# Laser granulometry of Holocene estuarine silts: effects of hydrogen peroxide treatment

J.R.L. Allen\* and D.M. Thornley

(Postgraduate Research Institute for Sedimentology, University of Reading, PO Box 227, Whiteknights, Reading RG6 6AB, UK)

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Abstract: The Holocene estuarine silts of the Severn Estuary Levels (southwest Britain) are representative of their kind in northwest Europe. They contain two broad types of plant material: particles codeposited with mineral grains from the estuarine water body, and extraneous debris (stems of indigenous prior plants; post depositional root matter) which is difficult to remove completely by physical means. Treatment with hydrogen peroxide before laser granulometry removes all plant material regardless of kind, drastically reduces values for the mean grain size and median size relative to untreated samples, but has little effect on the mode, except for a restricted group of bimodal-platykurtic, medium-coarse silts. It is concluded that, in the case of sediments of the general kind examined, no advantages acrue from the treatment of samples with hydrogen peroxide prior to analysis. Although a discrete rather than continuous variable, values of the mode obtained from untreated sediments are suggested to be acceptable for most purposes where a measure of central tendency is required.

Key words: Coasts, estuaries, grain-size analysis, laser granulometry, hydrogen peroxide, plant matter, silts, techniques, Holocene.

### Introduction

Sediment grain-size data gathered at high stratigraphical resolution are beginning to take a rightful place, alongside biological and geochemical proxies, in the environmental analysis of Holocene coastal, estuarine and lacustrine deposits (Laval et al., 1992; Plater, 1992; Borrego et al., 1995; Fenies and Faugères, 1998; Hewlett and Birnie, 1996; Last et al., 1998; Péndon et al., 1998; Bao et al., 1999; Spencer et al., 1998; Brew et al., 2000; Mellalieu et al., 2000; Psuty et al., 2000; Sidell et al., 2000; Evans et al., 2001; Lario et al., 2001; Allen and Haslett, 2002; Diz et al., 2002; Lavoie et al., 2002; Stupples, 2002). Gathered from estuarine and coastal sequences, for example, measurements of grain size are sensitive to such factors as the location of salt-marsh edges, relative water depth and sea-level rise on mudflats and salt marshes, and the degree of evolution of tidal creek networks (Allen, 1996; 2000; 2003; Allen and Haslett, 2002). These successions are characterized by alternations of peats and silts, although sands and gravels, representing environments ranging from coastal barriers to channel fills, are also commonly present and locally predominant. Insights secured through high-resolution textural studies all contribute towards an improved understanding

The minerogenic sediments that normally dominate these sequences are chiefly fine-grained and cohesive. Generally speaking, grain-size distributions are obtainable only after samples have been fully dispersed into a mixture of individual particles by a combination of physical and chemical means. As a means of analysing such dispersions, instruments using X-ray nephelometry or the scattering of laser or polarized light have largely replaced the older methods based on the pipette, hydrometer or Coulter Counter, on account of their greater rapidity, reproducibility and particle-size coverage. Whichever technique is employed, however, the handling and treatment of the samples strongly influences the outcomes of analysis. Long routine in soil survey (e.g., Avery and Bascomb, 1974; Klute, 1986), and favoured for work in modern estuaries (e.g. Kramer et al., 1994), the treatment of samples with the oxidizing agent hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is being increasingly adopted in Holocene environmental studies (e.g., Last et al., 1998; Spencer et al., 1998; Mellalieu et al., 2000; Psuty et al., 2000; Evans et al., 2001; Lavoie et al., 2002). The aim is to remove organic material of plant origin. However, the justification for, and outcomes of, this practice are far from clear. The evidence we give below strongly suggests that no advantages accrue from the practice.

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of Holocene environments and their development geographically and over time.

<sup>\*</sup>Author for correspondence (e-mail: j.r.l.allen@reading.ac.uk) In this note we report an examination of the effects of

hydrogen-peroxidetreatment on grain-size analyses obtained from Holocene estuarine deposits exposed at Redwick (National Grid Reference ST 4283), in the Welsh part of the Severn Estuary Levels, southwest Britain. Here an ongoing, high-resolution study is taking place into sea-level and environmental change throughout the Holocene, based on grain size, foraminifera assemblages and macroplant remains. Upward of 200 samples of fine-grained, minerogenic sediment have so far been examined from the sequence, of which 39 were judged to be 'contaminated' with extraneous plant matter which could not be fully removed by hand-picking prior to dispersion and grain-size analysis. The remaining samples, which we regarded as 'normal', contained either no visible extraneous plant material or such a small amount that it could not be fully removed by hand. We compared the contaminated samples before and after treatment with hydrogen peroxide solution, and carried out a similar test on a smaller but representative set of normal samples. The results suggests a more cautious approach to the use of hydrogen peroxide than has previously been evident.

