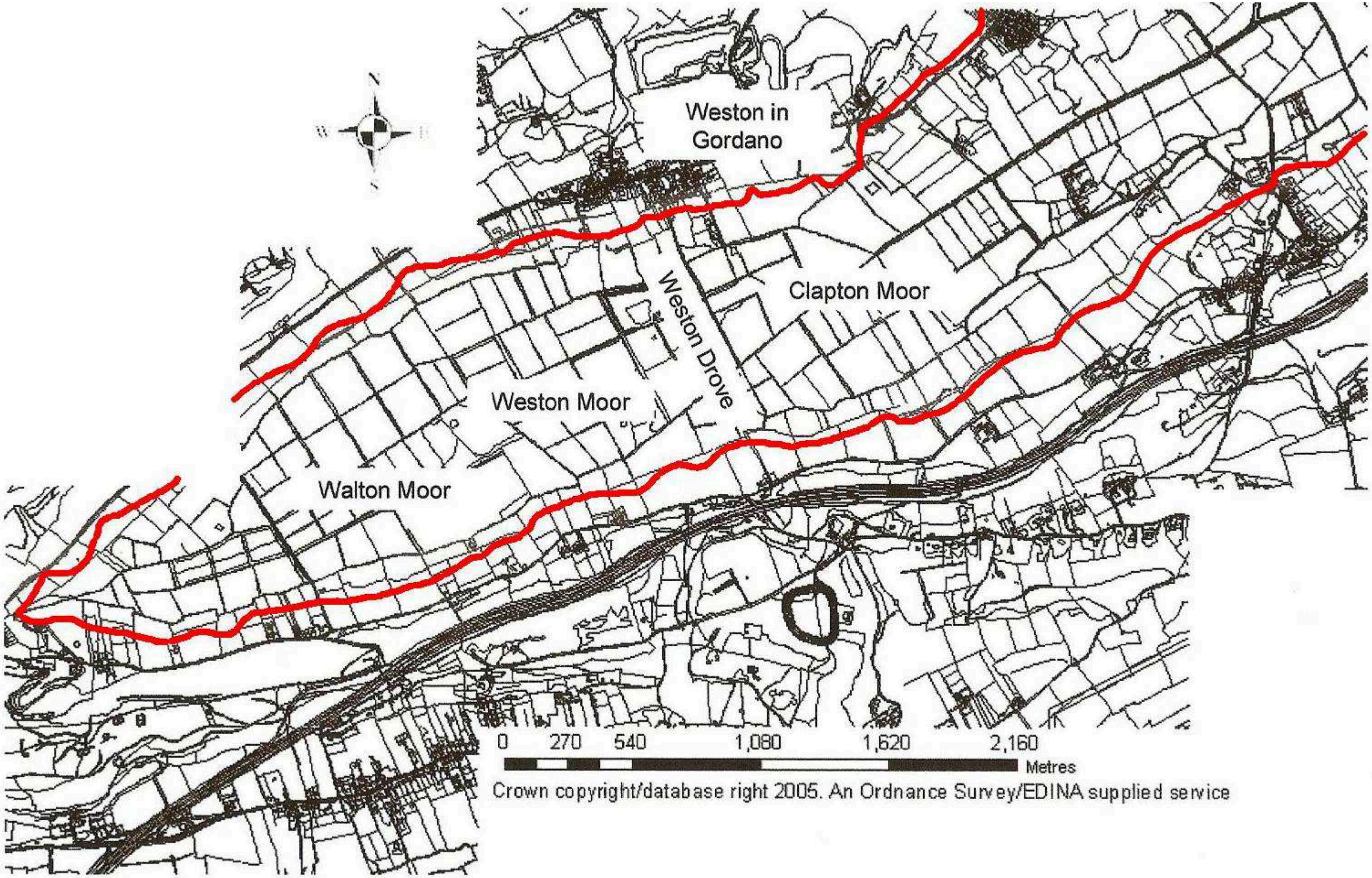


Figure 4.1: Key areas within the Gordano Valley. The boundary of the valley floor, which approximates to the 10 m contour, is picked out in red

so this would potentially maximise the quantity of information that could be obtained. Analysis of the core was carried out using the procedures set out in sections 4.7, 4.8 and 4.9; the results and their implications are presented and discussed in the relevant sections.

4.3 Fieldwork methodology and procedures

Data acquired by field sampling techniques were used to characterise and assess the aerial extent, surface morphology and stratigraphy of the valley floor minerogenic sediments and provide an indication of their geometries. Field sampling techniques were chosen which would obtain stratigraphic data from sediments below the peat surface at sufficient resolution to provide the detail that the pilot study (section 4.7) suggested was possible.

4.4 Determination of the aerial extent, surface morphology and geometries of the minerogenic sediments

Determination of the areal extent and surface morphology of the minerogenic sediments in the Gordano Valley forms an important preliminary stage in the investigation of the Pleistocene palaeoenvironments of the Gordano Valley, because it forms the basis for selection of locations for cores for further analysis. Geomorphology of landforms can often reveal a distinctive planform or three-dimensional shape that is diagnostic of a particular environment, and which in turn can provide valuable palaeoenvironmental information (Goudie 1990, Lowe & Walker 1997). It is sometimes possible to determine this from existing maps or aerial photographs, so that fieldwork is preceded by mapping (Goudie 1990).

However, because the Pleistocene topography in the Gordano Valley is masked by a thick covering of Holocene peat, no features are visible from maps, aerial photographs or satellite images that suggest the presence of any sub-peat landforms. Determination of the areal extent and surface morphology of the minerogenic sediments was therefore carried out in two stages. Stage one relied on information provided by previous authors (Jefferies *et al*. 1968, Hill 2006) for the choice of sampling area, and is described in the next section. Stage two involved field sampling and is described in sections 4.4.2 to 4.5.2.

4.4.1 Choice of sampling area within the field site

Details of the sampling area are provided in Figure 4.2. Choice of sampling area within the field site formed the first stage in determination of the aerial extent and surface morphology of the minerogenic sediments. As part of their valley-wide surveys Jefferies *et al.* (1968) and Hill (2006) found that Pleistocene minerogenic sediments were thicker in the area around Weston Drove, hence providing the greatest potential for the reconstruction of Pleistocene palaeoenvironments.

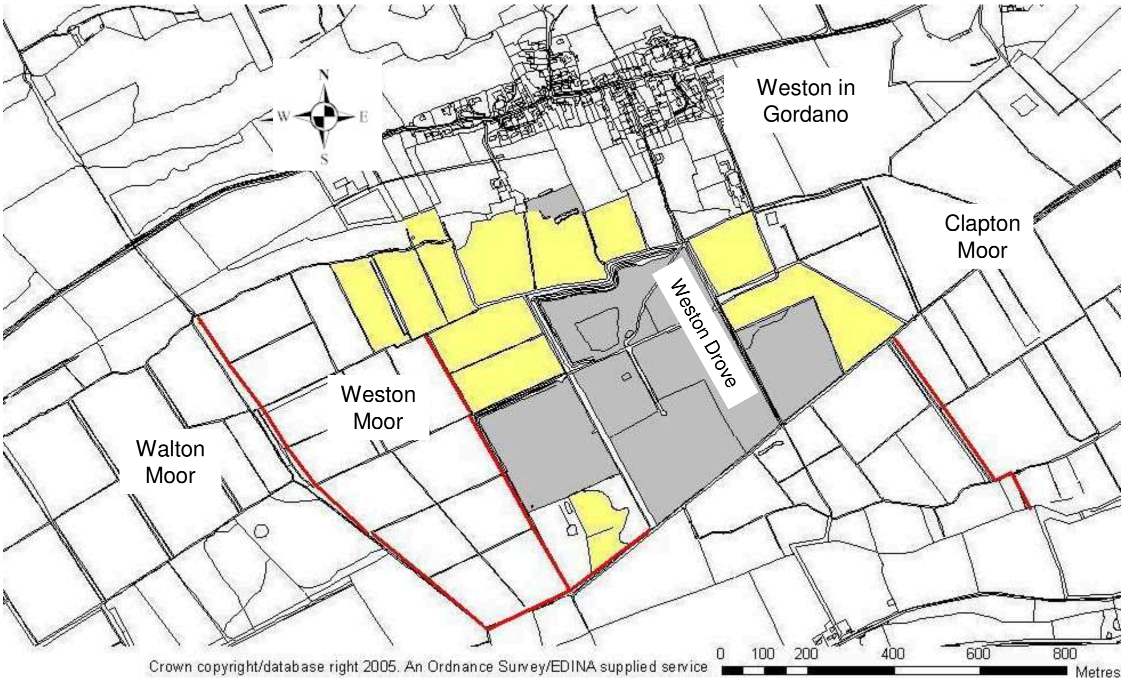


Figure 4.2: Location of field site showing sampling area (yellow) and cross- and down-valley transects (red lines). Areas shaded grey are those to which access was unavailable

Direct access to much of this area is presently restricted by waste disposal sites reputed to contain asbestos. The sampling area was therefore confined to the edges of the waste disposal sites, where access was granted by landowners. In order to improve the representativeness of the dataset the sampling area was extended by three transects across the valley floor and one down-valley transect along the southern edge of the accessible area.

4.4.2 Field sampling techniques

Field sampling formed the second stage in the determination of the aerial extent and surface morphology of the minerogenic sediments. At this stage of the research no dating of the valley floor minerogenic sediments had been carried out. Peat formation is known to have commenced by 9520 Cal BP, i.e. during the early Holocene (MIS 1), whilst biogenic sedimentation on Weston Moor is known to have commenced between 15060 and 13820 Cal BP (Hill *et al.* 2008), i.e. during the Devensian Lateglacial (MIS 2). Although the minerogenic sediments immediately below the peat could potentially be both Holocene and Pleistocene, in the absence of dating Pleistocene minerogenic sediments were assumed to be those immediately underlying peat or biogenic mud.

Two approaches were used for field sampling: manual coring was used to establish the surface morphology, but there was poor penetration of the sediments with this technique, so percussion coring was used to recover deeper sediments for laboratory analysis.

4.4.3 Manual coring

Because thick peat surface deposits restricted direct access to the minerogenic sedimentary sequences, manual coring using a 2.5 cm manual corer was used to retrieve subsurface samples. This technique facilitated identification of stratigraphic changes at depths of up to 5.28 m and permitted elucidation of the areal extent and surface morphology of the minerogenic sediments. Alternative methods either lacked the necessary resolution or involved removal of large volumes of peat overburden.

Manual coring generated a range of field information, such as thickness of sediments, grain size and sorting and clast lithology. Although sedimentary structures and architecture were often distorted during recovery of core samples, and the cohesiveness and compaction of the sediments often made their retrieval difficult, it was still possible to determine the vertical and lateral extent of the upper lithofacies from data obtained in this way. The surface of each core was levelled to OD and coring was conducted until sediments which could not be recovered or penetrated using this equipment were reached. Stratigraphies were established by retrieving successive cored samples from measured depths. This technique facilitated the identification of stratigraphic changes at centimetre resolution within each core. These relationships were then used to reconstruct a sequence of deposition with measured depths permitting determination of the surface morphology and the establishment of a three-dimensional representation of the sedimentary units and their geometries. Although occasional poor penetration with the manual corer hampered the process of sediment mapping, plotting and mapping the peat/minerogenic sediment interface provided an indication of minerogenic sediment surface morphology prior to Holocene peat or, where present, biogenic mud formation and lateral changes in the sediments. A total of 489 cores was sampled.

In order to provide adequate coverage of the study area and ensure representativeness of data a sampling grid was used. The position of a sampling grid in the study area was controlled by:

1. The WSW-ENE trend of valley.
2. Field boundaries/rhynes.
3. Accessibility.
4. Replicability; the ability to return to sample points for further material, or material for dating, if necessary.

The trend of the valley and the position of field boundaries meant that it was not possible to impose a uniform grid across the field sampling site. Datasets are therefore only representative of the sediments within these restrictions.

In order to maximise evidence on a field by field basis each field was sampled using a separate grid with a sampling interval of 25 m. This allowed variations in the valley stratigraphy to be interpreted at spatially high-resolution, and permitted the identification of subtle but significant sedimentological changes. Such systematic sampling was utilised to minimise subjective bias and produce representative results (Goudie 1990). Additionally, field sampling in this manner provided a higher-resolution survey from which to assess the sedimentary archive than that of either Jefferies *et al.* (1968), who used a coarse sampling strategy of essentially seven cross-valley transects and one down-valley transect, or Hill (2006), who used a 125 m grid to survey the whole valley, thereby reducing uncertainties in the geometries of the sedimentary units.

Each field was assigned a letter and each core within a field was identified by an alphanumeric commencing with the field letter, for example C23 would be the 23rd core in field C. Figure 4.3 shows the field identity letters and an example of the grid sampling system used during fieldwork.

© Crown copyright/database right 2006. An Ordnance Survey/EDINA supplied service.

Figure 4.3: A. Field identity letters used during fieldwork. B. Example of sampling grids applied during fieldwork

The 25 m sampling grid was laid out from an origin as close to the corner of the field as possible at the northeast corner each field west of Weston Drove and the northwest corner of fields to the east of Weston Drove. Coring was carried out at the grid intersections. From the origin 25 m was measured southwards using a 30 m measuring tape to the next sample point and so on until the end of the field was reached. The first sample point of the next leg of the grid was measured 25 m west of the origin (for sample grids west of Weston Drove; sample grids east of Weston Drove mirrored this scheme) i.e. working parallel to and away from Weston Drove (Figure 4.4). Where the next sampling point coincided with a rhyne, sampling was carried out as close to the rhyne edge as possible. This scheme inevitably introduced a measure of bias to the field data collection, because poorly accessible locations were excluded.

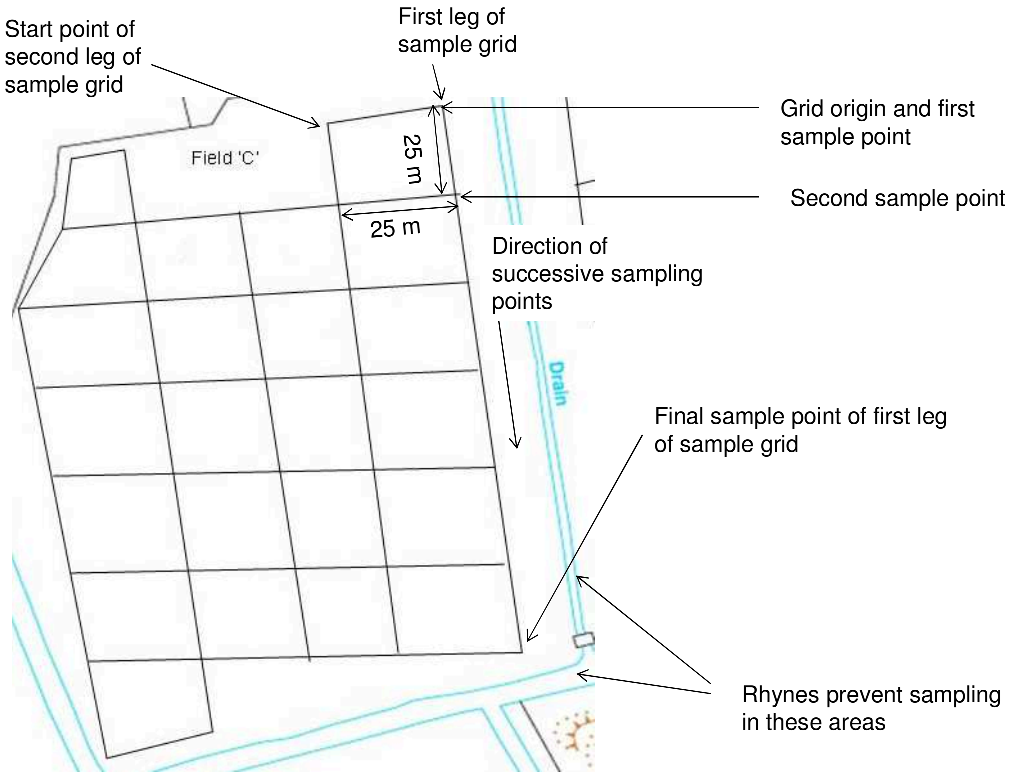


Figure 4.4: Coring scheme for a field west of Weston Drove. Coring was carried out at grid intersections. Where the next sampling point coincided with a rhyne, sampling was carried out as close to the rhyne edge as possible

4.4.4 Aerial extent of the minerogenic sediments

A hand held Global Positioning System (GPS) (Garmin GPS 12 Personal Navigator) was used to record the latitude and longitude (to three decimal places of minutes) at each core location. This system provides a positional accuracy of ±5 m, although in practice positional accuracy was found to be ±1 m and enabled a return to be made to each sample point for the collection of further material for analysis or dating purposes as required. However, the GPS system used lacked acceptable altitudinal accuracy, so altitudes were levelled using a Topcon GTS-210 total station, related to a benchmark.

The GPS co-ordinates of each manual core location were used together with Digimap Landline Plus (Ordnance Survey/EDINA 2005) and ESRI ArcMap 9.1® software to map the core locations and their various deposits. This was extrapolated to produce maps of the aerial extent of uniform deposits, with delineation based on homogeneous units. Figure 4.5 shows the core sampling sites imposed on the study site.

4.4.5 Surface morphology of the minerogenic sediments

Uncertainty about the altitude of the minerogenic surface is created not only by shrinking and swelling of the overlying peat in response to changes in the water table, thereby altering its altitude, thickness and surface topography, but also through vertical lowering of the surface(s) through the reduction in post-depositional sediment volume by compression of the sediment overburden (sediment autocompaction). This can seriously impact on vertical references for the reconstruction of palaeoenvironments because it lowers the original elevation of the sediments (Kidson & Heyworth 1976, Haslett *et al.* 1998, Allen 1999, 2001b, Waller & Long 2003, Hill 2006, Massey *et al.* 2006a).

Sediment autocompaction also has an effect on silt and clay (Massey *et al.* 2006a), although muds compress only a moderate degree and gravels and sands have low potential for compaction (Allen 1999, 2000b, Edwards 2006, Massey *et al.* 2006b). However, sediment autocompaction has proved difficult to measure or model (Allen 2000b) because it is influenced by unit thickness, depth of overburden, passage of time since deposition and sedimentary geotechnical properties including unknown variables such as water content and loading history (Edwards 2006, Massey *et al.* 2006a and b, Hill *et al.* 2007). There is presently no accepted method to correct for the influence of sediment autocompaction and consequently it is commonly set aside (Allen 2000b, Massey *et al.* 2006a). Although techniques to account for sediment autocompaction have been developed, for example Haslett *et al.* (1998) and Massey *et al.* (2006b) and a number of techniques reviewed by Allen (2000b), these are unstandardised and provide variable results which may reflect differential local response (Edwards 2006). Hill (2006) was unable to apply any of the available techniques to his research due to, for example, lack of peat onlap to solid rock, and was unable to account for autocompaction within the Holocene sedimentary archive of the Gordano Valley. Since adjustments for sediment autocompaction tend to be site specific (Edwards 2006), and there are presently no values available for the Gordano Valley, no corrections for sediment autocompaction were applied in this thesis.