### **Geological background**

The Holocene sequence in the Severn Estuary Levels (Allen, 2001) is 10-15 m thick and comprises mainly silts (mudflats, salt marshes) with several subordinate, rooted peats (highest intertidal/terrestrial marshes). In the main, the sequence accumulated continuously, but is erosively disrupted by ubiquitous tidal channel-forms and, locally, by diastems that record the retreat and subsequent rebuilding of mudflats and salt marshes. An ubiquitous, repeating stratigraphic element in the sequence is a couplet of silt and peat/root bed, recording a local fluctuation in relative water levels. Figure 1 shows the sources of organic matter of plant origin within silt in this couplet, in order to illustrate the difference between what we have called 'contaminated' and 'normal' samples. In terms of weight, the total organic matter in the Holocene silts of the Severn Estuary Levels is negligible, exceeding a small fraction of 1% ( $\leq$ 2%) only in the case of deposits formed within the last 100 years or so (e.g., Rae and Allen, 1993). The



Figure 1 The idealized sediment couplet of Holocene coastal and estuarine sequences, showing the sources, nature and location of plant material in the silt facies. The peats are of the rooted kind, and it is implicit that they consist of indigenous plant material.

sediments on which we report are not less than about 800 years old, and many date back several millennia.

Some of the organic matter present in the silts is part of the sediment deposited from the estuarine water body, in which it was held in suspension as discrete particles and as aggregates with mineral grains (floccules, faecal debris). Much of this matter, clearly visible in smear slides and on the surfaces of laminae when these are peeled back, consists of millimetre- and mainly submillimetre-scale fragments of macerated leaves and stems, together with occasional seeds. This kind of debris is likely to record chiefly the autumn dieback of halophytes that populated the salt marshes bordering the estuary, although there could also be contributions from riverside vegetation. Of lesser importance are detrital fragments of Holocene peat from beds exposed to erosion along the margin of the estuary and, except perhaps from the mid-nineteenth century, detrital grains of coal from the Carboniferous coalfields within the catchment (Allen, 1987; French, 1998). The evidence of smear slides shows that some organic matter of these kinds is present in all of the silts, regardless of their age and relative level within a couplet. It seems to be the only sort present in silts that are stratigraphically remote from peats. It is these silts which form the majority of our normal samples.

Extraneous plant material is of two types, both of which can lead to contaminated samples in the above sense (Figure 1). Neither sort relates to the hydraulic and geochemical factors that determined the properties of the silt as it existed in the water body and as it was deposited. The first type comprises the stems of indigenous plants, especially reeds, which had survived decay and wave attack, and so continued to project above the surface of a peat deposit as it underwent marine transgression and burial beneath silt. This material antedates the silt subsequently deposited among the stems. Postdating the silt are roots, rootlets and rhizomes which grew downward into the already-formed deposit from the base of the next peat.

### Laboratory methods

The silts we describe were collected as bulk spot samples of about 100 g moist weight, which were stored at 4°C. Our standard treatment for their analysis is detailed below. No attempt was made under this procedure to remove saline porewater, and the samples were not treated with hydrogen peroxide to remove organic matter or with hydrochloric acid to dissolve carbonate grains.

The samples were removed from their bags and broken up by hand. As much visible extraneous plant material as possible was removed at this stage using a spatula and scalpel. After thorough homogenization using a large spatula, the sample was spread out as a thin layer on a stiff plastic sheet with the aid of the same instrument. The tip of a small spatula was dug into this layer at 20-30 evenly scattered places, in order to build up on the spatula an unbiased subsample of 0.3-0.4 g weight. Transferring the subsample to a polythene watch-glass, a rubber pestle was used over a standardized period to disperse the silt into a few drops of aqueous sodium hexametaphosphate (3.3 wt %) buffered with sodium carbonate (0.7 wt %). At the end of this process as much as possible of any extraneous plant material that remained visible in the watch-glass was removed using tweezers or a needle. The dispersion was then diluted with 25 ml of the dispersant and flushed into the sample chamber of a Coulter LS 230 laser granulometer with PIDS (polarization intensity differential scattering). Using this combination of light-scattering techniques, highly reproducible, differential grain-size distributions, composed of up to 100 logarithmic classes, could be generated over the size range 0.04-2000 µm. Repeat analyses were made at intervals in order to ensure test reproducibility. Although the samples were saline, and small proportions of detrital, silt-sized carbonate particles were

present, the quantity of dispersant we used in each analysis was sufficient to maintain the full disperson of the particles.