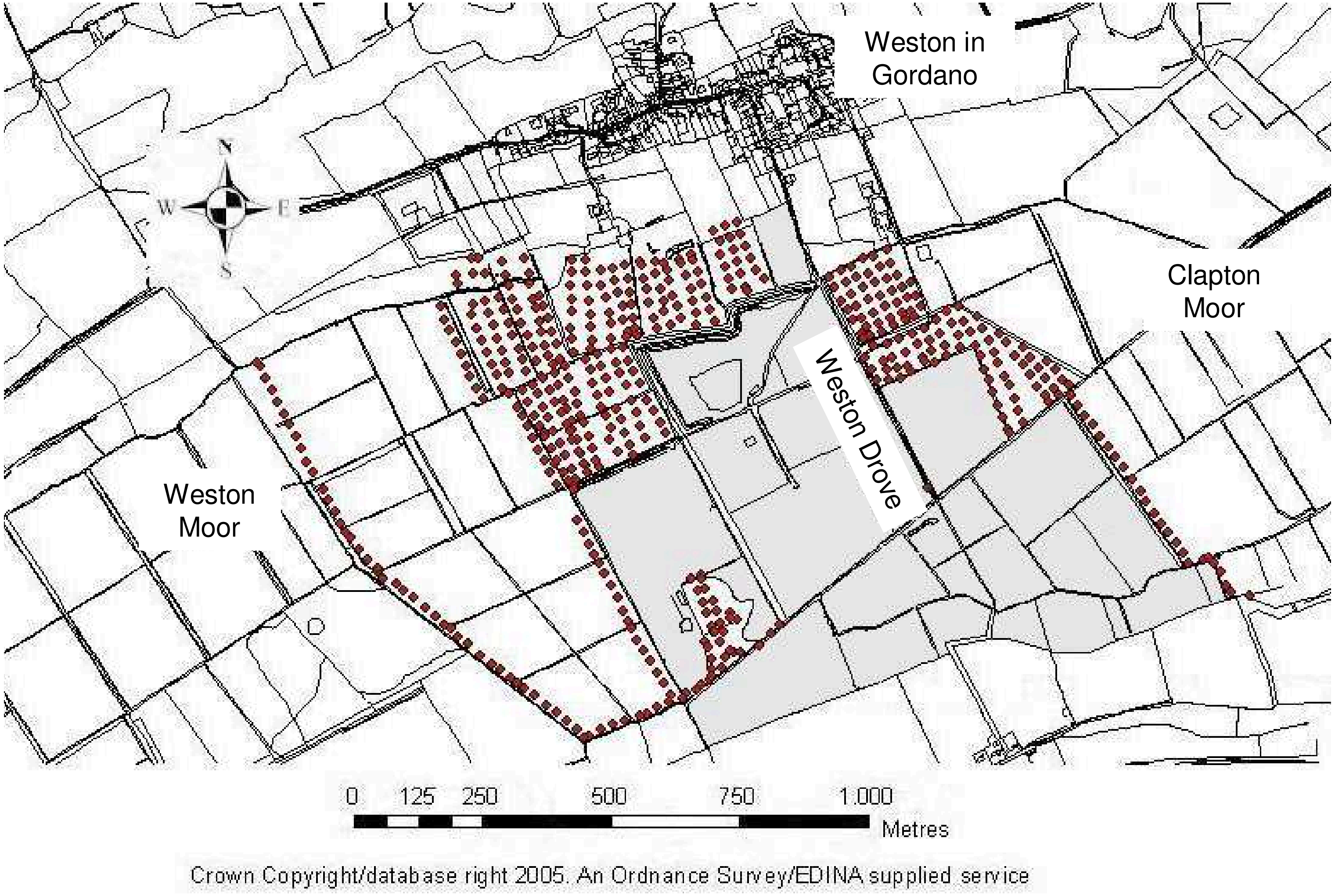


Figure 4.5: Manual core sampling sites ◆ imposed on study site. Areas shaded grey are those to which access was unavailable

Levelling was used to relate surface altitudes to OD albeit with the caveat that mitigation for the influence of peat shrinking and swelling by carrying out all levelling on the same day under the same meteorological and groundwater conditions was unfeasible for the number of cores involved, nor was it possible to quantify peat shrinking and swelling. Surface altitudes which could not be levelled due to dense vegetation or landuse changes were obtained from LiDAR (Light detection and ranging) elevation data. This has positional accuracy comparable to the GPS system used and vertical accuracy of ±40 cm at a 2 m resolution (Gao 2007, Gonga-Saholiariliva *et al.* 2011, Wilson 2012), with the advantage that all data are obtained on the same day, under the same meteorological and groundwater conditions. The measured thickness of peat, or where present, the measured thickness of both peat and biogenic mud together, was then subtracted from the relevant altitude to give the altitude of the minerogenic surface for each manual core.

A three-dimensional representation of the overall form of the minerogenic sediment surface was achieved using Surfer® 7 (Golden Software 1999, version 7.04, 2001) computer software. This software was used by Hill (2006) to produce three-dimensional representations of sub-surface features in the Gordano Valley and its use would therefore allow comparison with previous research. Coordinate data were plotted in conjunction with recorded sediment thicknesses and this software was used to interpolate the irregularly spaced XYZ data collected during fieldwork into a regularly spaced grid to produce contour and wireframe maps. This interpolation is integral to the Surfer® software and a suite of gridding methods, which define the way in which XYZ data are interpolated when producing a grid file, are available. Gridding fills holes between points where data are missing by extrapolating and interpolating Z values at those locations where no data exists (Golden Software Inc. 1999). The gridding methods in Surfer use weighted average interpolation algorithms; in this thesis the kriging algorithm was used. This is a geostatistical gridding method that attempts to express trends suggested by the data. It has been shown to be one of the most reliable two-dimensional spatial estimators and can be expected to produce reliable elevation data (Chappell *et al.* 2003, Heritage *et al.* 2009).

However, Heritage *et al.* (2009) found that if measured data are sparse in regions of (relatively) high topographic variation, then topography is generally more poorly modelled by the interpolator and that errors are highest in areas were there are no measured data. This can create a misleading impression in areas where data are missing or not collected, for instance where access was denied. In order to mitigate for the effects of large unsurveyed areas, separate three-dimensional models were produced of three main surveyed areas (Weston Moor North, Weston Moor South and Clapton Moor) where coring density was greatest (Figure 4.6) and these were subsequently used to guide further work.

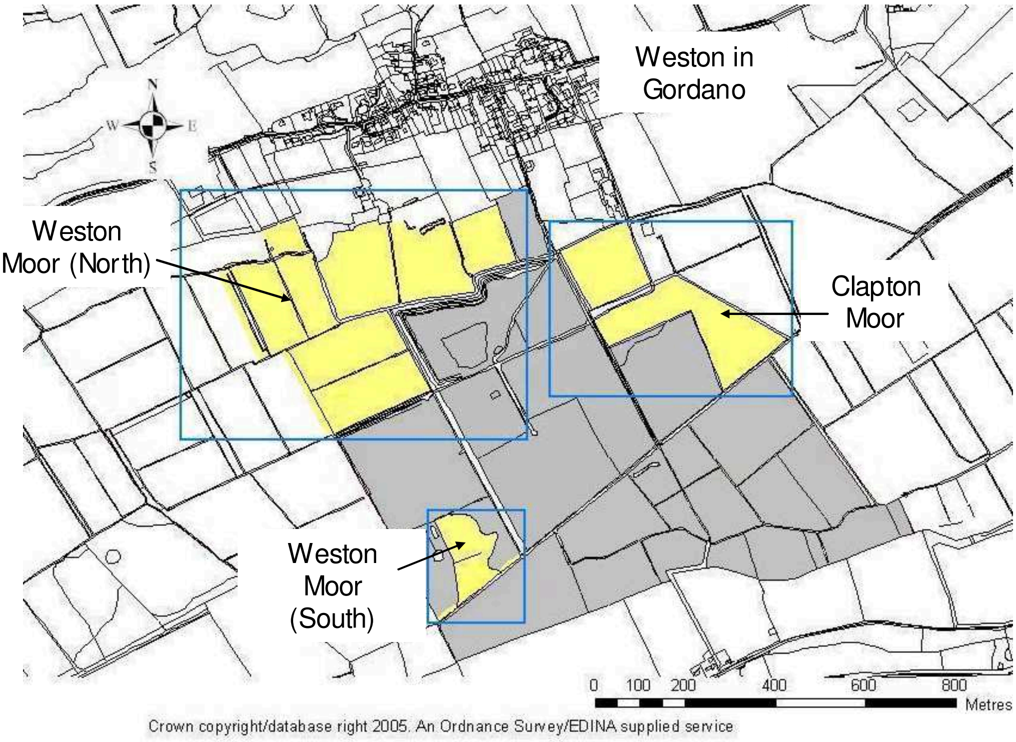


Figure 4.6: Approximate areas of Surfer® plots of the minerogenic surface (blue boxes) corresponding to areas of intensive manual coring (yellow). Separate plots are provided for Weston Moor (North), Weston Moor (South) and Clapton Moor. Unsurveyed areas to which access was unavailable are shaded grey

4.5 Establishing the stratigraphy and geometries of the minerogenic sediments

Sedimentary logging of stratigraphy in the field is a standard procedure which was used to record stratigraphic changes, highlight vertical trends, which in a core represent change over time, and allow rapid visual comparisons to be made (Jones *et al*. 1999). The geometry, shape or thickness of sedimentary units reflects the processes and environments of deposition (Evans & Benn 2004). These may be laterally extensive, as for example, gravel or sand sheets or isolated bed forms, for example, channel fill, or irregular, which may indicate post-depositional disturbance or partial reworking (Evans & Benn 2004). Contact between beds was used to provide additional information; gradational or conformable contacts indicate continuous deposition or deposition uninterrupted by erosional episodes; unconformable contacts may indicate the geometries of former erosion surfaces, such as channel forms from which channel dimensions and patterns of migration can be reconstructed (Evans & Benn 2004).

4.5.1 Establishing the stratigraphies of the minerogenic sediments

Stratigraphy in the field was recorded using a scheme based on conventional symbols and notation for sedimentary rocks (Jones *et al.* 1999, Tucker 2003, Evans & Benn 2004). Similar schemes have been widely applied in the study of Pleistocene sediments and environments, thus ensuring consistency in the recording of sedimentary characteristics and allowing inter-site comparisons. An example of the personalised log compiled in the field is provided in Figure 4.7 and an explanation of the symbols used is shown in Figure 4.8. Depth of the sedimentary units below the surface was recorded using a 5 m steel tape measure and the following stratigraphic aspects were logged directly into a field notebook:

1. Lithology: composition of the sediment.
2. Texture: grain-size and arrangement of grains in the sediment. This was recorded by combining the column for lithology with a horizontal scale for peat, clay, silt, fine, medium or coarse sand and gravel as shown in the left-hand column of Figure 4.7, and using lithofacies codes (Table 4.1). Roundness and shape of individual clasts was also noted.
3. Colour: This was the field moist colour noted using Munsell® soil colour charts (U.S. Department of Agriculture 2000), and included details of any mottling present.
4. Sedimentary structures, bedding surfaces and the nature of vertical changes defined by changes in sediment grain size and colour.
5. Fossils: Principle fossil groups were recorded.

Where partial recovery of some sections occurred, particularly at the base of the sections, this was also recorded, as were details of any photographs of the sediments and specimens taken.

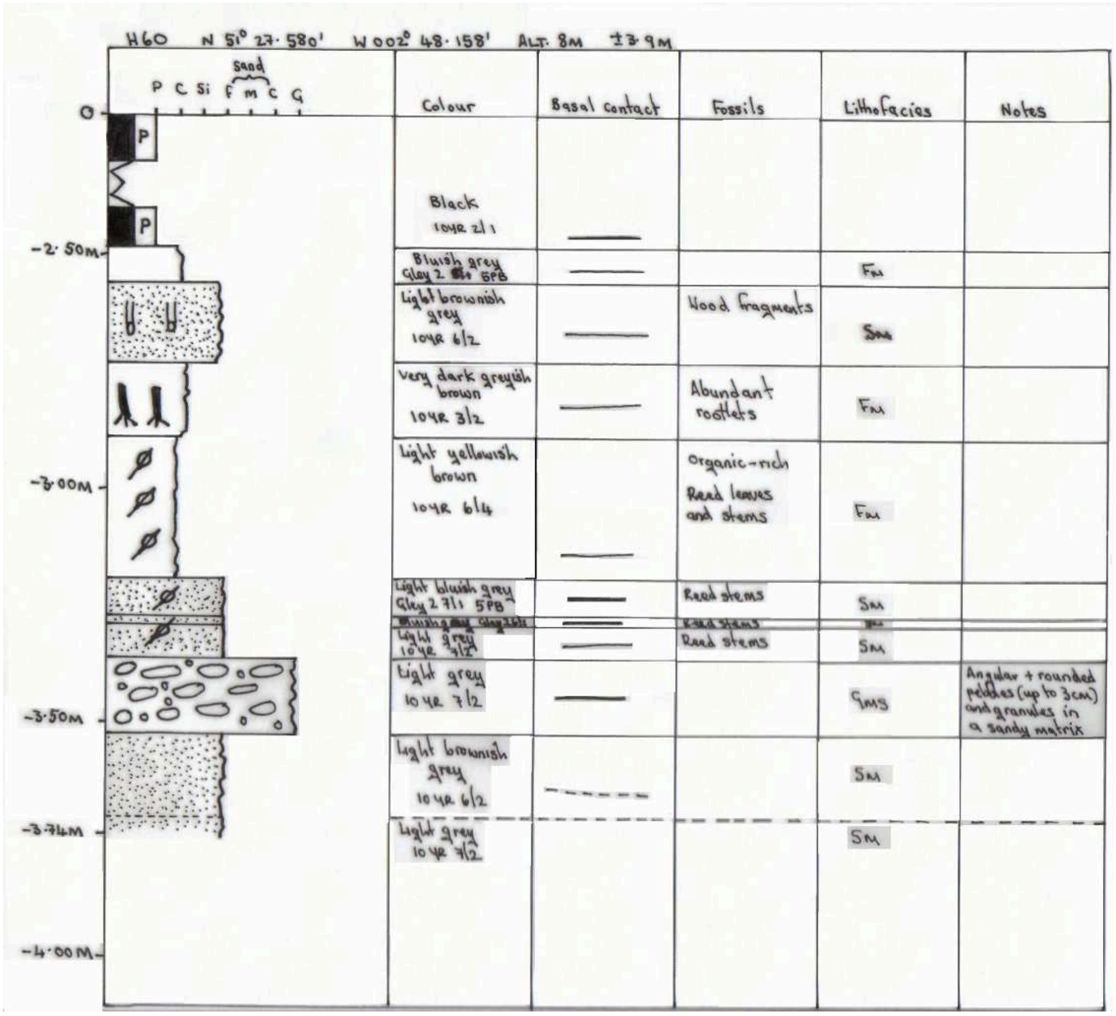


Figure 4.7: Example of a stratigraphic log drawn up from field record

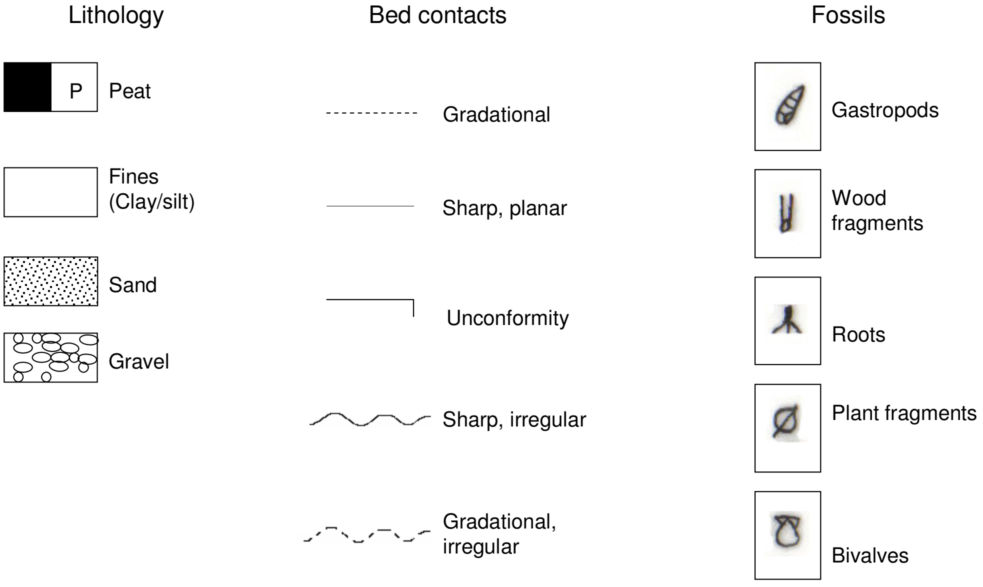


Figure 4.8: Notation and symbols used in the field (sources: Tucker 2003; Evans & Benn 2004)

Table 4.1: Lithofacies identified in this study; codes based on Tucker (2003); Evans & Benn (2004)

Lithology	Prefix	Qualifier	Code	Description
Gravel (G)	C		CG	Coarse gravel
		ms	Gms	Matrix supported, massive gravel
		m	Gm	Clast supported, massive gravel
Sand (S)	f	m	fSm	Massive fine sand
	m	m	mSm	Massive medium sand
	c	m	cSm	Massive coarse sand
		uf	Suf	Upward fining sand
		uc	Suc	Upward coarsening sand
Silt & clay (F)		m	Fm	Massive silt or clay
Peat (P)			P	Peat

The feel method (Rowell 1994, Brady & Weil 2004) was used during fieldwork to provide estimations of texture and to facilitate the stratigraphical reconstruction. This was necessary because whilst much of the stratigraphical reconstruction relies upon textural properties, only a relatively small proportion of core samples could be subjected to laboratory particle size analysis. Although the feel method was developed to determine soil texture classes it provides a broad limit to the sediment particle-size distribution and allowed the sediment to be allocated to a textural class from which a stratigraphical reconstruction could be produced (Rowell 1994, Brady & Weil 2004). Textures were allocated based on the guidelines shown in Table 4.2.

Sand textures were further subdivided into fine, medium and coarse depending on the visually dominant grain size distinguished by using a hand lens and comparison with a standard chart, although use of such charts introduces a degree of subjectivity. Comparison with standard visual comparison charts was also used to assess sedimentary particle sorting and the percentage cover of, for example, mottling. Colour was assessed using Munsell® soil colour charts (U.S. Department of Agriculture 2000), the most widely used colour reference.

Information from field data was used to provide two- and three-dimensional representations of the geometries of the minerogenic sediments, as outlined in the next section.

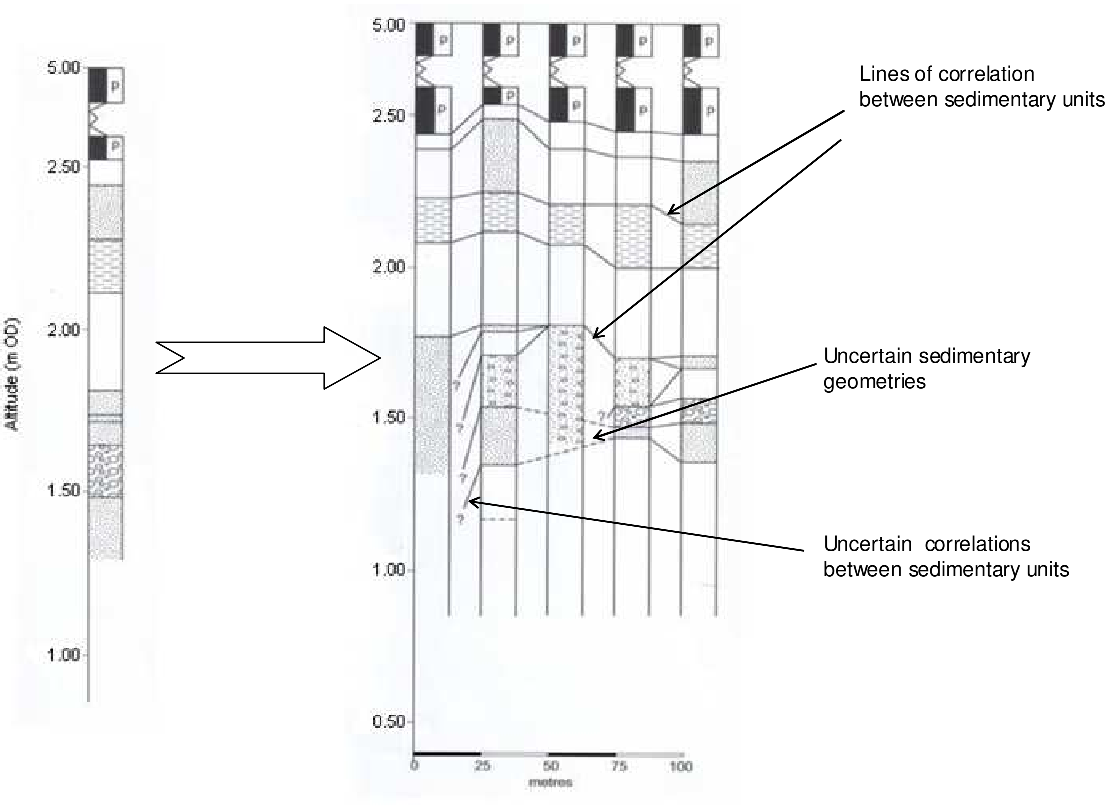
Table 4.2: Guidelines used to assign sediment texture in the field (source: Rowell 1994, Figure 1.2)

Guideline		Textural class
Does not form a cohesive ball. Hardly adheres to fingers. Very sandy feel	Yes →	Sand
No ↓		
Forms a cohesive ball. Rolls into a short, thick cylinder but not a thread. Sandy feel. Very little adheres to fingers.	Yes →	Silty sand
No ↓		
Rolls into a thread. Thread does not bend into a U. Adheres to at least one finger. Silky/soapy feel.	Yes →	Silt
No ↓		
Thread bends into a U and rolls into a ring. Adheres to finger and thumb. Silky/soapy feel. Moderately sticky	Yes →	Clayey silty sand
No ↓		
Sandy feel, very sticky. Takes a polish but sand grains stand out on surface	Yes →	Sandy clay
No ↓		
Very sticky with silky/soapy feel. Takes a polish	Yes →	Silty clay
No ↓		
Extremely sticky. Very stiff to work	Yes →	Clay

Notes:
Start with approximately 2.5 cm diameter of sediment with moisture content which, on being wetted, just begins to adhere to fingers
Cylinder: Approximately 5 cm long and 1.5 cm diameter
Thread: Approximately 13 cm long and 0.6 cm diameter
Ring: Approximately 2.5 cm diameter formed from about 8 cm of above thread

4.5.2 Establishing the geometries of the minerogenic sediments

The thickness of sedimentary units, calculated from the measurements taken in the field, was used to establish their geometries and to determine lateral changes. A series of transects linking core stratigraphies was constructed to form a two-dimensional representation with lines of correlation drawn between sediment units and lateral relationships recorded. Transects were related to the field sampling grids and sketches produced which showed the variation in thickness of different sedimentary units along transects. These provided a visual impression of the changing thicknesses and geometries of the Pleistocene sedimentary units, which reflect the processes and environment of deposition (Evans & Benn 2004), and allowed changes along a transect to be tracked. An example of how this was achieved is shown in Figure 4.9.



Stratigraphy

Geometry

Figure 4.9: Diagram showing how a series of stratigraphies were linked together to provide a two-dimensional impression of changes in thickness and geometries of the Gordano Valley Pleistocene sedimentary units

Three-dimensional diagrams were constructed for key transects selected based on their representativeness of features identified during field work. The relationships of sedimentary units were used to construct a three-dimensional representation of the sedimentary units in which geometries of the various units were highlighted, providing further information on their depositional environments. An illustration of how this was applied is shown in Figure 4.10.

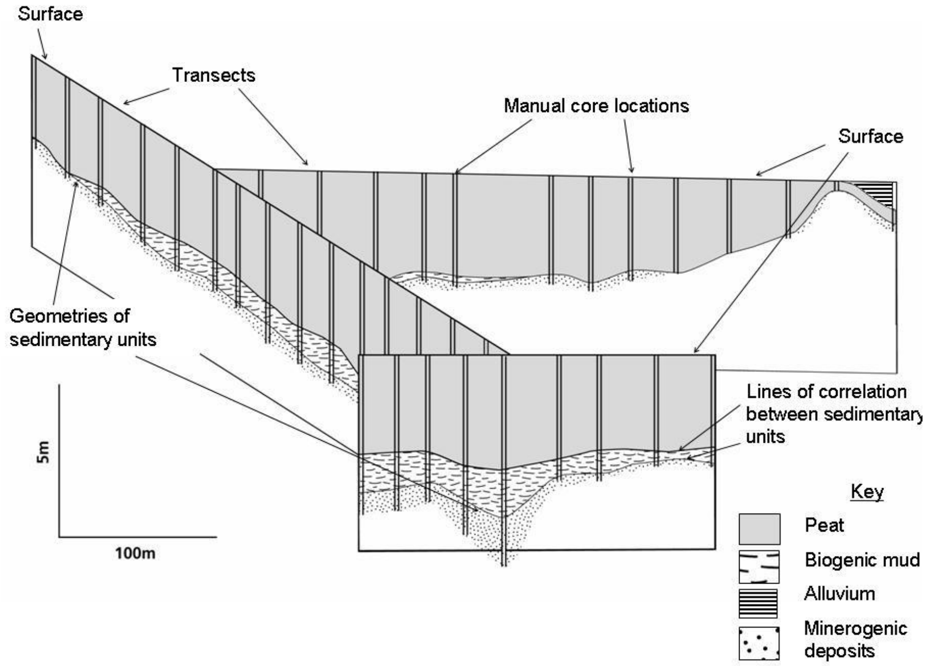


Figure 4.10: Diagram showing a three-dimensional representation of the geometries of sedimentary units from aggregated two-dimensional transect diagrams

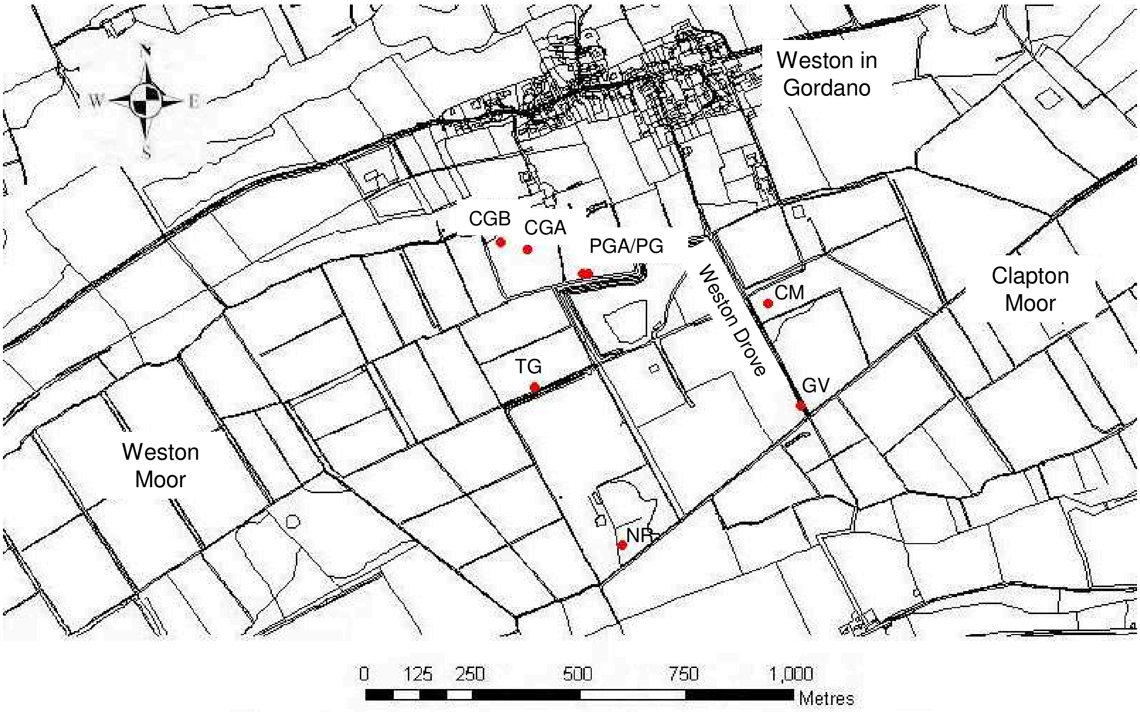
The methods described above allowed interpretation of the stratigraphy of the area, enabling locations to be chosen that would maximise the quality of the percussion cores obtained for subsequent laboratory analysis.

4.6 Percussion cores

On completion of the field stratigraphic survey, percussion cores were extracted for the purpose of extending the stratigraphies recorded in the field and providing material for laboratory analysis. In addition to the pilot study, seven locations were selected for the extraction of cores, on the basis of their representativeness of features identified from manual coring.

4.6.1 Locations of percussion cores for laboratory analysis

To address the research objective of establishing the stratigraphy and ages of the minerogenic sediments, percussion cores were extracted for laboratory analysis. Percussion cores were retrieved from areas that had the thickest deposits of sub-peat minerogenic sediments, potentially maximising the quantity of information that could be obtained. The locations of percussion cores are shown in Figure 4.11; justification for the locations is summarised in Table 4.3. Cores PG and PGA are less than 1 m apart because of difficulties in recovering core PG, which was retained because the cores demonstrate rapid lateral sedimentary changes.



Crown Copyright/database right 2005. An Ordnance Survey/EDINA supplied service

Figure 4.11: Locations of percussion cores (red dots)

Table 4.3: Summary of justifications for percussion core locations

Core	Justification for location
GV	Located where minerogenic deposits were reportedly thickest (Jefferies *et al*. 1968)
PG/PGA	Represent the sediments at the edge of topographic variation on Weston Moor (North), identified from section diagrams of manual core evidence (Figure 4.12)
CGA	Represents sediments on the northern boundary of biogenic mud sedimentation
CGB	Represents sediments found on Weston Moor (north) outside the area of biogenic mud sedimentation
NR	Represents the sediments found on Weston Moor (south)
CM	Represents the sediments of Clapton Moor
TG	Represents sediments of the valley axis within the area of biogenic mud sedimentation and also allows investigation of topographic variation identified from manual core evidence (Figure 4.12)

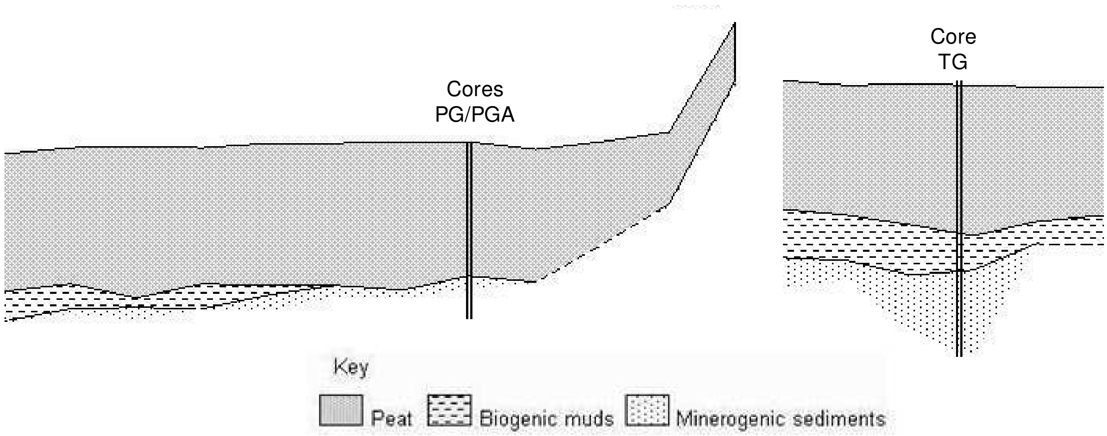


Figure 4.12: Section diagrams (not to scale) showing locations of cores PG/PGA and TG in relation to topographic variation

4.6.2 Method of percussion core recovery

The location and altitude of each percussion core was recorded as for manual cores. Core GV (pilot study) was retrieved from near the southern end of Weston Drove (Figure 4.11) using an open-face percussion corer to achieve maximum penetration of the sediments. For subsequent percussion cores peat overburden was removed using an open face corer of wider diameter than that used to recover the minerogenic sediments. This reduced contamination from peat falling back down the borehole and provided a margin of error for the insertion of the sediment recovery corer. For sediment recovery, a percussion corer of 1 m length and 50 mm diameter lined with a 2.8 mm thick PVC tube was used. Sediment was held in place during recovery by a ‘tulip’. Each 1 m length of core in its PVC liner was removed from the corer, capped, sealed and labelled in the field prior to return to the laboratory for analysis. In order to prevent condensation and growth of green algae, cores were stored under refrigeration at 3° C (Tan 2005) until processing could be carried out in the laboratory.

No clasts larger than the diameter of the corer were encountered during coring, although in that event either the corer would have stopped cutting downwards or it would have cut through the clast, which would have been subsequently identified by observable freshly cut edges.

Use of a percussion corer limited the availability of information on sedimentary structures and architecture, as these are usually destroyed during the coring process (Evans & Benn 2004). However, although gravels, sands and muds have low to moderate potential for compaction (section 4.4.5), there are potential problems when coring in this manner from *coring-induced compaction* of sediments, whereby structures are induced through vertical compression during coring, resulting in up- or down-turning of beds or laminae at the vertical edge of the core and edge dragging of intraclasts (Evans & Benn 2004). Recovery by this method also limited the volume of material available for analysis. It was therefore necessary to extract as much information as possible from the available material.

4.7 Laboratory analysis of physical, chemical and sedimentological characteristics of sediments

Laboratory analysis of the physical, chemical and sedimentological characteristics of sediments (stratigraphic changes, particle size, sediment texture and fabric, lithology and extent of weathering of clast assemblages and mineralogical and chemical analyses) was used to provide data on the nature of former depositional environments, permitting a more detailed reconstruction of environmental conditions than sediment surface morphology alone (Lowe & Walker 1997).

4.7.1 Stratigraphy

The PVC liners containing sediment cores were cut in half lengthwise to enable a flat surface to be seen and the contained sediments cleaned prior to recording. Stratigraphy of the percussion cores was recorded in the laboratory in 1 m sections using the notation outlined in section 4.4.1. Thicknesses of individual units were measured using a steel tape measure. Photographs of percussion core sections were taken prior to processing for reference purposes. Stratigraphic logs were drawn for each core to summarise changes in bed characteristics through the core profile. Textural changes through the core profile were summarised by the inclusion of a textural scale bar at the bottom of each log; the width of each bed corresponds to the dominant particle sizes within that bed. Textural classes have been given the following abbreviations: C = clay; Si = silt; f = fine sand; m = medium sand; c = coarse sand; G = gravel; CG = coarse gravel. The symbols used in the stratigraphic logs are shown in Figure 4.13.

Sediments from each 1 m core section were divided into two; one for physical characterisation of the sediments, the other for determination of its biological characteristics. Analytical methods used to determine the physical characteristics of the sedimentary units are outlined below.

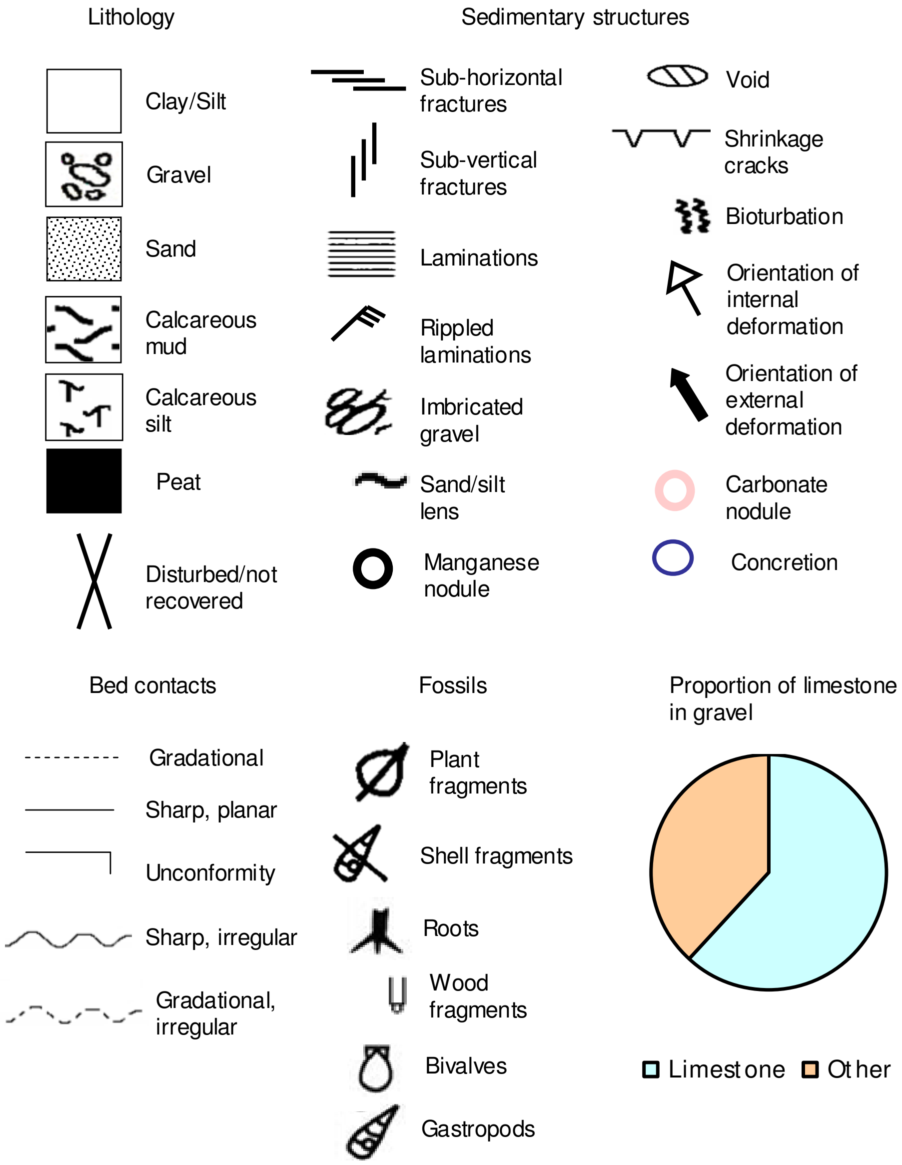


Figure 4.13: Key to symbols used in stratigraphic logs

4.7.1.1 Pilot study stratigraphy

The stratigraphy of core GV (Figure 4.14) was logged in the field. The surface altitude was 4.822 m OD and 3.60 m of peat overburden was discarded. The nature of the transition from peat to minerogenic sediment was not recorded. Surface altitude of minerogenic deposits was 1.222 m OD and 2.40 m of minerogenic sediments were recovered. Each unit was bagged separately, labelled and returned to the laboratory for analysis.