Those silts which, after analysis with our standard procedure, remained contaminated were treated with hydrogen peroxide as follows. From each silt a subsample was procured as described above. This was transferred to a test tube with 8 ml of de-ionized water, to which 2 ml of 30% hydrogen peroxide was added. The mixture was allowed to digest for one week, when a further 1 ml of 30% hydrogen peroxide solution and 5 ml of de-ionized water were added. This was followed by immersion for 30 minutes in an ultrasonic bath. The bubbling reaction was found to have ceased after three to four weeks. Finally, the mixture of sediment and liquid was mixed with 25 ml of the dispersant and transferred to the granulometer. This treatment appeared to remove all reactable plant material. The samples became almost white, regardless of whether originally they were pale to mid-grey (contaminated silts) or pale greyish green (normal silts), and no particulate plant matter remained identifiable.

# Comparison of treated and standard samples

Figure 2(A–C) compares the grain-size distributions of three representative contaminated samples analysed, in each case, following our standard procedures and then after treatment with hydrogen peroxide (see also Table 1). Plotted below each pair of curves is a single curve representing the apparent percentage difference between the two.

The standard curves are typified by relatively long coarse tails, extending to as much as 600–700  $\mu$ m (coarse sand), marked by two or more minor modes. These features disappear after treatment with hydrogen peroxide. The coarse tails now plunge steeply to meet the grain-size axis at diameters of 30-80 µm (very coarse silt-very fine sand), that is, at particle sizes roughly an order of magnitude less than in the standard procedure. The fine tails are also long and, as indicated in Figure 2A, typically display one or more shoulder-like feature, which may also appear on the coarse tails. Treatment with hydrogen peroxide tends to emphasize these features on the fine tails (e.g., Figure 2B), and in some cases reveals shoulders where none were previously seen. In the case of the coarse tails, the effect of hydrogen-peroxide treatment is generally to either weaken or remove the shoulders apparent in some samples (e.g., Figure 2B). The difference graphs show that the overall effect of the treatment is to create an area between the two curves of comparatively large magnitude.

A similar comparison is made in Figure 2(D–F) for three representative normal samples (see also Table 1). The coarse tails obtained under the standard procedure are steep, cut the grain-size axis generally between 150 and 400  $\mu$ m (fine-medium sand), and rarely show more than one weak mode and a shoulder-like feature. Treatment with hydrogen peroxide markedly steepens the coarse tails, which typically intersect the grain-size axis at 40–90  $\mu$ m (very coarse silt-very fine sand), and may either weaken or remove any shoulders, in addition to removing minor modes (e.g., Figure 2D). However, as with the contaminated samples, the treatment tends to emphasize shoulder-like features on the long, fine tails (e.g., Figure 2E). Size for size, normal samples present much less area between the the two curves than contaminated ones.

Figure 3 compares values of central tendency – mean diameter and modal diameter (principal mode) – measured on our set of 39 contaminated samples. Hydrogen peroxide treatment drastically reduces the mean size (Figure 3A), the value after treatment falling by upwards of 65%. In contrast, values for the mode are hardly affected and remain clustered about the parity line (Figure 3B). The exceptions, with modes substantially reduced by treatment, are a group of eight contaminated samples with standard modal values of  $13-22 \ \mu m$  (medium-coarse silt). Samples in this range tend to yield standard distribution curves with either two closely spaced, main modes of about equal strength, or a broad, in some cases flat-topped, single mode. The effect of peroxide treatment in these cases is to either diminish or remove the coarser mode from a bimodal sample, or to sharpen the peak of a platykurtic one by emphasizing the finer part of the feature.

Six representative normal samples were also compared. Treatment with hydrogen peroxide has much less effect than in the case of contaminated silts The plot suggests that at sufficiently large mean values – probably in the very coarse silt–sand range – there could be little difference between treated and standard samples (Figure 3A). As with the contaminated samples, modal values are little affected, except as before in the case of bimodal or platykurtic silts (Figure 3B).

We do not give here our full results, but the effect of treatment with hydrogen peroxide on median diameters is similar in kind and magnitude to the effect on the mean. Table 1 gives comparative values for the samples illustrated as grain-size distributions (Figure 2).