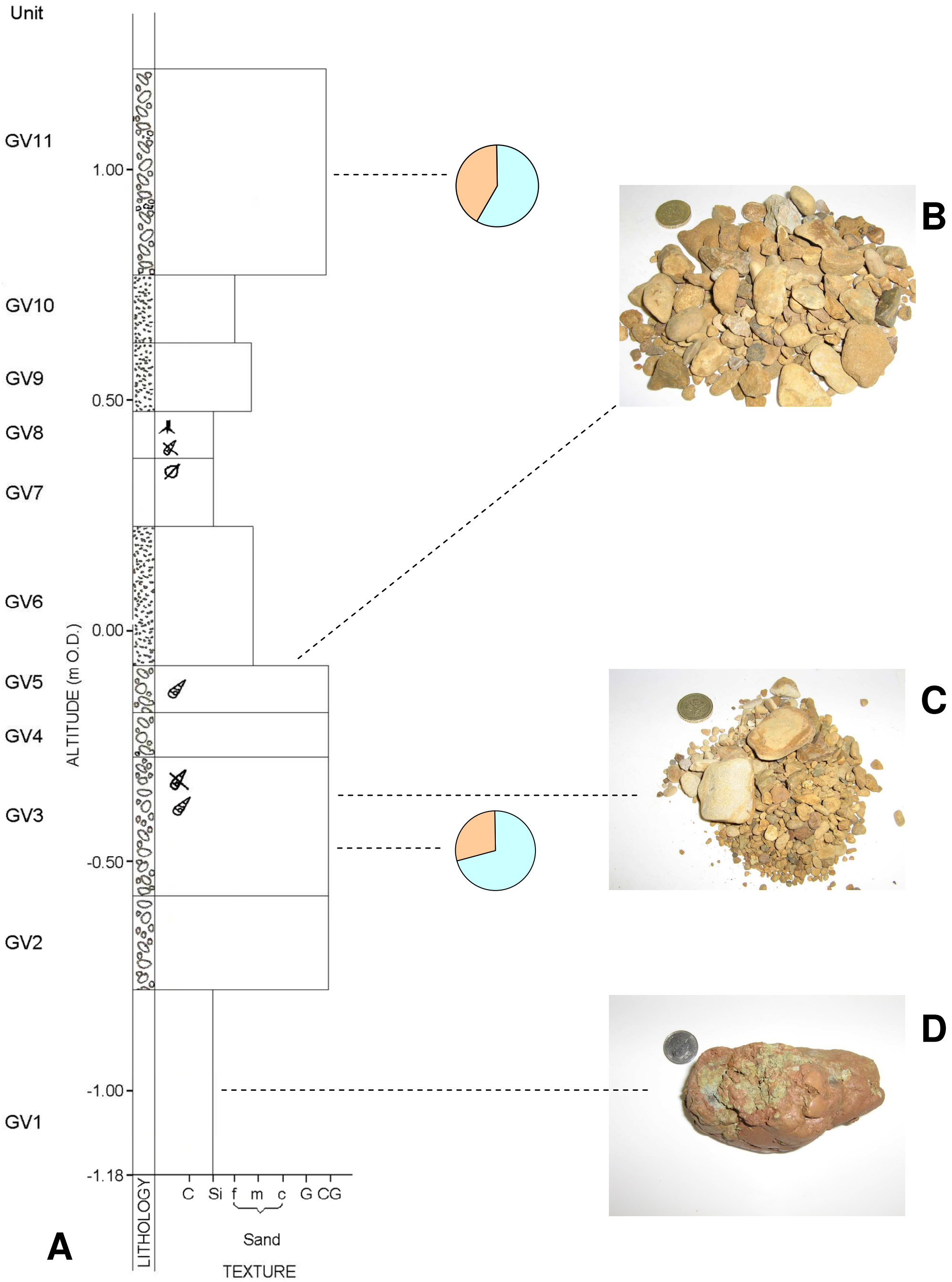


Figure 4.14: A. Stratigraphy of core GV; stratigraphic units are shown on the left. B. Detail of GV5 gravel, £1 coin for scale. C. Detail of GV3 gravel, £1 coin for scale. Note greater variation in clast size. D. Surface of bedrock (Mercia Mudstone Group) from GV1, 10 pence coin for scale. See Figure 4.13 for key

The deposits are medium or thickly bedded and all boundaries between units are sharp and planar, indicating the minerogenic sediments at this site are thicker and more complex than those described by Jefferies *et al.* (1968) and Hill (2006), being neither the homogeneous sands described by Jefferies *et al.* (1968) nor the clast dominated pebbly sand and gravels described by Hill (2006), revealing an inconsistency with previous studies. In terms of the subsequent sampling strategy, the stratigraphy of core GV indicated that there were potentially a range of depositional environments and processes within the wider valley responsible for the minerogenic sediments and each unit would need to be analysed and interpreted separately.

4.7.2 Bulk sample preparation

Bulk samples were prepared using the protocols set out in Avery and Bascomb (1982) as a guide. Each bulk sample was first air dried at room temperature for 2 to 4 days to preserve it as near as possible in its original condition and prevent the occurrence of further chemical and biochemical reactions (Tan 2005). Each air-dried sample was then gently disaggregated with a mortar and pestle and passed through a -1 φ sieve. The >-1 φ and < -1 φ fractions were weighed and these weights combined to give a total air-dried weight. The percentage >-1 φ and <-1 φ fractions of the bulk sample ($\%_{>-1\ \varphi \text{ or }} \%_{<-1\ \varphi}$) were calculated using the equation:

$$\%_{>-1\ \varphi \text{ or }} \%_{<-1\ \varphi} = \frac{W_{>-1\ \varphi \text{ or } <-1\ \varphi}}{W_b} \text{ x } 100 \qquad [4.1]$$

where $W_{>-1\ \varphi \text{ or } <-1\ \varphi}$ is the weight of the >-1 φ or <-1 φ fraction and W_b is the weight of the combined bulk sample.

Sub-samples of the >-1 φ fraction were created using a riffle box. This is a random, unbiased approach to ensuring that every particle has an equal chance of being sub-sampled, enabling sediment characteristics to be accurately identified using a single analysis (Tan 2005). Samples were kept in separate sealable plastic bags to avoid contamination.

4.7.3 Organic matter and total carbonate content

Analysis of organic matter and total carbonate content was used to characterise the post-depositional environments of sediments and to provide an indication of pedogenesis. The susceptibility of carbonate minerals to weathering processes through vertical profiles of total carbonate concentrations was used as an indicator of past climates and to assess the depth and degree of post-depositional weathering of sedimentary units (Jenkins 1985, Evans & Benn 2004). In addition, total carbonate and organic matter content was used as an indication of variation in biological productivity and biogeochemical conditions (Lowe & Walker 1997, Verrecchia 2007) and to provide a guide to pre-treatments required for particle size analysis.

Sequential loss on ignition (LOI) was used to provide a broad indication of the total carbonate and organic content of samples. This is a widely used technique in which organic and carbonate content of sediment is approximately indicated by weight loss following its combustion in a furnace (Ball 1964, Bengtsson & Enell 1986, Lowe & Walker 1997, Heiri *et al.* 2001). Although more accurate results for organic content can be achieved by standard titration or colorimetry (Lowe & Walker 1997), and for carbonate content using either gasometric methods or a calcimeter (Bascomb 1982), the technique provides simple, accurate, rapid and inexpensive determination of carbonate and organic contents of sediments, with a precision and accuracy comparable to more sophisticated methods (Ball 1964, Mooers 1999, Heiri *et al.* 2001). Structural water loss from clays with a high mineral content may affect the accuracy of the results obtained (Ball 1964, Catt 1990, Mooers 1999*)*; however, clay content was generally low (8.43-0.03 %) for Gordano Valley sediments.

The protocol of Bengtsson & Enell (1986) was used throughout and the recommendations of Heiri *et al.* (2001) regarding weight, temperature and duration of ignition were followed. All weights were recorded to 0.01 g to ensure consistent precision.

The LOI method removes moisture as well as organic and carbonates content from samples. Therefore, in order to convert results to an oven-dried basis, the air-dry moisture content was calculated. Heiri *et al.* (2001) found LOI at 550°C is partly dependent on sample size; therefore the same sample size was used throughout. A pre-weighed crucible and *c*. 2 g of air-dried sub-sample material were dried overnight in an oven at 105°C. The crucible and contents were cooled in a desiccator to ensure no moisture absorption from the air by the sediment, as this would potentially increase the dry weight measurement (Heiri *et al.* 2001), then re-weighed.

The oven-dry weight of each sample (W_{105}) was calculated as follows:

$$W_{105} = W_s - W_c \tag{4.2}$$

where W_c represents the weight of the crucible and W_s represents the oven dried weight of the crucible and sub-sample. The oven-dry sub-sample was then used to determine the organic matter and carbonate content by sequential LOI, following the method of Heiri *et al.* (2001). Porcelain lids were placed on crucibles during ignition in order to prevent loss of material by explosive combustion. Crucibles containing oven-dry sub-samples were heated in a furnace at 550°C for 4 hours. At this temperature organic matter is combusted to ash and carbon dioxide. The LOI at 550°C (LOI_{550}) was calculated for each sub-sample as follows:

$$LOI_{550} = \frac{W_{105} - W_{550}}{W_{105}} \text{ x } 100 \tag{4.3}$$

where W_{550} is the weight of the sub-sample after ignition at 550°C and cooling in a desiccator. Weight loss is proportional to the organic carbon content of the oven-dried sub-sample.

The sub-sample was then heated in a furnace at 950°C for 2 hours. During this combustion carbon dioxide is evolved from carbonate, leaving a calcium oxide residue. LOI at 950°C (LOI_{950}) was calculated as follows:

$$LOI_{950} = \frac{W_{550} - W_{950}}{W_{105}} \text{ x } 100 \tag{4.4}$$

where W_{950} is the weight of the sub-sample after ignition at 950°C and cooling in a desiccator. Weight loss is proportional to the carbonate carbon content of the oven-dried sub-sample. Sediments were then classified according to their LOI_{950} carbonate content. Classification and descriptive terms follow Catt (1990) and are set out in Table 4.4.

Table 4.4: Classification of carbonate content (after Catt 1990, Table 14)

< 0.5%	Non-calcareous
0.5-1%	Very slightly calcareous
1-5%	Slightly calcareous
5-10%	Calcareous
>10%	Very calcareous

4.7.3.1 Pilot study organic matter and total carbonate content

Results for LOI applied to the >4 φ fraction of core GV are shown in Table 4.5. There was insufficient sample available to produce data for GV11; this is marked in the table by a dash. Percentage organic content ranges between 0.83% (GV10) and 2.56% (GV7) and percentage carbonate content ranges between 4.26% (slightly calcareous, GV7) and 15.33% (very calcareous GV3). Low carbonate content is most evident in GV5, GV6 and in GV7, where it coincides with a relatively high organic content.

Table 4.5 Loss on ignition for core GV

Unit	GV1	GV2	GV3	GV4	GV5	GV6	GV7	GV8	GV9	GV10	GV11
% Organics	1.50	2.15	1.48	1.51	1.00	1.50	2.56	1.17	1.17	0.83	-
% Carbonates	11.02	13.08	15.33	13.54	4.51	4.49	4.26	8.16	7.51	8.43	-

The results also indicate that pre-treatments are required for particle size analysis.

4.7.4 Particle size analysis

Particle size analysis was carried out to confirm the stratigraphic description based on visual assessment of sediments, to enable detailed examination of component particle sizes and to achieve a fuller understanding of the Pleistocene depositional environments of the Gordano Valley. In this context, absolute values of particle-size distribution were considered less important than comparative values down a core profile which can provide important evidence regarding the origin and processes responsible for the deposition of sediments. Particle sizes of sedimentary units were used to give a broad indication of the processes of erosion, transportation and deposition and the source of material that produced a deposit (Briggs 1977, Rowell 1994, Evans & Benn 2004). However, because particle size variability also depends on lithology and prior processes such as weathering and previous phases of erosion, transport and deposition, it is rarely possible to relate particle size directly to process (Evans & Benn 2004). Therefore, particle size analysis has been used in combination with other forms of evidence to enable interpretation of sediments.

The technique chosen to measure particle size depends on the nature of the sediment under consideration. Conventionally the measurement of size is taken to refer to the measurement of the diameter (or intermediate axis) of the particle (Briggs 1977). Particle axes of coarse sediments can be measured directly, or alternatively the material can be sieved (Briggs 1977). Sands are usually measured using indirect and therefore less precise methods (Briggs 1977), the most commonly used of which is sieving (Jones *et al.* 1999). Using sieves to determine particle size eliminates the problem of operator error that is inherent in manual measuring techniques (Bunte & Abt 2001).

Particle size determination was carried out using two methods; sieving of the $< 4\ \varphi$ fraction, a widely used method in particle size analysis (Whalley 1990), and laser diffraction measurement of $>4\ \varphi$ fraction. Particle size distribution was measured using whole phi classes. Although this interval may be considered too coarse to reveal the details of the distribution, leading to inaccurate determination of moment statistics (Evans & Benn 2004), whole phi classes were found to provide a readily understandable framework that was simpler and quicker to use over the wide range of sizes of the Gordano Valley sediments, and allow a cumulative particle size distribution for each sample to be produced. The particle size class intervals used follow the standard classification (Jones *et al.* 1999) of Udden-Wentworth (Table 4.6).

The PSS Accusizer 780 Automatic Particle Sizer (Accusizer 2003) was used to measure particle sizes $>4\ \varphi$ from which the contribution of clay and silt was calculated. The advantage of this is the speed and improved reproducibility with which samples can be analysed compared to traditional techniques such as the pipette method (Konert & Vandenberghe 1997, Isphording *et al.* 2003). The Accusizer 780 programme was set up to provide the particle size results in terms of the “volume weighted differential distribution” of each sample in which the computer programme provides a volume weighted function to the dataset of each sample, where volume (V) is calculated using the equation:

$$V= 4/3\ \pi\ (d/2)^3 \qquad [4.5]$$

Table 4.6: Particle size class parameters (source: Jones *et al.* 1999)

Description	Metric size-class	Equivalent phi (φ)-class
Cobbles	>64 mm	>-6 φ
	32-64 mm	-5 φ to -6 φ
Pebbles	16-32 mm	-4 φ to -5 φ
	8-16 mm	-3 φ to -4 φ
	4-8 mm	-2 φ to -3 φ
Granules	2-4 mm	-1 φ to -2 φ
Very coarse sand	1000-2000 μ m	0 φ to -1 φ
Coarse sand	500-1000 μ m	1 φ to 0 φ
Medium sand	250-500 μ m	2 φ to 1 φ
Fine sand	125-250 μ m	3 φ to 2 φ
Very fine sand	63-125 μ m	4 φ to 3 φ
	31.25-63 μ m	5 φ to 4 φ
Silt	15.63-31.25 μ m	6 φ to 5 φ
	7.8-15.63 μ m	7 φ to 6 φ
	3.9-7.8 μ m	8 φ to 7 φ
Clay	<3.9 μ m	>8 φ

This statistical approach renders results broadly comparable with other methods of particle size analysis, although the clay fraction may be under/over estimated in comparison to some techniques (Konert & Vandenberghe 1997, Beuselinck *et al.* 1998, McCave *et al.* 2006). However, Konert & Vandenberghe (1997) found that results are comparable if a higher particle size level is used for the clay fraction. Therefore, a level of 8 φ was used to delimit the clay fraction. Accusizer channels were set to metric-equivalent whole phi classes to maintain consistency with the sieved fraction. These were subsequently converted to phi for method of moments calculations. Each sample was analysed by Accusizer at least three times, until the particle size distribution histograms of the silt and clay fraction matched visually.

4.7.4.1 Analysis of the < - 1 φ fraction

The < - 1 φ fraction of the air-dried bulk sample was sub-divided into whole phi fractions from -2 to -6 φ by sieving through a stack of sieves on a mechanical shaker for 10 minutes (Goudie 1990). The sediment remaining on each sieve was transferred to a pre-weighed dish and weighed. This was then calculated as a percentage of the total bulk sample ($\%_t$) using the equation:

$$\%_t = \frac{\text{Weight of gravel in phi class}}{\text{Weight of bulk sample}} \times 100 \qquad [4.6]$$

4.7.4.2 Pre-treatment procedure for >- 1 φ fraction

In the Gordano Valley calcium carbonate occurs geologically as limestone, and its presence was a possibility in all the sediment particle-size classes, either as inherited minerals in the pebble-, sand- and silt-sized fractions, or as a mixture of inherited and pedogenic minerals in the clay-size fraction. Because it is relatively soluble and may be moved down the profile and re-precipitated (Rowell 1994) calcium carbonate is likely to form a major component of the clay-size fraction (Rowell 1994) and this may have a significant influence on particle size distribution of the sediments. To reduce the influence of secondary carbonate deposition on particle size distribution of the >- 1 φ fraction, calcium carbonate was removed as part of the pre-treatment processes.

In order for comparisons to be meaningful, a standardised procedure of analysis of particle size distribution was used. Loss on ignition data for core GV (Table 4.5) indicated variable sample organic and carbonate content, with a range of 0.83 to 2.56% organic content and carbonate content of 4.26 to 15.35%. It was important to consider their effects when considering pre-treatment procedures for particle size analysis. Konert and Vandenberghe (1997) found the presence of organic and carbonate matter in sediments had an enormous effect on particle size measurements. Therefore, in order to produce particle size distributions which are representative of their constituent particles, pre-treatments were used to remove the organic and carbonate content.

The most common pre-treatments for particle size analysis use hydrochloric or acetic acid to remove the carbonate content and treatment with hydrogen peroxide to remove the organic content (Avery & Bascom 1982, Gee & Bauder 1986, Catt 1990, Konert & Vandenberghe 1997, Murray 2002, Mikutta *et al.* 2005). The method of Catt (1990) was adopted as a guide and the following pre-treatment procedure was applied to the prepared bulk samples in order to analyse their particle size:

10 g (or 5 g where there was insufficient sample to allow this) of air-dried sub-samples were placed in a 50 ml centrifuge tube and treated with 40 ml of 1M acetic acid, buffered with sodium acetate to pH4, and stirred. Treatments were repeated until effervescence stopped. Sub-samples were centrifuged at 2000 – 3000 rpm for 10 minutes between each treatment and the supernatant discarded. After the final centrifugation, 2 drops of 6% aluminium sulphate in 50 ml of distilled water was added to the sub-sample and the centrifuge tube was shaken, centrifuged and the supernatant discarded. The sub-sample was then transferred to a beaker placed in a fume cupboard and 10 ml of 30% hydrogen peroxide (H_2O_2) was added. Once the reaction was initiated, the beaker was heated at approximately 80°C and further aliquots of H_2O_2 were added until the reaction ceased. The sub-sample was left overnight then excess H_2O_2 was boiled off. The sub-sample was left to cool, then transferred to a centrifuge tube and centrifuged at 2000 – 3000 rpm for 10 minutes. The supernatant was discarded and the sub-sample was oven-dried overnight at 50°C, cooled in a desiccator and weighed. This weight was used as the basis for calculation of the proportions of the fine fraction. To ensure complete dispersion, each sub-sample was treated with a 5% solution of sodium hexametaphosphate (calgon) and shaken overnight.

4.7.4.3 Separation and analysis of the sand fraction

The sand fraction was removed from the dispersed sediment by wet sieving through a 4 φ sieve using a wash bottle of distilled water with a fine jet to fully wash the sand retained on the sieve and ensure all finer material passed through the sieve. Silt and clay passing through the sieve was collected in a 500 cm^3 beaker and transferred to sealable polyethylene containers for later analysis by Accusizer.

Sand remaining on the sieve was transferred to a 250 ml beaker and dried overnight at 105°C. It was then weighed and sub-divided into whole phi fractions from -1 to 4 φ by sieving through a stack of sieves on a mechanical shaker for 10 minutes (Goudie 1990). The sediment remaining on each sieve was transferred to a pre-weighed dish and weighed. The percentage of sand in each phi fraction was found using the equation:

$$\%_{phi} = \frac{W_{phi}}{W_{sand}} \times 100 \qquad [4.7]$$

where $\%_{phi}$ is the percentage of particles in a phi fraction, W_{phi} is the weight of particles in that phi fraction in the sub-sample and W_{sand} is the weight of the sand fraction of the sub-sample.

4.7.4.4 Analysis of the silt and clay fraction

The >4 φ fraction was transferred from its sealable polyethylene container to a 300 ml beaker. A wash bottle of distilled water with a fine jet was used to ensure the entire sample was transferred. A magnetic stirrer was used to homogenise the sample, enabling a representative *c.* 1 ml sub-sample to be added to the Accusizer for analysis.

The percentage of silt and clay in each phi fraction was found using the % Cum(ulative) Vol(ume) >=Diam(eter) ($\%_{cv}$) output for metric-equivalent phi intervals. This was converted to a percentage of the > -1 φ fraction ($\%_{>-1\,\varphi}$) using the equation:

$$\%_{>-1\,\varphi} = \frac{\%_{phi} \times \%_{>4\,\varphi}}{100} \qquad [4.8]$$

where $\%_{phi}$ is the percentage in that phi class of the percentage silt or clay, and $\%_{>4\,\varphi}$ is the percentage of > 4 φ sub-sample material.

4.7.4.5 Combining data from sieve and Accusizer analyses

The percentage of sand, silt or clay in each phi fraction of the >-1 φ fraction was converted to its equivalent percentage of the bulk sample ($\%_t$) using the equation:

$$\%_t = \frac{\%_{phi} \text{ of } >\!-1\,\varphi \text{ sub-sample} \times \% >\!-1\,\varphi \text{ of bulk sample}}{100} \qquad [4.9]$$

where $\%_{phi}$ is the percentage of sand/silt/clay in a phi class. The percentage of gravel, sand, silt and clay in each phi fraction (from >8 to -6 φ) was then tabulated to produce complete particle size distributions. In the past using a combination of different methods has caused problems when presenting and interpreting the results obtained (Evans & Benn 2004). However, by minimising the number of techniques used to two, sieving and Accusizer, by using a cut-off of 4 φ between the two techniques to minimise the impact of discontinuities in the sand fraction and by using the Gradistat software package (Blott 2000, v7 2009), the particle sizes were integrated to a single distribution for each sedimentary unit.

4.7.4.6 Pilot study particle size analysis

Particle size analysis, outlined above, was applied to core GV and the results are summarised in Table 4.7; full details, including particle size distribution histograms, are provided in Appendix III.

Table 4.7: Summary of particle size data for core GV

Unit	%		Particle size distribution				
	Gravel/Sand/Silt/Clay	Mode	Median particle size (φ)	Mean particle size (φ)	Sorting (σ_{φ})	Skewness (Sk_{φ})	Kurtosis (K_{φ})
GV11	97.69/1.38/1.17/0.03	Bimodal	-4.106	-3.404	1.672	3.069	18.48
GV10	24.28/61.06/13.36/1.14	Trimodal	1.831	1.455	2.976	0.044	2.587
GV9	8.49/45.69/40.82/1.49	Trimodal	1.941	2.786	2.951	-0.091	2.197
GV8	19.56/20.91/56.49/3.64	Trimodal	5.199	3.732	3.674	-0.811	2.381
GV7	0.05/27.29/67.97/4.54	Bimodal	5.651	5.233	2.008	-0.459	2.574
GV6	2.54/65.22/26.38/1.80	Bimodal	2.650	3.265	2.320	0.380	2.890
GV5	77.32/13.41/8.10/0.71	Unimodal	-5.259	-3.207	3.945	1.540	4.004
GV4	88.11/6.76/4.58/0.44	Unimodal	-4.312	-3.351	2.742	2.739	9.664
GV3	92.50/1.12/2.73/0.29	Unimodal	-3.949	-3.343	2.090	3.601	17.36
GV2	32.16/10.12/50.86/5.96	Polymodal	5.474	2.942	4.880	-0.559	1.642
GV1	9.49/14.98/64.99/8.43	Bimodal	6.255	5.142	3.273	-1.435	4.380

Mean grain size ranges from *c*. -3.4 φ to 5.2 φ (medium gravel to coarse silt) and particle size distribution is mostly multimodal; three gravels, GV3, GV4 and GV5 are unimodal. The sediments are mostly very poorly sorted (σ_{φ} = 2.0 to 4.0 φ); GV2, a mainly sandstone gravel buried in the weathered surface of bedrock, is extremely poorly sorted (σ_{φ} = 4.9 φ) and GV11 is poorly sorted (σ_{φ} = 1.7 φ). Skewness ranges from very fine to very coarse (3.6 to -1.4) and kurtosis from platykurtic to very leptokurtic ($K_{\varphi} > 7.4$).

Variations in the relative proportions of gravel, sand, silt and clay confirm that core GV is composed of a number of different sedimentary units. Gravel clast analysis is confined to those units which were identified from particle size analysis as having a gravel content of ≥30%.

4.7.5 Calculation of particle size parameters

The Gradistat software (Blott 2000, v7 2009) program was used to compute the particle size parameters of mean, median, mode, skewness standard deviation and kurtosis for each sample, by the logarithmic method of moments. Statistical moments have been used to produce descriptive statistics. Each statistical moment indicates sedimentary characteristics which have been used to provide interpretations of palaeoenvironmental conditions (Friedman 1961, Tanner 1991, Lario *et al.* 2002) and provide a means of comparison with other research. Using a software programme reduces the possibility of inaccurate determination of moment statistics that might otherwise occur from using a 1 φ particle size interval (Evans & Benn 2004). Calculation of statistical particle size parameters by the logarithmic method of moments is defined by the following equations, where f is the frequency in per cent of each size fraction and m_φ is the mid-point of each size class in phi units.

Descriptive statistics measure the central tendency of the distribution (mean), the spread around the mean (standard deviation or sorting), the symmetry of the distribution around the mean (skewness) and the peakedness of the distribution (kurtosis) (Table 4.8). In computing summary statistics, statistical moments include the whole dataset and are therefore preferred to graphical computational techniques in which only a part of the distribution is used (McBride 1971).

$$\text{Mean} = \bar{x}_\phi = \frac{\sum fm_\phi}{100} \qquad [4.10]$$

$$\text{Sorting} = \sigma_\phi = \sqrt{\frac{\sum f(m_\phi - \bar{x}_\phi)^2}{100}} \qquad [4.11]$$

$$\text{Skewness} = Sk_\phi = \frac{\sum f(m_\phi - \bar{x}_\phi)^3}{100\sigma_\phi^{\ 3}} \qquad [4.12]$$

$$\text{Kurtosis} = K_\phi = \frac{\sum f(m_\phi - \bar{x}_\phi)^4}{100\sigma_\phi^{\ 4}} \qquad [4.13]$$

Table 4.8: Descriptions of particle size statistical parameters (Blott 2000)

Sorting (σ_φ)		Skewness (Sk_φ)		Kurtosis((K_φ)	
Very well sorted	<0.35	Very fine skewed	$>^{+}1.30$	Very platykurtic	<1.70
Well sorted	0.35 – 0.50	Fine skewed	$^{+}1.30$ - $^{+}0.43$	Platykurtic	1.70 – 2.55
Moderately well sorted	0.50 – 0.70	Symmetrical	$^{-}0.43$ - $^{+}0.43$	Mesokurtic	2.55 – 3.70
Moderately sorted	0.70 – 1.00	Coarse skewed	$^{-}0.43$ - $^{-}1.30$	Leptokurtic	3.70 – 7.40
Poorly sorted	1.00 – 2.00	Very coarse skewed	$<^{-}1.30$	Very leptokurtic	>7.40
Very poorly sorted	2.00 – 4.00				
Extremely poorly sorted	>4.00				

Sorting, skewness and kurtosis statistics are unreliable for multimodal distributions because they do not approach a normal distribution (McBride 1971). Multimodal particle size distributions are usually taken to indicate the presence of more than one population of sediments; most hydraulic and aeolian sediments are multimodal and represent different transport or depositional processes (Sun *et al.* 2002, Weltje & Prins 2007). However, particle-size parameters of bulk samples have been commonly used as environmental indicators in sedimentary investigations. Given that particle-size components in polymodal sediments reflect different transportation or depositional processes (Sun *et al.* 2002), for the Gordano Valley the presence of multimodal sediments, as demonstrated for core GV (Table 4.7), is likely to be an indication of recycling of pre-existing sediment, which is equally useful for an environmental interpretation.

4.8 Clast lithological analysis

Clast lithological analysis was used to identify the provenance of sediments from the range of lithologies present (Bridgland 1986, Hubbard & Glasser 2005) and hence, the direction of movement of the transporting medium (Briggs 1977, Evans & Benn 2004). This simple technique, requiring minimal sample preparation, is most useful when carried out in conjunction with other methods (Bridgland 1986), as in this thesis. Identification of a suitable number of clasts allows the proportions of each lithology represented in the sediment to be calculated. Clast assemblages can be compared for correlation and related to particular source areas to determine provenance. Although non-durable lithologies that are less resistant to mechanical or chemical weathering, for example limestone in the Gordano Valley, may be under represented due to abrasion and progressive removal during transport, recycling of older deposits or post-depositional weathering (Evans & Benn 2004), durable-only counts are of little value in areas where these lithologies provide the overwhelming bulk of local deposits (Bridgland 1986).

Two important considerations were the size range to be sampled and the number of clasts to be identified to ensure a representative sample (Hubbard & Glasser 2005). Clasts are usually restricted to narrow size-range limits because of the tendency for different concentrations of lithologies at different sizes (Bridgland 1986). Hubbard & Glasser (2005) recommend a range of 0.5 or 0.25 phi; 4-8 mm (-2 to -3 φ) and 8-16 mm (-3 to -4 φ) were used by Lee *et al.* (2002). Limitations on the use of small clasts (>-3 φ) are that their cores are often affected by weathering, some recognition features such as fossils or mineral structures are unlikely to be encountered and breaking them open may prove impracticable/impossible (Bridgland 1986). Sample sizes of *c*. 300 clasts are considered the norm for statistical validity of a dataset, although counts of >50 can still give a good approximation of the general composition of a deposit (Bridgland 1986, Hubbard & Glasser 2005). However, borehole samples provide small and restricted volumes of material. Amalgamating different sedimentary units from a greater vertical range in order to obtain a sufficient number of clasts for a statistically valid sample would have resulted in loss of important evidence of stratigraphical changes, and stratigraphic integrity was considered to be of primary importance. In order to improve the statistical validity of the dataset and reduce statistical bias that might accrue from too few clasts being available in a sample a more extensive dataset, the smallest range with the greatest proportion of clasts (-2 to -5 φ) was used. All available clasts in this size range were first divided on the basis of the main geological formations of the Gordano Valley. Clasts were examined with a hand lens and compared with known examples. Characteristic examples of each rock type were retained and used to prevent changes to some of the more subjective subdivisions as work proceeded. Notes on weathering and surface texture features were made at the same time to facilitate identification of pedogenesis and/or redeposition. Where the weathered state of smaller sizes made identification difficult they were studied under a binocular microscope.

4.8.1 Procedure for clast lithological analysis

Clasts were washed before being assigned to one of two groups: a local group of rocks outcropping in the Gordano Valley, which was subdivided into limestone, brown sandstone and other local lithologies, and an exotic group of rocks from outside the Gordano Valley, which was subdivided into quartz/quartzite, flint and other exotic lithologies. Divisions were based on composition, colour, texture and hardness, and follow those of Hunt (2006e); this permits comparison with previous studies whilst not requiring an extensive knowledge of geology. Chert has been included in the other local lithologies class because although Greensand chert is a common exotic lithology in the Bristol region (Hunt 2006e), chert bands have been identified within local limestone outcrops (Reynolds 1916, Kellaway & Welch 1948, Green 1992, Simms 1997, Waters *et al*. 2007); no attempt was made to differentiate between the two. Quartz and quartzite have been placed in the exotic class because these are durable rocks which may have a long transport history (Hunt 2006e). A flow chart outlining the procedures adopted for clast lithological analysis is shown in Figure 4.15. Limestone clasts were identified by testing with a 10% solution of hydrochloric acid (HCl) (Bridgland 1986, Catt 1990). Those that effervesced were given a repeat treatment because of the possibility of non-calcareous clasts reacting with HCl as a result of calcite precipitation onto clast surfaces and/or infiltration of calcite in porous rocks (Bridgland 1986).

4.8.1.1 Pilot study clast lithology

Results for clast lithological analysis applied to all clasts in the -2 to -5 φ size fraction of core GV gravel units are presented in Table 4.9; full details of gravel analysis data are provided in Appendix IV. Table 4.9 shows that most gravels are dominated by limestone, with components of brown sandstone and other lithologies. An exotic component, comprising flint (GV3) and quartz and quartzite (GV3, GV5 and GV11) accounts for a significant proportion of clasts. However, the most numerous lithology in GV2 (6 of 7 clasts) is brown sandstone.

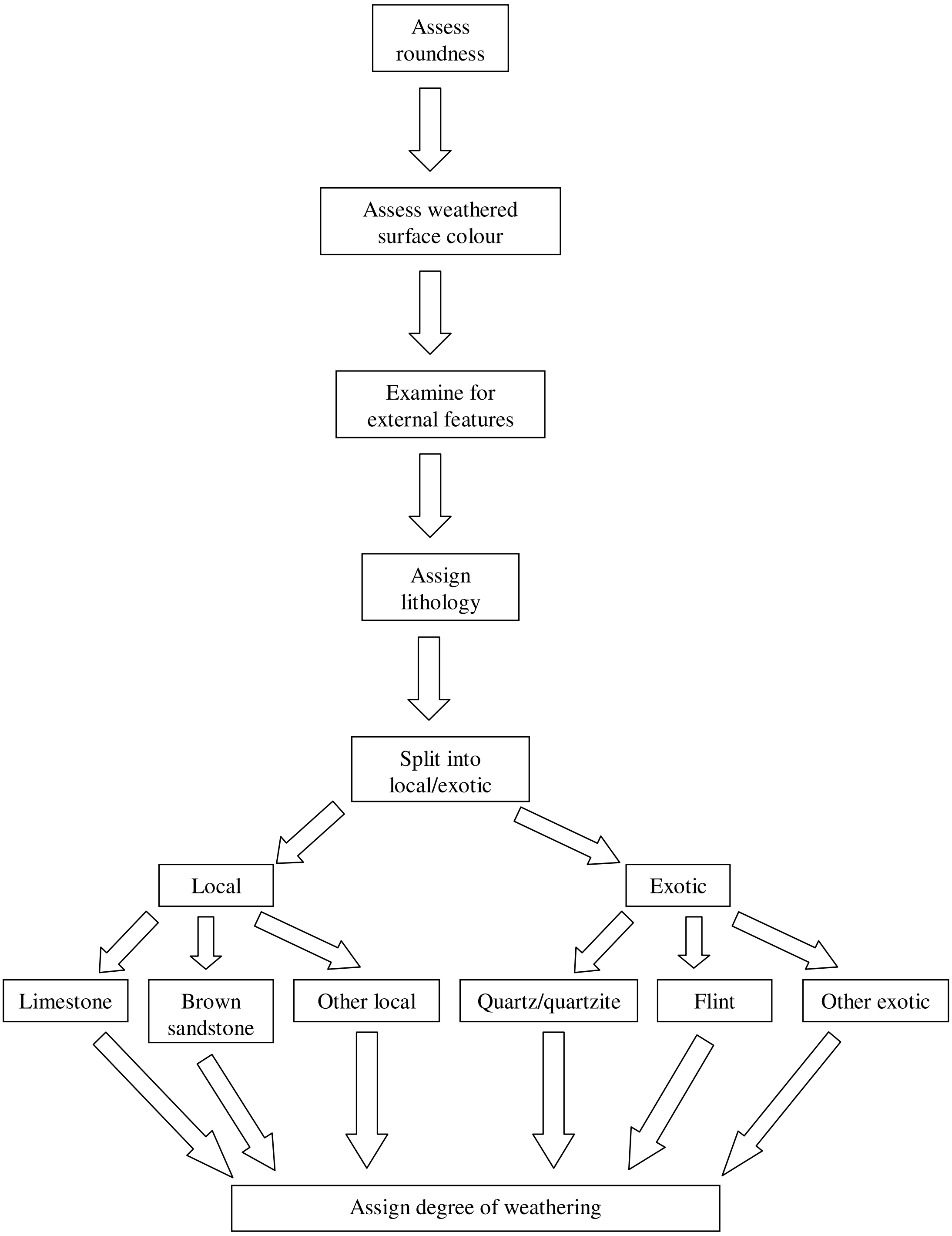


Figure 4.15: Flow chart outlining the procedures adopted for clast lithological analysis

Table 4.9: Clast lithological analysis of core GV gravel units based on percentages of the -2 to -5 φ fraction

Unit	Local				Exotics				N^{o} of clasts
	Limestone %	Brown sandstone %	Other local %	Total %	Quartz & quartzite %	Flint %	Other exotics %	Total %	
GV11	58.14	13.95	13.96	86.05	13.95	0.00	0.00	13.95	43
GV5	57.14	14.29	7.14	78.57	21.43	0.00	0.00	21.43	14
GV4	60.00	40.00	0.00	100.00	0.00	0.00	0.00	0.00	15
GV3	70.69	14.65	7.77	93.11	6.03	0.86	0.00	6.89	116
GV2	14.29	85.71	0.00	100.00	0.00	0.00	0.00	0.00	7

However, most core GV gravel units have low clast counts for one or more lithology and units GV2, GV4 and GV5 have very low clast numbers in the -2 to -5 φ fraction. A number of clasts of GV2 were completely weathered and disintegrated when immersed in water for cleaning prior to counting; it is not possible to state with certainty how many of these clasts there were or what their lithology may have been. In order to maintain statistical validity of datasets in further gravel analysis, only results where counts are ≥30 are presented in tables, although lower counts are discussed as they are used to provide supplementary interpretative evidence.

4.8.2 Clast surface features

The presence or absence of minor surface features and the weathered condition of clasts was used to provide information on transport mechanisms and depositional and post-depositional environments. Identification of surface features, which in this thesis includes evidence of weathering, is subjective, but provides a useful line of evidence for palaeoenvironmental reconstruction (Reineck & Singh 1973, Evans & Benn 2004, Hubbard & Glasser 2005). For example, chattermarks (trails of crescent-shaped gouges) on rounded surfaces may indicate attrition between clasts in a littoral or marine environment, ventifact morphology of clasts may indicate exposure to abrasion by aeolian sand, frost pits may indicate that the clast has been subject to cold climate conditions and surface striations are commonly associated with glacially transported clasts although similar scratching of clast surfaces can occur during mass movement of various types (Bridgland 1986, Hubbard &

Glasser 2005). Their development is strongly dependent on lithology; hard rocks rarely display striations, whereas soft or fine-grained rocks, such as limestone, do (Hubbard & Glasser 2005). Weathering leads to post-depositional discolouration, decomposition and disintegration of clasts (Tucker 2003).

Clast surface features, including weathered condition, of the local lithology component were used to provide a general transport and depositional history which could be compared with other lines of evidence such as clast morphology. Assessment was carried out on all clasts in the -2 to -5 φ size range in conjunction with lithological analysis and all visible features recorded. Clast surface features were visually assessed using the features listed by Whalley (1990, Table 3.3) and Evans and Benn (2004, section 4.2.4) as a guide and comparison with known examples. Surface features recorded includes chattermarks, pitting, striations, grooves, gouges, cracks, characteristic ventifact morphology, surface polishing and evidence of secondary carbonate deposition. The weathered condition of clasts was noted using the weathering scales of Mourne *et al.* (2000) and Tucker (2003) adapted to suit the Gordano Valley sediments (Table 4.10).

Table 4.10: Weathering scale for Gordano Valley sediments (adapted from: Mourne *et al.* 2000, Tucker 2003)

Scale	Term	Criteria
5	Fresh	No visible sign of rock weathering
4	Slightly weathered	Discoloured; little reduction in strength of rock; lightly corroded; tiny perforations
3	Moderately weathered	Perforated or powdery surface; fresh rock present as corestone
2	Highly weathered	Can be broken by hand; friable, but with corestone still present; does not disintegrate in water
1	Completely weathered	Very rotted, broken shell, core exposed; very friable – crumbles easily between fingers; disintegrates in water

4.8.2.1 Pilot study clast surface features

Surface features of core GV gravel clasts were recorded as present or absent; results are shown in Table 4.11. The most common feature on brown sandstone clasts is a powdery white surface which reacted vigorously with dilute HCl indicating the presence of calcium carbonate. Pitting is mainly a feature of limestone clasts. Gouges recorded for GV3 occur on limestone and sandstone clasts and include a crescentic gouge; for GV5 gouges occur only on limestone. Deep cracks and pitting of carbonate deposits are recorded for the sandstone of GV11.