#### **Discussion and conclusions**

The samples we describe come from a sequence (Allen, 2001) which is representative of many Holocene estuarine and coastal deposits in Britain (e.g., Waller, 1994; Long *et al.*, 1998; Sidell *et al.*, 2000) and the European mainland (e.g., Streif, 1972; Morzadec, 1974; Vos and van Heeringen, 1997). These sequences are normally dominated by alternation of peats and silts, although as noted other lithologies can also be represented.

Laser granulometry is an increasingly popular and available method for the grain-size analysis and comparison of silts and sandy silts that require dispersion. Its chief advantages are speed, precision and a wide grain-size coverage ( $\leq 2000 \,\mu$ m) and, when combined with PIDS in the Coulter LS 230 instrument, a much improved representation of the clay-sized fraction. A disadvantage in relation to sediments which include particles of plant origin (Figure 1) is that frequency is measured in terms of volume. Most detritus of this sort found in Holocene deposits has a cellular to microporous structure, and consists of material with a density comparable with that of water. Hence when not already aggregated in some way such debris tends to be laid down from a water body in the form of much larger particles than codeposited quartz and similar mineral grains. Extraneous organic matter - indigenous plant stems antedating silt deposition and postdepositional roots - also tends to be of large size, and cannot always be fully removed from samples by physical means. Consequently, an emphasis tends to fall on the coarse tails of laser-based differential grain-size distributions (Figure 2).

Grain-size analysis after hydrogen-peroxide treatment is superficially appealing for the characterization and comparison of finegrained sediments containing troublesome plant material. Using this method, all samples, regardless of the amount and origin of the organic matter contained therein, are reduced to a common basis. However, as the response of our normal samples emphasizes (Figure 2 D-F), the treatment removes all material of plant origin, including detritus that was a proper, codeposited part of the sediment. In the case of Holocene silts from the Severn Estuary Levels, values for the mean particle diameter, strongly influenced by percentiles remote from the centre, are drastically reduced by the treatment (Figure 3A). There is no systematic trend between the reduced mean values and those obtained without peroxide treatment. The median particle diameter, also sensitive to the extremities of distributions, is affected in a similar way (Table 1). In contrast, the mode (Figure 3B) is little influenced by treat-



Figure 2 Representative differential grain-size distributions for treated and untreated samples of Holocene silt from the Severn Estuary Levels (see also Table 1). (A–C) Silts contaminated with extraneous plant material. (D–F) Normal silts with no extraneous plant matter.

 Table 1
 Values of central tendency for the representative samples

 depicted in Figure 2 (values after treatment with hydrogen peroxide in brackets)

Sample	Mean diameter (µm)	Mode (µm)	Median (µm)
A	9.2 (5.2)	6.5 (5.4)	6.2 (5.4)
В	39.6 (11.7)	23.8 (28.7)	15.6 (7.3)
С	40.3 (16.4)	38.0 (38.0)	17.3 (10.3)
D	11.0 (7.9)	7.1 (6.5)	6.5 (4.9)
E	23.8 (12.1)	26.1 (28.7)	12.1 (7.7)
F	31.9 (19.5)	41.7 (45.8)	18.3 (13.4)

ment with hydrogen peroxide, except for a restricted set of bimodal or platykurtic silts, calling further into question the value of the procedure. Even when some extraneous plant material unavoidably survives to the point of analysis, values for the mode from untreated samples appear to offer the best basis for the establishment of textural trends and the broad comparison of sediments from different parts of a sequence or area. A minor disadvantage of the mode is its discreteness when derived from classified data such as laser granulometers deliver.

Laser granulometry is inappropriate for the characterization of peats, except perhaps those of a purely detrital nature (e.g., 'coffee-grounds' facies), but the question does arise as to when meaningful results can be secured in the general case of mixed organic-minerogenic fine sediments. The silts we describe have a relatively low organic content and contain extraneous plant material that is readily recognized as such in both the field and laboratory. Provided that codeposited and extraneous plant material are distinguishable and separable, and the codeposited debris is not too large, there seem to be no objections in principle to the application of the laser method to silts with a higher organic content than those typical of the Holocene in the Severn Estuary Levels.

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standard samples, grain size (µm)

Figure 3 The effects of treatment with hydrogen peroxide on (A) the mean diameter and (B) the mode of contaminated and normal silts from the Holocene of the Severn Estuary Levels.

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