Table 4.11: Surface features of core GV gravel clasts. X = present, O =absent

	GV2	GV3	GV4	GV5	GV11
Pitting	O	X	X	X	X
Gouges	O	X	O	X	O
Cracks	X	O	O	O	X
Carbonate deposits	X	O	X	X	X

The weathered condition of core GV gravel clasts is presented in Table 4.12. All the gravels demonstrate some degree of weathering. In GV3 limestone is slightly weathered and sandstone weathering is more variable, from highly weathered to fresh, but is mainly moderate whereas in GV11 limestone is highly weathered, brown sandstone is moderately weathered and other local sandstones show variable degrees of weathering. All clasts in GV2 are highly or moderately weathered and, as already noted, a number of clasts (lithology unidentified) were completely weathered. In GV4 limestone is slightly weathered and sandstone weathering ranges from completely to slightly weathered, whereas in GV5 limestone weathering is variable, from highly weathered to slightly weathered, whilst sandstone clasts are moderately weathered.

Table 4.12: Weathered condition of clasts in core GV gravel units based on percentages of the -2 to -5 φ fraction. (1 = Completely weathered; 5 = Fresh)

	1	2	3	4	5	N° of clasts
GV11						
Limestone	0.00	52.00	20.00	16.00	12.00	25
Brown sandstone	0.00	0.00	66.67	33.33	0.00	6
Other local sandstones	20.00	20.00	40.00	20.00	0.00	5
GV5						
Limestone	0.00	37.50	12.50	50.00	0.00	8
Brown sandstone	0.00	0.00	100.00	0.00	0.00	2
GV4						
Limestone	0.00	0.00	11.11	77.78	11.11	9
Brown sandstone	16.67	33.33	16.67	33.33	0.00	6
GV3						
Limestone	0.00	4.88	14.63	79.27	1.22	82
Brown sandstone	0.00	23.53	41.18	29.41	5.88	17
Other local sandstones	0.00	0.00	100.00	0.00	0.00	1
GV2						
Limestone	0.00	0.00	100.00	0.00	0.00	1
Brown sandstone	66.67	0.00	33.33	0.00	0.00	6

4.9 Clast morphological analysis

Analysis of clast morphology usually involves description of the two- or three-dimensional properties of clasts, although no single quantitative measure can provide a full description of three-dimensional shape (Evans & Benn 2004). In this thesis shape, sphericity, roundness and surface features were used to characterise the deposits and to establish their depositional environments. This follows Blott & Pye (2008) who have argued that a combination of several shape indices provides the best method of grouping and discriminating between clasts. Clast morphological analysis is valuable for palaeoenvironmental reconstruction because clasts often exhibit contrasting morphologies as the result of their different erosion, transport and deposition histories (Bridgland 1986, Benn & Ballantyne 1993, Evans & Benn 2004, Lukas *et al.* 2009), although difficulties in distinguishing between some transportational modes have been acknowledged (Lukas *et al.* 2009). Quantitative analysis of clast morphology can therefore potentially provide information on aspects of sediment history prior to and during deposition (Evans & Benn 2004).

Factors which determine the morphology of a clast and its susceptibility to rounding include: the geological composition or structure which controls the initial shape of the rock fragment; its hardness and resistance to abrasion, controlled by its chemical and mineralogical properties; its size; its distance of transport and the transporting agent, which control the amount of abrasion to which it is submitted; the effects of post-depositional processes such as weathering (Sneed & Folk 1958, Fisher & Bridgland 1986). Overall morphological characteristics of a deposit are therefore controlled by the proportions of the different lithological types it contains which respond differently to similar wear processes. For these reasons, morphological characteristics are usually restricted to a single lithological type (Fisher & Bridgland 1986, Evans & Benn 2004). Gale & Hoare (1991) recommend using only clasts of isotropic lithologies, i.e. showing physical properties equally in all directions, because lithologic controls may be so dominant on anisotropic gravel clasts that they may be unable to develop environmentally diagnostic shapes. Limestone tends to split along bedding planes and wears anisotropically, tending to evolve to plate and blade shapes in hydrodynamic situations, and may not therefore provide good environmental discrimination (Gale & Hoare 1991), although limestone was used by Krüger & Kjær (1999) in their interpretation of environments on Møn, southeast Denmark.

Bennett *et al.* (1997) have suggested the influence of lithology on clast shape may be less than previous authors (e.g. Sneed & Folk 1958, Bridgland & Fisher 1986) have implied. However, the impact of mixed lithologies on clast shape measurements for reconstructing transport processes, often assumed, has only recently been assessed by Lukas *et al.* (2009) who found that lithology has a marked effect on clast shape results.

Within the limitations of the available material, and following the recommendations of Gale & Hoare (1991) conventional practice has been adopted in this thesis and clast morphological analysis has been carried out on clasts of a single, uniform lithology within a limited size range. For core GV the most abundant clasts are limestone in the -2 to -5 φ size range (Table 4.9). Samples for morphological analysis usually comprise of a minimum number of clasts in order to ensure that the random effects of chance on clast morphology are minimised (Briggs 1977, Gale & Hoare 1991, Evans & Benn 2004, Hubbard & Glasser 2005). However, sample size limitations imposed by coring meant that there were often fewer than 30 clasts available for analysis. All available identifiable limestone clasts in the

-2 to -5 φ size range in a gravel unit up to a maximum count of 250 pebbles were analysed, thus avoiding bias in the choice of clasts for morphological analysis, although only results where there are counts of ≥30 clasts are presented.

It has also been shown that the morphological properties of clasts vary with size, which exerts a distinct control on sphericity; sphericity decreases as clasts get larger (Sneed & Folk 1958). For this reason samples are normally kept within narrow size ranges (Evans & Benn 2004). Additionally, because of its bedding, limestone tends to show no consistent changes in sphericity regardless of duration of transport (Sneed & Folk 1958). Therefore the recommendations of Sneed & Folk (1958) have been followed; sphericity was used in combination with morphology to assess and interpret gravel depositional environments.

In contrast to sphericity, roundness is independent of shape and refers to the degree of wear exhibited by a clast, the relative rounding of edges and corners and its overall smoothness (Blott & Pye 2008). In the fluvial environment, for example, roundness is the product of abrasion during transport and the degree of roundness is a function of clast size, lithology, distance of transport and degree of recycling, although clast roundness may also decrease in response to recycling (Pettijohn 1975, Lindsey *et al.* 2005). Additionally, limestone is more readily rounded than some lithologies (Bridgland 1986, Lindsey *et al.* 2005). For this reason limestone is usually avoided for roundness analysis because it rapidly reaches a limit of roundness (Sneed & Folk 1958) hence cannot be used to estimate distance of transport. However, high angularity of a limestone clast may indicate that it has not been transported over a long distance (Bunte & Abt 2001). This thesis therefore uses angularity to indicate a short transportation.

4.9.1 Clast shape

In this thesis, shape refers to the overall form of a clast defined by its relative dimensions. To reduce any error involved in clast measurement this was visualised as the smallest box that the clast will fit into (Briggs 1977, Blott & Pye 2008). The dimensions of the box, termed the a or Long, b or Intermediate and c or Short axes (Figure 4.16), are determined by the length of the three orthogonal axes of the clast, which need not intersect at a common point (Evans & Benn 2004, Hubbard & Glasser 2005, Blott & Pye 2008). Blott & Pye (2008) have suggested orienting the clast so that it exhibits the smallest projected area to the eye, a combination of the b and c dimensions, then measuring the a dimension perpendicular to the b and c dimensions (Blott & Pye 2008). However, in this thesis the method of Krumbein (1941) was adopted; the a dimension (defined as the maximum calliper dimension) was identified first, with b and c dimensions measured orthogonal to a. Clast axes were measured using callipers and measurements were entered into the tri-plot spreadsheet of Graham & Midgely (2000), which provides a rapid means of generating ternary diagrams.

Image withheld for copyright reasons

Figure 4.16: Measurements of clast diameters (after: Krumbein 1941, Figure 2, p 66)

Based on the ratios of the relative dimensions of the three axes, clasts are usually classified into four basic categories (Tucker 2003, Bunte & Abt 2001), termed spheres/equant, discs/oblate, blades and rods/prolate (Zingg 1935, Tucker 2003), or equant, tabular, prolate and bladed (Benn & Ballantyne 1993), or compact, platy, bladed and elongate (Sneed & Folk 1958), although Blott & Pye (2008) offer their own, five-class, method of describing particle form. Shape can be plotted as a biaxial diagram (Zingg 1935) or as a ternary diagram (Sneed & Folk 1958). The Zingg (1935) method has only four shape categories, and it has been shown to be less useful and versatile than the ternary plot (Benn & Ballantyne 1993, Evans & Benn 2004), making it less suitable for the detail required in this research than the more commonly used ternary diagram of Sneed & Folk (1958), which has ten shape categories (Figure 4.17) (Fisher & Bridgland 1986, Graham & Midgely 2000, Evans & Benn 2004) and has been adopted in this thesis. Each axis of the ternary diagram represents one of the end-members, all possible shapes are represented without distortion of the continuum of form and different forms are distributed evenly across the diagram, although bladed and elongate forms are compressed into the bottom right hand corner of the diagram, making them difficult to distinguish (Evans & Benn 2004, Blott & Pye 2008).

Image withheld for copyright reasons

Figure 4.17: Clast shapes plotted according to Sneed & Folk (1958)

4.9.2 Clast sphericity

Sphericity is a measure of the degree to which the shape of a clast approaches that of a true sphere (Tucker 2003, Blott & Pye 2008) and is a measurement which combines clast surface area and clast volume (Fisher & Bridgland 1986), although Waddell (1935) suggested the use of circularity as an alternative to sphericity because of the impracticality of measuring surface area or volume on natural clasts (Waddell 1935, Blott & Pye 2008). The relationship between sphericity and abrasion/attrition during transport is unclear; cubic clasts will turn into spheres, but clasts of fissile rocks are unlikely to reach this state (Fisher & Bridgland 1986). However, for single lithologies, the variation of sphericity has been shown to be closely related to hydrological factors (Sneed & Folk 1958, Fisher & Bridgland 1986). In this thesis, clast sphericity has been used in a hydraulic context as an indication of the effective settling, tendency to remain suspended in flow and as a measure of the ability of a clast to remain in transport once entrained (Benn & Ballantyne 1993, Bunte & Abt 2001, Blott & Pye 2008).

Estimates of sphericity can be made using a visual comparator, which requires measurements to be made in the three orthogonal orientations to obtain average sphericity values (Blott & Pye 2008). However, Maximum Projection Sphericity (MPS, ψ_p) (Sneed & Folk 1958), which is derived from actual measurements of clasts, bears the closest relationship to clast hydraulic properties (Fisher & Bridgland 1986) and has therefore been used in this thesis. It is obtained using the following equation:

$$\psi_p = \sqrt[3]{c^2/ab} \qquad [4.14]$$

where c is the length of the shortest principal axis, b is the length of the intermediate principal axis and a is the length of the longest principal axis and gives a range of values between 0 (least spherical) and 1 (most spherical) (Sneed & Folk 1958).

4.9.3 Pilot study clast morphology

The results of clast morphological and sphericity analysis applied to the limestone fraction of gravel units in core GV are summarised in Table 4.13.

Table 4.13: Morphology, OPI and sphericity of limestone clasts of core GV
(after Sneed & Folk 1958, Dobkins & Folk 1970)

Morphology												Sphericity	N^o of clasts
Unit	Compact	Compact-Platy	Compact-Bladed	Compact-Elongate	Platy	Bladed	Elongate	Very-Platy	Very-Bladed	Very-Elongate	Mean OPI	Mean Sphericity	
GV11	0.00	14.71	17.65	0.00	23.53	17.65	11.76	8.82	5.88	0.00	-3.13	0.63	34
GV3	8.75	10.00	11.25	5.00	17.50	26.25	8.75	3.75	6.25	2.50	-1.21	0.65	80

In GV3 the largest proportion is the bladed class with a significant additional proportion in the four compact classes, although mean sphericity of 0.65 indicates an overall less compact morphology. In GV11 the largest proportion of clasts are platy. In units with low clast numbers, the most numerous morphology classes are bladed and elongate in GV4 and bladed in GV5. The single limestone clast of GV2 is compact-elongate with a sphericity of 0.86.

4.9.4 Clast roundness

Roundness may be assessed by direct measurement using formulae, such as those of Waddell (1935), Krumbein (1941) or Cailleux (1947), but these methods are time consuming, and have not been universally adopted (Hubbard & Glasser 2005). Instead, roundness is most often assessed by using visual comparators which, although less precise than direct measurement, provide a flexible, practical and speedy method of sample description and comparison, and assigning the clast to a roundness category (Briggs 1977, Evans & Benn 2004, Blott & Pye 2008). The most commonly used visual comparator is that of Powers (1953), which has six categories (Table 4.14) and is used in this thesis.

Where ambiguities in roundness categories arose regarding the classification of, for instance a round pebble with broken edges, the additional information was recorded (e.g. round, broken) and the advice of Hubbard & Glasser (2005) was followed, whereby a round clast with a single broken corner, for example, was classified as round (Hubbard & Glasser 2005). All other cases were treated in the same manner as the rest, as advocated by Gale & Hoare (1991).

Table 4.14: Roundness categories (Powers 1953)

Class	Description	Roundness indices
Very angular	Strongly developed faces. Corners and edges very sharp with no discernible blunting. Reserved for frost-fractured and other freshly broken clasts	0.12-0.17
Angular	Strongly developed faces with sharp corners	0.17-0.25
Sub-angular	Strongly developed flat faces with incipient rounding of corners	0.25-0.35
Sub-round	Poorly developed flat faces with corners well rounded	0.35-0.49
Round	Flat faces nearly absent, with all corners gently rounded	0.49-0.70
Well round	No flat faces or corners. A uniform outline	0.70-1.00

4.9.4.1 Pilot study clast roundness

Results for clast roundness analysis, applied to the limestone fraction of core GV gravel units are shown in Table 4.15. The largest proportion of clasts in GV3 and GV11 are sub-angular although 27.50% of those in GV3 were formerly round but are now broken. There are also large proportions of sub-round and round clasts. No core GV gravel unit contains any very angular clasts; in units with low clast numbers, GV4 has mostly sub-angular and clasts in GV5 are sub-round and round.

Table 4.15: Roundness of limestone clasts in core GV

	Roundness							N^{o} of clasts
Unit	% Very Angular	% Angular	% Sub-Angular	% Sub-Rounded	% Rounded	% Well Rounded	% Broken	
GV11	0.00	14.71	58.82	20.59	5.89	0.00	11.76	34
GV3	0.00	10.98	40.24	20.73	21.95	6.10	27.50	80

4.10 Palaeontology

Fossils form proxy indicators of the environment in which they lived. When combined with other sedimentary evidence they enable a more comprehensive palaeoenvironmental history of sedimentary units to be inferred (Whalley 1990, Lowe & Walker 1997, Haslett 2002, Mackay *et al.* 2003, Evans & Benn 2004). However, most fossil remains of the Gordano Valley sediments consist of very small shell fragments and fine organic fragments. Because of their fragmentary nature and small size they are considered to be derived; therefore no attempt was made to identify them. Fossil evidence in this thesis is mainly confined to that of the pilot study (core GV) and two fossilferous units in core TG and is drawn from molluscs, algae, ostracods, foraminifera, coleoptera, pollen and plant macrofossils; as many biological proxies as possible have been used to give a representative analysis of the fossil assemblage and to allow conflicts in the evidence to be resolved (Evans & Benn 2004).

The following sections give a brief overview of the potential contribution of each fossil to the overall Pleistocene environmental reconstruction in the Gordano Valley in this thesis. This is followed by a description of sample preparation and identification techniques used.

4.10.1 Molluscs

Mollusc shells are preserved in a wide range of calcareous sediments and have been widely used in reconstructing palaeoenvironments; for example, Preece *et al*. (2007) were able to infer changes in Pleistocene fluvial discharge and vegetation at West Stow, Suffolk from the molluscan fauna. Molluscs occupy a wide range of ecological niches and their sensitivity to changes in the environment makes them useful indicators of local habitat conditions (Birks & Birks 1980, Ložek 1986, Keen 1987, Lowe & Walker 1997). Their present-day ecology and distribution is well known, facilitating comparisons with palaeoenvironments (Ložek 1986, Lowe & Walker 1997). However, whilst land taxa have been used to determine local habitat conditions, especially the degree and type of vegetation cover and whether ground conditions were dry or marshy (for example; Preece *et al*. 2007), freshwater and marshland species tolerate a wider range of habitats and climates, making inferences more difficult (Sparks 1964, Ložek 1986). Molluscs are therefore used with caution in this thesis to infer both their habitat and the depositional environment of the sediment they are preserved in.

4.10.2 Algae

Algae may be used to enhance the palaeoenvironmental reconstruction, providing detail of hydrological conditions, water chemistry and palaeoclimate. The use of algae in palaeoenvironmental reconstruction is less common than other fossils, although Preece *et al*. (2007) used *Chara* as part of their reconstruction of palaeoenvironments at West Stow, Suffolk. *Chara* are epipelic macroscopic algae found on all types of sediment on the littoral zone of lakes extending down to the lower limit of photosynthetically available light (Round 1973). They usually grow submerged in mainly still, occasionally flowing, fresh water. *Chara* frequently populate calcareous waters of high pH; although a very few species of *Chara* are found in slightly brackish waters near coasts, none are fully marine (Round 1973, Bryant & Stewart 2002).

Chara are often dominant and long-lived perennials, particularly in limestone areas in the northern temperate zone (Round 1973, Bryant & Stewart 2002). They are highly adaptable and are found in a wide range of habitats. They can be pioneer colonizers of newly created habitats, ephemerals in transient habitats, dominant deepwater perennials in large lakes or background members of aquatic vascular plant communities. They are intolerant of high levels of nutrients, generally indicating absence or low levels of nutrients, and are important in stabilizing sediment thus contributing to clear water conditions and water clarity (Bryant & Stewart 2002).

Normal metabolic activity results in encrustation with calcium carbonate (Prescott 1969, Round 1973, Bryant & Stewart 2002). Calcium carbonate deposition may be appreciable, and the process may continue in a particular habitat over thousands of years, resulting in considerable marl accumulations in lake bottoms (Prescott 1969, Bryant & Stewart 2002).

4.10.3 Ostracods

Although they are used less routinely than other fossils ostracods are an abundant and diverse group of small crustaceans which have been successful in colonising most aquatic habitats and have a readily fossilised carbonate carapace (Boomer 2002). They show limited evolutionary change during the Pleistocene, migrate rapidly in response to climate amelioration and their faunal and shell chemistry response to environmental change can be used to qualitatively and quantitatively reconstruct patterns of Pleistocene climate change (Jones & Keen 1993, Boomer 2002).

Ostracods are sensitive to changes in a wide range of environmental variables and some have restricted ecological preferences, making them useful palaeoenvironmental indicators, particularly in the transition between marine and non-marine facies in marginal marine environments where assemblages of marine and non-marine waters tend to be mutually exclusive (Jones & Keen 1993, Lowe & Walker 1997, Griffiths & Holmes 2000, Boomer 2002). Potentially ostracods could be used as proxies of past environmental change through transfer functions similar to those already established for diatoms and foraminifera. Parameters which could be indicated are salinity, water chemistry, water depth, substrate, oxygen, productivity, temperature and climate (Frenzel & Boomer 2005). Ostracod transfer functions have been used mainly in North America to reconstruct the solute history of lakes (Griffiths & Holmes 2000).

However, environmentally stressed environments are often dominated by a single taxon, their carapaces tend to be fragile and can be easily destroyed by mechanical abrasion and chemical corrosion, which can make interpretation of palaeoenvironmental changes difficult (Boomer 2002). Such difficulties are best resolved by examination of other taxa (Boomer 2002). Fossil assemblages may be biased by selective preservation of the more thick-shelled species or the incorporation of fragments of older or younger material, although *in situ* species can often be recognised by the presence of instars, reflecting the life cycle of indigenous fauna (Lowe & Walker 1997). Additionally, the modern ecology of many species is poorly understood, limiting their use in respect of modern analogue techniques (Boomer 2002).

The most extensively used approach to palaeoecological reconstruction using ostracods has involved qualitative methods based on the perceived autecology of individual species to estimate qualitatively a range of past environmental conditions, most notably habitat type, including salinity and water temperature (Griffiths & Holmes 2000). This is the approach used in this thesis, where ostracods are employed in conjunction with other fossil evidence as was done, for example, by Bates *et al.* (2002, 2007) to infer local marginal marine environments for the Medway estuary at Allhallows, Kent and Roe *et al.* (2009) to distinguish intertidal from true marine environments at two locations in Essex.

4.10.4 Foraminifera

Most foraminifera are marine and benthic, although a small number are adapted to freshwater environments (Lowe & Walker 1997). Reworking and redeposition of foraminifera tests is a frequent occurrence (Lowe & Walker 1997), and robust forms are amenable to preservation in sands and gravels (Jones & Keen 1993). Foraminifera have been used in quantitative and semi-quantitative palaeoenvironmental reconstructions to infer changes in sea-level (e.g. Gehrels *et al.* 2001, Allen *et al.* 2006), and are used in this thesis in support of other fossil data as indicators of local sea-level conditions as part of a multi-proxy approach.

4.10.5 Coleoptera

Coleoptera are often abundant in a wide range of Quaternary deposits, particularly those conducive to the preservation of plant debris, and are often adapted to narrow temperature or vegetational niches. Their rapid colonization ability makes them ideally suited to palaeoenvironmental reconstruction (Coope 1986, Jones & Keen 1993, Lowe & Walker 1997). Although best preserved in Devensian (MIS 5d-2) deposits, where they are often abundant (Coope *et al.* 1997, Allen *et al.* 2009), coleoptera have been found in various stages of preservation in Mid-Pleistocene sediments (Murton *et al.* 2001, Ashton *et al.* 2008, Roe *et al.* 2009). In this thesis coleoptera remains are used to support the vegetational and landscape evidence of other fossil remains.

4.10.6 Pollen and plant macrofossils

Pollen analysis is a widely adopted technique in the reconstruction of palaeoenvironments in the context of local vegetational history (Moore *et al.* 1991, Lowe & Walker 1997, Haslett 2002). Pollen grains survive better and longer than other biological materials because their sporopollenin is resistant to decay (Moore *et al.* 1991), although they may be destroyed in soils with a high pH value (Andersen 1986). Pollen grains are usually better preserved in fine-grained lake and peat sediments than in coarse grained sediments (Moore *et al.* 1991, Haslett 2002).

The advantage of using plant macrofossils rather than pollen analysis is that plant macrofossil taxa can frequently be distinguished to species level. They can therefore provide greater detail about palaeoenvironments than would have been provided by pollen (Lowe & Walker 1997, Birks 2004, Mauquoy & Van Geel 2007). However, the preservation-state of the fossil material may be variable, so that identification to species level is sometimes precluded (Lowe & Walker 1997). Furthermore, vegetational productivity is variable between species and changes in response to environmental conditions, and there may be a considerable time lag in vegetational response at times of rapid environmental change (Walker 1995, Lowe & Walker 1997, Mayle *et al.* 1999, Mauquoy & Van Geel 2007) and selective decomposition of vegetation, predation or microbial or fungal attack may limit the usefulness of reconstructions of plant assemblages.

4.10.7 Sample preparation

Palaeontological analysis of core GV was carried out using conventional protocols (Murray 1979, Coope 1986, Grosse-Brauckmann 1986, Löffler 1986, Ložek 1986, Moore *et al.* 1991). Other samples for palaeontological analysis were prepared following the guidelines outlined in Murray (1979), Berglund (1986), Griffiths & Holmes (2000) and Haslett (2002). In order to permit the maximum amount of fossil material to be extracted, no chemical treatments were carried out on samples used for fossil analysis. Thus, solutions of sodium carbonate and sodium/potassium hydroxide were not used to facilitate disaggregation because this has been known to make fossil insects thin and frail (Berglund 1986). It was also considered preferable to pick insect remains directly from the sediment rather than use kerosene flotation for analysis of beetle remains because partially decomposed insect remains, such as heads, are often filled with sediment and remain in the heavy fraction (Berglund 1986).

A sub-sample of material was taken from the middle 2 cm of each unit and any obvious plant macrofossils were first picked from the sediment and placed in a vial containing a small amount of glycerol/alcohol mixture to preserve the material. The sub-sample was then air dried at room temperature for 24 hours and weighed to allow relative concentrations of fossils (expressed as number of individuals/gram of sediment) to be determined. The sub-sample was then rehydrated in tap water and stirred to disaggregate it. Small quantities of sample were then washed through a nest of sieves (1, 2, 3 and 4 φ aperture), again using tap water. Each fraction was then air dried for a minimum of 24 hours before being placed in a glass petri dish and examined under a low-power (20x magnification) binocular microscope using transmitted light against a matt black surface. A 0000 sable-hair paintbrush was used to pick specimens. All foraminifera, ostracods and molluscs between 4 φ and 1 φ from both units were picked, identified and counted; juvenile molluscs and ostracods were not excluded from counts.

Any plant macrofossils or beetle remains were placed in a vial containing a small amount of glycerol/alcohol mixture. Mollusc specimens too large to be mounted on a micropalaeontological slide were also placed in a vial. Smaller mollusc specimens and those of ostracods and foraminifera were glued to micropalaeontological slides using water soluble adhesive gum. Unused clastic material was archived.

Only sediments of pilot study core GV were analysed for pollen content. Samples were prepared using the conventional protocols of oxidation and acetolysis to reduce organic content (Berglund & Ralska-Jasiewiczowa 1986). The pollen-containing residues were mounted on glass slides and all identifiable pollen grains were counted using a light microscope (Moore *et al.* 1991). Identification was made to family/genus level based on distinctive exine characteristics.

Plant macrofossils were more abundant, but time constraints prevented more than a cursory examination. However, this limited plant macrofossil analysis improved the detail of palaeoenvironmental reconstruction.

4.10.8 Identification of fossils

Fossil specimens were identified by comparison with published taxonomic keys (Table 4.16) and verified by comparison to reference material. Identifications were then recorded photographically, which allowed earlier identifications to be used for comparison with later material.

Table 4.16: Keys used in the identification of fossils

Fossil	Key
Algae	John *et al.* (2002)
Coleoptera	E. Tetlow (Pers. comm. 2009)
Foraminifera	Murray (1979)
Molluscs	Ellis (1969)
Ostracods	Athersuch *et al.* (1989); Griffiths & Holmes (2000)
Pollen	Moore *et al.* (1991)

4.10.9 Pilot study palaeontology

Palaeontological analysis as described above was applied to core GV. However, the sediments proved to be largely unfossiliferous, with low counts of poorly preserved fossils. The exceptions were of rare pollen grains (one grain each) of *Potentilla*, *Ranunculus* and Chenopodiaceae in GV7, Cyperaceae, *Filipendula* and *Ranunculus* in GV8 and *Ranunculus*, Cypereaceae and *Juniperus* in GV9, two mollusc shells (tentatively, because of its poor preservation state, *Belgrandia marginata* (Michaud) in GV3 and *Viviparus* *diluvianus* in GV5) and shell fragments and detrital plant remains which were found throughout the core between GV4 and GV11. Because of their fragmentary nature and small size, no attempt was made to identify the small shell fragments and very fine plant debris. Otherwise, the sediments of core GV are largely unfossiliferous.

Because the sediments of core GV were almost barren of fossils, detailed palaeontological analysis of further percussion cores was not carried out, with the exception of two obviously fossiliferous units. Palaeontology therefore forms an additional source of palaeoenvironmental information that in combination with readily determined sedimentological information such as grain size, sorting, clast morphology and lithology would improve the palaeoenvironmental interpretation.

4.11 Establishing the ages of the minerogenic sediments

Dating is important to enable reconstruction of environmental change (West 1985). A number of dating techniques have been used in Quaternary studies to estimate the age of the material of interest (Lowe & Walker 1997, Walker 2005, Elias 2007). Each dating technique has problems at the required level of resolution or with analytical errors that can lead to uncertainties in interpretation (Lowe & Walker 1997). Contamination and reworking of sediments form particular problems for the application of dating techniques, and many records cannot be dated precisely (Lowe & Walker 1997, Walker 2005), whilst many of the dating techniques currently employed in Quaternary science can be applied only to restricted timespans and some methods, for instance U-series dating, require geochemically closed-system behaviour (in which matter is not exchanged with the surroundings) while others, such as AAR, only give relative ages (Lowe & Walker 1997, Lian & Roberts 2006).

However, choice of dating technique is largely constrained by the nature of the material available. For this project this was mostly sand, silt and gravel, with some pedogenic and biogenic material. Much of the biogenic material was detrital, which limited its usefulness for dating. However, the presence of *in situ* mollusc shells and pedogenic material afforded the opportunity to obtain both radiocarbon dates and correlation through AAR geochronology, whilst OSL dating was applied to minerogenic material. Otherwise, relative ages of sediments were established from their stratigraphic superposition (Lowe & Walker 1997).

4.11.1 Radiocarbon dating

Radiocarbon (^{14}C) dating has been the most commonly used technique to establish Quaternary geochronology (Richards 2000, Duller 2004, Lian & Roberts 2006). Despite its use being limited to approximately 60,000 years, radiocarbon dating provides a technique for dating at least part of the Devensian (MIS 5d-2). It can be undertaken on a range of biogenic material such as wood, plant macrofossils or peat.

There are two approaches to measuring ^{14}C activity in a sample: conventional radiocarbon dating and AMS. Although the AMS method cannot inherently provide a more accurate age than the conventional method, particularly on bulk sediment samples, dating by AMS has the advantage that very small samples, 1 mg of organic carbon or less, can be dated compared with 5-10 g required for conventional radiocarbon dating. The precision of AMS is comparable to conventional radiocarbon dating (Walker 2005) and can provide dates at higher resolution (Grimm *et al.* 2009). The AMS technique was selected for radiocarbon dating of organic carbon in this thesis because of the small sample sizes available.

Limitations of radiocarbon dating include hardwater and mineral carbon errors, reservoir effects in marine fossils, and biological and chemical fractionation. Some of these are site specific and can be mitigated through careful site and/or sample selection and/or application of correction factors (Lowe *et al.* 1999). The hardwater effect may be a particular problem for the Gordano Valley sediments where dissolved carbonates from the solid geology may be incorporated into the valley floor sediments. Additionally, the accuracy of older radiocarbon dates, particularly those which are at or just over what is considered to be reliable for conventionally pre-treated radiocarbon ages, has recently been questioned because they are potentially sensitive to contamination by modern carbon (Briant & Bateman 2009). Standard pre-treatments have been found insufficient to remove contamination in older samples (Hatté *et al.* 2001), and Bird *et al.* (1999) found that radiocarbon ages obtained using standard chemical and extraction techniques often underestimate true radiocarbon ages. Pigati *et al.* (2007) have therefore urged caution in the interpretation of radiocarbon dates that exceed 40 ka; Briant and Bateman (2009) suggest this limit should be drawn at 35 ^{14}C ka BP. This introduces an element of doubt concerning the reliability of radiocarbon ages, which will therefore need to be interpreted with care.

To mitigate for contamination samples were carefully selected to avoid obvious foreign matter, such as roots or reworked material, collected using clean, inorganic implements, placed in fresh plastic bags and stored under refrigeration at 3° C to prevent fungal or algal growth (Tan 2005, Briant & Bateman 2009). In addition, routine pre-treatment was carried out at the radiocarbon laboratory. Whilst this will not counteract all contamination, it minimises this potential source of error in radiocarbon dates (Walker 2005).

4.11.1.1 Radiocarbon dating of mollusc shells

Dating mollusc shells often incurs problems with contamination. This may be of older or younger carbon, and can result from terrestrial molluscs ingesting older carbonates (limestone or soil carbonates) during their lifetime which may be incorporated into the shell resulting in anomalously old radiocarbon dates. A further problem is that fossil terrestrial molluscs often have secondary (pedogenic) carbonate deposition on them and after death recrystallisation, in which the aragonite of mollusc shells is converted to calcite, can occur resulting in anomalously young radiocarbon dates (Walker 2005).

The presence of secondary carbonate (calcite) on mollusc shells composed of aragonite was checked at the radiocarbon laboratory using X-ray diffraction (XRD). Shells were prepared for analysis by using acid hydrolysis to remove the outer portion of the shell to obtain the inner portion for AMS radiocarbon dating (Walker 2005).

4.11.1.2 Radiocarbon dating of bulk soil samples

Radiocarbon dating is commonly used to date organic matter from buried soils, within the limits of the technology (Catt 1990). However, soils are dynamic systems, receiving organic matter over long periods of time. This is further complicated by the constant recycling that takes place within the soil profile, the biological activity of, for example, earthworms, the circulation of humic acids and root penetration, and correction factors are difficult to apply when the sediment is composed of a heterogeneous mix of clastic and organic material (Lowe & Walker 1997, Walker 2005). Radiocarbon dates from soils are therefore influenced by the mean residence time of the various organic fractions in the soil, and a radiocarbon date reflects both the mean residence time as well as the time that has elapsed since burial. Because of the continuous input of organic material into soil, decomposed humus from the uppermost part of a buried soil is therefore likely to provide a radiocarbon age that is generally younger than the true age of the soil by an unknown amount (Catt 1990, Walker 2005), and therefore a minimum age for the cessation of soil formation. Radiocarbon dating of the uppermost pedogenic units is therefore used in this project to establish the age at which pedogenesis and landscape stability ceased.

4.11.2 AAR geochronology of mollusc shells

Amino acid geochronology has the potential to determine relative Pleistocene age and enable correlation within the British Isles and also with continental Europe (Rink *et al.* 1996, Penkman 2009). Application of this technique has been particularly important in the Bristol Channel/Severn Estuary region for dating interglacial deposits and for recognising complexity in the Pleistocene sequence (Davies 1983, Bowen *et al.* 1985, Bowen *et al.* 1986, Bowen *et al.* 1989, Campbell & Bowen 1989, Bowen 1991, Campbell *et al.* 1998, Scourse & Furze 2001).

Past use of amino acid ratios has not been without problems; early methods of sample preparation have been replaced, making direct comparison with previous work difficult (Bowen *et al.* 1986). This led to frequent reassessments of earlier interpretations, which were then called into question (Hunt 1998a, Meijer & Cleveringa 2009), and uncertainty surrounding the central position of aminostratigraphy to Pleistocene correlation. However, recent advances involving a new method (reverse-phase high-pressure liquid chromotography; RPC) which allows the analysis of multiple values from the same shell and thus provides a cross–check on the behaviour of the sample (Penkman 2009), and using the chemically protected intra-crystalline fraction of shell (Penkman *et al.* 2008), have widened the time range and resolution possible (Penkman 2009). The level of temporal resolution is better for sites of MIS 7 age or younger although in some cases results allow discrimination between older stages (Penkman *et al.* 2007, Penkman 2009).

There are caveats in its application; samples need to be of the same species for direct comparison (Bowen *et al.* 1986) and the thermal history of samples needs to be the same (Miller *et al.* 1979; Davies 1983; Andrews *et al.* 1984). AAR ratio measurements do not provide chronometric dates and rely on absolute dating to calibrate the aminostratigraphic sequence (Rink *et al.* 1996). McCarroll (2002) considered amino acid ratios should therefore be viewed as a guide to relative age rather than a definitive stratigraphical or dating tool.

AAR geochronology would potentially allow some of the difficulties involved with radiocarbon dating of mollusc shells, such as temporal limit of the technique, hard water effect and potential for contamination, to be overcome and provide a useful check on radiocarbon dates obtained. Mollusc shell forms a tightly closed system that is affected by a minimum of external factors (Sykes 1991). Unlike radiocarbon dating, contamination by handling is generally not a problem because the samples are rigorously cleaned during preparation for analysis (Sykes 1991). However, protein breakdown is temperature dependent, which means it is important to consider temperature variation when correlating AAR geochronology over geographically wide areas (Penkman 2009).

Three species of freshwater gastropod (*Bithynia tentaculata*, *Bithynia troschelli* and *Valvata piscinalis*) and the bivalve *Corbiucula fluminalis* are commonly used for AAR geochronology (Penkman *et al*. 2007). In this research, AAR of *Valvata piscinalis* from an *in situ* deposit was used to determine the age of deposition. This was the first use (to the knowledge of this author) of the RPC/intra-crystalline fraction technique to provide AAR geochronology in the Bristol Channel/Severn Estuary region, although results cannot be directly compared with old datasets (Penkman 2009).

4.11.3 OSL dating of minerogenic sediments

OSL dating is achieved by measuring ionising energy stored by natural minerals (usually silicate material) that results in a luminescence phenomenon, providing an indication of the time elapsed since mineral grains were last exposed to sufficient sunlight (Walker 2005, Lian 2007, Duller 2007). Instead of relying on the decay of a single isotope, as with radiocarbon dating, OSL dating exploits the presence of naturally occurring minerals such as quartz and feldspar recording the amount of radiation to which they have been exposed (Duller 2007). In the case of sediments, the luminescence clock can be zeroed by exposure to sunlight, a process known as ‘bleaching’ (Duller 2007).

OSL dating is commonly used to date the time of formation and alteration of sedimentary landforms (Lian & Roberts 2006), although the quality of results obtained depends on the suitability of samples analysed (Duller 2007). Sediments should contain quartz and/or feldspar of sand or silt-size and consist of grains deposited in an environment which enabled them to be well exposed to light (Richards 2000). Much research has focused on sediments for which zeroing (bleaching) of the luminescence signal prior to deposition was assured, such as loëss, coastal dunes or desert sands (Wintle 2008), but the technique has recently been applied, with varying degrees of success, to fluvial and colluvial sediments (Richards 2000).

One of the primary limitations on the precision of OSL dating is the uncertainty in the water content of the sediment being dated and the impact this has on the dose rate. However, the main problem with OSL dating is complications that arise from the original sediment not being completely bleached by sunlight before the accumulation of the dose under study, or that partial bleaching occurs (Walker 2005, Lian 2007). OSL dating of sediments relies on the resetting of latent luminescence to a low level by sunlight. This is attenuated by turbidity particularly during fluvial transport, which slows the rate of bleaching for grains (Richards 2000). Other reported problems include: low luminescence sensitivity and difficulties in isolating pure quartz (Richards 2000).

The advantage of OSL dating is that sediments are directly dated (Richards 2000). Another advantage is that OSL dating is applicable over a longer timespan than ^{14}C, giving calendar ages without the need for complex calibration. OSL techniques are capable of providing dates typically in the 75-150 ka range, although the age range over which OSL dating can be applied is variable, and it is not possible to give a precise upper age limit as this is controlled by saturation of the luminescence signal, which varies from one sample to another, coupled with the rate at which a sample receives dose, which varies from one site to another (Richards 2000, Lian & Roberts 2006, Duller 2007). The lower age limit is equally difficult to define and is controlled by how well the luminescence signal was reset at the time of the event being dated and the brightness of the signal obtained from the mineral being studied (Duller 2007). One major advantage of OSL dating is the ability to make replicate measurements on sub-samples using the same material (Duller 2007), making the technique particularly suitable for use where sample sizes are small, as in this research.

OSL dating of minerogenic sediment is used in this research to extend the chronology beyond the age limitation of the radiocarbon technique and to validate the mollusc AAR geochronology by attempting to bracket the sediments dated using those techniques. Sample preparation was carried out at Research Laboratory for Archaeology and the History of Art, Oxford. Sections of core were opened under controlled (orange) light conditions, and although ideally sampling would not be carried out either close to the ends of core sections or within 30 cm of a stratigraphic boundary, because most of the sedimentary units are less than 30 cm thick, samples were taken from unit mid-points. Six samples were taken for dating and samples were assigned numbers x3780-x3785 for ease of identification; X3785 and x3781 were taken from gravel units and x3780, x3782, x3783, and x3784 from fine sand units.

The samples were wet sieved to separate the 180-255 µm sand fraction, treated with dilute HCl to remove any carbonates and immersed in sodium polytungstate to achieve quartz separation. The quartz samples were treated with hydrofluoric acid (HF) for 30 to 60 minutes in order to remove feldspars and the outer layer exposed to alpha radiation. Finally, the samples were dry sieved. Three test discs for preliminary OSL dating were prepared for each sample to ensure sample viability. Sample was deposited onto aluminium discs using silica gel as an adhesive and each disc was then placed in an aluminium tray.

All luminescence measurements were performed using an automated Risø TL-DA-15 luminescence reader (Bøtter-Jensen, 1988, 1997, Bøtter-Jensen *et al.* 2000). Optical excitation was provided by filtered blue diodes emitting at 410-510 nm operated at 90% power and the quartz luminescence signal was detected using an EMI 9635Q bialkali photomultiplier tube, filtered with Hoya U340 glass filters. OSL measurements were made at 125°C and sample irradiation was provided by a calibrated sealed ^{90}Sr source. The calculated palaeodose for each sample was based on the weighted mean result obtained from 12 repeat measurements made on medium sized aliquots (~ 4 mm). A preheat combination of 260°C and 220°C for 10s was used in all cases using a standard single aliquot regenerative-dose measurement protocol (Murray and Wintle 2000, Banerjee *et al.* 2001, Wintle and Murray 2006).

4.12 Characterisation of sediment attributes to determine depositional environments

To characterise the sediment attributes and determine the depositional environments of the Gordano Valley it was necessary to integrate the different lines of evidence to produce an overall synthesis. A multi-faceted approach, in which mutually supporting lines of evidence converge on the most appropriate interpretation with the highest probability of being correct (Birks & Birks 2006), has been adopted for this thesis. This permits a higher degree of confidence to be placed on the palaeoenvironmental reconstruction for the

Gordano Valley, enabling different aspects such as sedimentary processes, provenance and relative chronology to be inferred (Lowe & Walker 1997, Evans & Benn 2004). This approach also provides opportunities to recognise and resolve apparent conflicts, overcome the sporadic occurrence of fossils and the bias that selective transport and differential destruction can introduce into the fossil assemblage, and reduces the possibility of a proxy providing misleading palaeoenvironmental information (Lowe & Walker 1997, Walker *et al.* 2003). A multi-faceted study was used, for example by Walker *et al.* (2003) to resolve problems of reworked sediments, low counts of biological proxies and conflicting evidence. A multi-faceted approach also facilitates comparison with regional sites of known history (Evans & Benn 2004), allowing the Pleistocene sedimentary sequences of the Gordano Valley to be set in context with regional sequences (Lowe & Walker 1997).

4.12.1 Characterisation of sediment attributes

The sedimentary attributes of marine, fluvial, colluvial, aeolian, glacial and periglacial processes and environments have all either been suggested by previous authors for the Gordano Valley minerogenic sediments and/or are likely to be present in a coastal lowland setting. In order to discriminate between these processes and environments a range of approaches was used to characterise the depositional environments. Options were limited, particularly because the depositional environment was not known in advance. Accepted models of interpretative treatments that had been used successfully by specialists in the various modern environments were selected and applied. Once included, models were applied consistently to all the data; where models were applicable to only a part of the population, only the appropriate population was used.

Some general inferences were made from sediment particle size distributions to provide a preliminary assessment about the palaeoenvironments. For example, till usually comprises poorly sorted material containing a range of particle sizes from coarse gravel to clay, although this also applies to slope deposits, debris flows and alluvial fan deposits (Gale & Hoare 1991); fluvial gravels may be poorly sorted and are typically bimodal (Reineck & Singh 1973), whereas fluvial sands are usually moderately sorted and fine skewed and riverbank deposits usually consist of silts and fine sands deposited from suspension (Gale & Hoare 1991). In almost all environments there are low- and high-energy sub-environments. High-energy sub-environments show coarser, better sorted sediments, whereas low-energy environments show finer-grained and poorly sorted sediments with skewness >1 (Reineck & Singh 1973). Modality of particle size distributions was also used to infer palaeoenvironments. For example, many tills have polymodal or uniform distributions, whereas englacial and supraglacial debris often possess unimodal particle size distributions (Gale & Hoare 1991). Multimodal particle size distributions have commonly been used to argue for the presence of more than one population of sediments (Weltje & Prins 2007) or of more than one process (Evans & Benn 2004); both are likely in the Gordano Valley.

There have been numerous attempts to relate particle-size statistical parameters to different depositional environments (e.g. Folk & Ward 1957, Stewart 1958, Friedman 1961, Bull 1962, Visher 1969, Tanner 1991, Long *et al.* 1996, Lario *et al.* 2002). The most commonly used approaches are bivariate plots using particle size distribution summary statistics, identification of truncated log-normal subpopulations or multivariate statistical approaches using principle components analysis, factor analysis or discriminant analysis (Gale & Hoare 1991). For example, Long *et al.* (1996) used particle size data (sorting and skewness) to infer energy conditions of a coastal marsh. However, these approaches have had limited success as generally applicable methods (Reineck & Singh 1973, Gale & Hoare 1991). An investigation of the ability of techniques commonly used to discriminate sediments from different depositional environments found that none of the tested methods was successful (Solohub & Klovan 1970, cited in Gale & Hoare 1991), and had the approaches been applied to sediments of unknown origin, most sediments would have been wrongly categorised (Gale & Hoare 1991). Evans & Benn (2004) caution that there is rarely a unique set of particle size characteristics related to a particular process. Particle size distribution alone is therefore inadequate as a means of determining the depositional environment of sediments and interpretation depends on the evaluation of all the available evidence (Gale & Hoare 1991, Lowe & Walker 1997). A range of approaches was therefore applied to discriminate between different depositional environments.

Bivariate plots in which sediments from different environments appear to cluster in different areas (Gale & Hoare 1991) were used to investigate depositional environments by comparison with those of known modern environments. Divisions shown on the various plots are those recognised by the relevant authors. For example, Tanner (1991) plotted particle size parameters skewness against kurtosis to discriminate between beach, river, aeolian and settling environments. The environmental parameters derived from this are shown in Figure 4.18.

Image withheld for copyright reasons

Figure 4.18: Environmental parameters derived from analysis of modern environments (Tanner 1991). Boundary between aeolian/settling & river environments are shown as a dashed line; boundaries between beach & river or aeolian/settling environments are shown as solid blue line

Plots of particle size parameters skewness against kurtosis were used to differentiate between beach, river, aeolian or settling environments (following Tanner 1991); median particle size against skewness and against sorting was used to differentiate between river, wave and quiet water deposition (following Stewart 1958); mean particle size against sorting of the >4 φ fraction was used to differentiate between river and closed basin or settling environments (following Lario *et al.* 2002).

An approach which did not require the use of particle size summary statistics was also adopted. To discriminate between deposition from mudflow, river channel and braided stream flow, the first percentile of each sample (the particle size at which 1% of the distribution is coarser) was plotted against the median percentile (the particle diameter at which 50% of the distribution is coarser) (Bull 1962). Segment analysis (Tanner 1991), a triangular plot of the percentage by weight of coarse, fine and intermediate particle sizes was used to distinguish between beach (no tails), dune, sandy and silty river or closed basin deposition. Whilst these approaches permit differentiation between environments, there is some overlap between environmental envelopes as illustrated in Figure 4.19.

Image withheld for copyright reasons

Figure 4.19: Triangular diagram showing segment analysis environmental envelopes (Tanner 1991). Area of overlap between dune and river silts envelope is shown by hashes

Plots of gravel clast sphericity and oblate-prolate shape index (OPI) were used to distinguish between beach and fluvial deposition (following Dobkins and Folk 1970). OPI defines whether the intermediate axis is closer in size to the short or long axis and is based on the value of equation 4.15. Using this formula, all perfect blades have an OPI = 0.00, platy shapes have negative values and elongate shapes have positive values.

$$\mathrm{OPI} = \frac{10\left(\frac{a-b}{a-c} - 0.5\right)}{c/a} \qquad [4.15]$$

Dobkins & Folk (1970) showed that river gravels possess higher mean sphericities (ψ_p) than low energy beach gravels which in turn display higher sphericities than high energy beach gravels and applied a division between fluvial gravels of $\psi_p \geq 0.67$ and beach gravels of $\psi_p \leq 0.65$. They found the mean OPI of fluvial gravels is close to zero, becoming increasingly negative for beach gravels from increasingly higher energy environments, although differences are less marked than those for sphericity, and that for beach gravels mean OPI was almost invariably less than -1. The recommendation of Dobkins & Folk (1970) to use mean OPI in combination with ψ_p for environmental determination has been followed in this thesis.

Additionally, because it has been speculated that minerogenic deposits of the Gordano Valley are of glacial origin (Hawkins 1972), bivariate plots were used to discriminate glacigenic sediments as outlined by Benn & Ballantyne (1993, 1994), who have shown that the main difference between frost-shattered and subglacially transported clasts is the degree of blockiness as measured by the c:a ratio. Bivariate plots of RA (percentage of clasts which are very angular or angular) against C_{40} shape (percentage of clasts with c:a axes ratio of ≤ 0.4) permit differentiation of subglacially transported gravel clasts from those which were englacially, supraglacially or subaerially transported for a range of lithologies, in that scree and supraglacial samples have high RA and C_{40} values whereas till and subglacial samples have low RA and C_{40} values (Benn & Ballantyne 1994, Jones *et al*. 1999, Evans & Benn 2004).

Reworking of gravel deposits was identified by their bi- or poly-modal shape indices distribution when values of the (a-b)/(a-c) measurements were plotted as a frequency histogram (Sneed & Folk 1958, Bridgland 1986). Potential sources of minerogenic sediment in the Gordano Valley are bedrock, colluvial redeposition of surficial Pleistocene sediments located on the valley margins, transgressive marine beach deposits and fluvial deposits. The same order was used for all gravels; it would have been possible in some instances to re-order the shape classes to produce a normal distribution, but no single order could be consistently applied to all gravel units to achieve this.

A potential problem is that of inherited characteristics, where material has been reworked from pre-existing deposits. Depositional environments are rarely clear cut; the complexity of sedimentary processes means there is usually some degree of overlap between the characteristics of sediments of different environments and it is not always possible to make a confident determination. Where analysis suggested multiple possible depositional environments, that suggested by most analyses was selected. In cases where there was a tie, no analytical technique was given precedence, and an attempt was made to accommodate all possibilities in the interpretation. This is illustrated in Table 4.17 which shows two fluvial solutions, two settling/closed basin solutions and one mudflow solution. By accommodating all these solutions it is possible to interpret the depositional characteristics of the sediment as those of a slow-flowing muddy river.

Environmental interpretations are based solely on the results from sediment cores. There is therefore no evidence for diagnostic bed shapes which might aid interpretation and the use of statistical biological transfer functions was precluded by the sparseness of biological remains. Therefore as much evidence as possible, using a variety of techniques, was used. Five depositional modes are identified: river channel, braided stream, mudflow,

Table 4.17: Example of tied analytical solutions

Analytical technique	Indicated depositional environment
Segment analysis	Sandy river deposition
Bivariate plot of skewness against kurtosis	Fluvial deposition
Bivariate plot of mean particle size against sorting for the >4 φ fraction	Settling or closed basin deposition
Bivariate plot of median particle size against sorting	Settling in quiet water/slow deposition
Bivariate plot of median particle size against the coarsest 1 percentile	Mudflow

settling and flow intermediate between mudflow and river channel. In some cases the sedimentological characteristics indicate beach or settling deposition, possibly reflecting similarities in the mechanics of deposition and the inability of the analytical models used to adequately discriminate depositional environments rather than being an indication of the actual depositional environment. Autochthonous beach deposits are considered unlikely given the spatially extensive nature of the deposits. A beach solution has therefore been used to indicate reworking of pre-existing material through winnowing of finer material. Similarly, a settling solution has been used to indicate deposition in a closed basin environment (lagoon, estuary, lake, delta, floodplain, tidal flat, Tanner 1991) which probably reflects the configuration of the valley. Environmental interpretations of depositional environments were made using the criteria set out in Table 4.18.

4.12.2 Interpretation of post-depositional environments

Palaeosols have been successfully used in the reconstruction of local histories and, in certain circumstances, wider correlative schemes (Lowe & Walker 1997). However, a cautious approach was adopted in the use of pedogenesis in palaeoenvironmental interpretation in this thesis because buried profiles may be the product of more than one phase of pedogenesis (Lowe & Walker 1997). Colours 7.5YR or redder, or 5YR or redder in sediment coarser than sandy silt, are used as a criterion in the recognition of the ‘Palaeo-argillic Soil Group’ (Avery 1973), indicating the possibility of palaeosols.

Table 4.18: Environmental interpretation from analytical solutions

Sedimentological characteristics	Depositional mode	Environmental interpretation
Fluvial	River channel	River channel
Fluvial	Braided stream	Braided stream
Fluvial	Mudflow	Muddy river
Aeolian	Settling	Aeolian
Beach	River channel	Channel lag
Settling	Braided stream	Braided stream
Settling	Intermediate (between mudflow and river channel)	Muddy river
Settling	Mudflow	Mudflow
Settling	River channel/braided stream	Braided stream channel
Fluvial/settling	Braided stream	Braided stream
Fluvial/settling	Mudflow	Muddy river
Fluvial/beach	Braided stream	Braided stream lag
Settling/beach	Braided stream/river channel	Braided stream/river channel lag

In order to evaluate redness, a redness rating (Harvey *et al.* 1999) was calculated for each sedimentary unit using Munsell soil colours, where:

$$\text{Redness rating} = \text{hue x chroma/value} \qquad [4.16]$$

using numerical values of 10 for 10R hues down to numerical values of 1 for 10YR hues. A numerical value of 0 was given to 2.5Y, 5Y and Gley hues. Red colours could also have been inherited from locally present red Devonian or Triassic sandstones, or 5YR and 7.5YR hues be due to the presence of the mineral lepidocrite, common in poorly drained, fine-grained soils but not under permanently waterlogged conditions (Gale & Hoare 1991) or due to deposition in oxidative environments (Reineck & Singh 1973), so the rating was interpreted with caution.

Organic and calcium carbonate content derived from LOI have been used as an approximate index to infer climate-driven changes in minerogenic and organic sediment components. Mayle *et al.* (1999) were able to equate reduced organic and calcium carbonate content with climatic deterioration whilst attributing coincident peaks in organic and calcium carbonate production to well-developed, organic rich soil and lacustrine calcium carbonate production under conditions of climatic amelioration. By applying this to the Gordano Valley LOI results it was possible to infer periods of climatic deterioration and amelioration. However, low organic content may reflect periods of high productivity when significant amounts of organic material were lost through decomposition and, conversely, high amounts of organic matter may be preserved during periods of low productivity when decomposition rates are reduced (Mayle *et al.* 1999). These two scenarios could not be resolved without recourse to proxies such as beetles, not widely present in the Gordano Valley minerogenic sediments.

4.12.2.1 Pilot study redness rating

The redness rating for core GV was calculated using equation 4.16; results are shown in Table 4.19. Most sediments of core GV are brown or reddish brown and redness ratings range from 10.00 for GV1 to 0.67 for GV3; six units have redness ratings ≥5.00, suggesting potential pedogenesis in these units.

Table 4.19: Redness rating for core GV sediments

Unit	GV1	GV2	GV3	GV4	GV5	GV6	GV7	GV8	GV9	GV10	GV11
Redness rating	10.00	7.50	0.67	2.08	2.50	3.13	5.00	6.67	2.50	8.33	5.83

4.12.3 Use of modern analogues to determine processes and environments

It is common practice to interpret sediments with reference to modern analogues whose origin and environmental significance are well known. This is underpinned by the uniformitarian principle, that the present is the key to the past (Evans & Benn 2004) and is the approach adopted to guide the interpretation of both sedimentary and fossil evidence of the Gordano Valley archive. Modern analogues were used as guides, rather than as rigid templates because the range of past conditions, for instance during a glacial-interglacial cycle, may have no modern analogues (Evans & Benn 2004).

The basic assumption in this thesis has been that each sedimentary unit is a response to a definite set of environmental conditions (Krumbein 1941). However, sediments produced in a range of different environments may result in ambiguities further complicated by subsequent reworking (Lowe & Walker 1997, Evans & Benn 2004). Reconstruction of depositional processes and environments therefore relied on interpretation of the relationships between such processes and the observable sediment characteristics. Published accounts of modern environments that incorporate all the processes thought to have occurred within the Gordano Valley were used to provide reference points against which data were compared. This technique was used previously for the Gordano Valley by Mills (1984) who compared particle size parameters for sand with those of beach/dune sand.

Interpretation of depositional environments of the minerogenic sediments was supplemented by interpretation of fossil evidence. A uniformitarian approach was adopted, whereby factors influencing the abundance and environments of modern organisms enabled inferences to be made about the ecological context and provided a more detailed impression of environmental conditions than analysis of the sediments alone (Lowe & Walker 1997). This approach also depends on assemblages being interpreted with modern analogues (Birks & Birks 1980, Mauquoy & Van Geel 2007) and fossil remains identified to a sufficiently low taxonomic level in order that uniformitarian principles can be applied (Lowe & Walker 1997). The uniformitarian approach requires a number of assumptions to be made about present-day animal and plant populations which may not be valid. For example, it must be assumed that there is adequate understanding of modern plant and animal distributions; that modern analogues exist for past fossil assemblages, that the ecological affinities of fossils have not changed over time and that these are in equilibrium with their environmental controls. The extent to which these assumptions are met varies with type of fossil evidence and the nature of the assemblage, and all conditions are rarely satisfied (Lowe & Walker 1997). For example, terrestrial vegetation assemblages are not always in climatic equilibrium (Birks 1986).

A prerequisite for palaeoenvironmental reconstruction is an understanding of the processes that led to the formation of the fossil assemblages (Lowe & Walker 1997). Fossils are best preserved where deterioration is minimal. Calcium carbonate-rich waters of limestone regions such as the Gordano Valley influence the preservation of non-marine molluscs, which show a preference for chalk and limestone habitats (Lowe & Walker 1997) whereas pollen may be destroyed in soils with a high pH value (Andersen 1986).

Some fossils in the Gordano Valley were found *in situ*, whilst others had been transported and redeposited. This may have introduced bias into the eventual fossil assemblage through selective transport or differential destruction in which only the more robust species survive. Distinguishing derived fossils from primary fossils, important in palaeoenvironmental reconstruction (Lowe & Walker 1997), was achieved by careful recording of their stratigraphic context. This permitted the fossil assemblages, the majority of which have modern counterparts, to be used to reconstruct palaeoenvironmental conditions in the Gordano Valley. Where it was not possible to relate fossil assemblages directly to modern occurrences, abundances and environments, general relationships were inferred.

The limited volumes of material available for the pilot study resulted in small sample sizes which limited significance for any one line of analysis, but also indicated the potential for a multi-faceted approach in which, using the methodology discussed above, the amount of palaeoenvironmental information available from cores could be increased by using both biogenic and minerogenic material, providing mutually supportive data and producing a more secure environmental reconstruction (Lowe & Walker 1997). The results from applying these techniques to the minerogenic sediments of the Gordano Valley are presented in Chapters 5, 6 and 7. The next chapter deals with data from field sampling; the subsequent two chapters examine evidence from analysis of percussion cores.