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1 **Hydrogen peroxide treatment effects on the particle size distribution**

2 **of alluvial and marsh sediments**

3

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1   **Abstract**: Pretreatment of sediment with hydrogen peroxide to remove organic constituents and

2   aid deflocculation is a common component of particle size analyses of terrestrial and marine

3   sediments. This study quantitatively determined the effect of a range of treatment levels on

4   particle size distribution among four sediment types representing a range of mineral/organic

5   particle size distributions, organic content and particle characterization (charcoal or detrital plant

6   material). The hypothesis was that complete removal of organic particles would lead to improved

7   repeatability of results for a given sample and treatment level. Repeatability was assessed with a

8   coefficient of variance calculation and a comparison of particle size distribution patterns within

9   and across treatments. The effect of treatment levels on commonly used distribution descriptors

10   (e.g. texture ratios and measures of central tendency) were then examined for each sample.

11   Samples characterized primarily by detrital material responded most readily to treatment,

12   whereas charcoal-dominated samples required higher levels of treatment to achieve increased

13   repeatability and disappearance of large organic particles. Certain distribution descriptors such as

14   modal analysis were found to be more resilient to organic particle presence, although amplitude

15   of the organic distribution and the degree of overlap with the inorganic signal in some cases

16   obscured even this metric. Thus, final treatment recommendations are based on sample

17   characteristics and the types of distribution descriptors used in a study.

18

19   **Keywords**: laser granulometry, hydrogen peroxide, particle size analysis, particulate organic

20   material, sediment

21

1   **Introduction**

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3

4   Paleogeographic studies of alluvial sediments often include some consideration of particle size

5   distribution. Such analyses are now routinely brought to bear on questions involving geomorphic

6   and anthropogenic factors associated with sediment sourcing (Chen et al., 2000; Ghilardi et al.,

7   2008), fluvial processes governing these depositional environments (Visher, 1969; Orton and

8   Reading, 1993), and paleoclimate reconstruction (Tebbens *et al*., 1998; Allen and Haslett, 2006).

9   Advances in instrumentation now allow many more samples to be run at higher levels of

10   resolution and precision than was possible in the days of the pipette method and contemporaries

11   (Syvitski, 1991), increasing the feasibility of large-scale grain size analysis and the value of this

12   approach. Consequently, preparation and pretreatment of samples for such studies are now

13   required on a larger scale of production, which raises issues of procedural standardization within

14   and between studies.

15

16

17   Alluvial sediments commonly contain significant amounts of co-depositional and extraneous

18   organic matter that in most cases must be removed to analyze the inorganic particle distribution.

19   Extraneous organic matter in this study is considered to be any organic material that became

20   incorporated into the study sediments from local biotic sources, including plant litter and roots

21   which did not experience the transport regime that deposited the inorganic sediments. Co-

22   depositional organic matter was considered to be material transported hydraulically to the

23   sampling site along with the inorganic sediments of interest. Despite the common mode of entry

1 into the sedimentary record, co-depositional organic matter is commonly removed from the

2 inorganic fraction for particle size distribution analysis, as inorganic particles are denser than

3 organic particles, and uniformed particle density is a major assumption implicit to the

4 interpretation of depositing flow characteristics (Lewis, 1984).

5

6 While other strong oxidizing agents have been used to digest organics, isolation of the lithic

7 fraction is normally accomplished through treatment with 30% hydrogen peroxide (Robinson,

8 1922; Kunze, 1982; Lewis, 1984). The long history and widespread use of this treatment has lead

9 to a certain complacence that accompanies many such laboratory methods. Indeed, a survey of

10 current literature suggests that most studies where hydrogen peroxide was employed for organic

11 digestion did not report the specific protocol used, with only a few exceptions (Konert and

12 Vandenberghe, 1997). Furthermore, few recent studies have attempted to determine to what

13 extent different levels of treatment result in measurable differences in grain size distribution

14 (Matthews, 1991; Allen and Thornley, 2004). In fact, most protocols simply propose a

15 qualitative approach. Treatment with hydrogen peroxide is often prescribed, with or without

16 heating, until visible reaction (bubbling) has ceased and/or a desired lightening of color has

17 occurred.

18

19

20 However, qualitative assessment of organic digestion may be complicated by other reactions,

21 such as the rapid decomposition of hydrogen peroxide above 70 $^{\circ}$C and interactions with

22 inorganic constituents of sediments such as manganese oxide (Kunze, 1982; Lewis, 1984;

23 Percival, 1997). Both of these reactions can serve to obscure a definitive endpoint of organic

1 digestion. For example, the laboratory experience of the authors has shown that unheated

2 treatments left to react for days often reach an apparently inert state, only to begin liberating gas

3 again with the application of heat. Heated samples may continue to exhibit signs of reaction,

4 assumed to be the presence of organic carbon, with each additional hydrogen peroxide aliquot,

5 even after many treatments. In order to ensure comparability across and within studies, a

6 standardized method for organic removal with hydrogen peroxide that does not rely solely upon

7 such qualitative assessments of the reaction's conclusion should be developed.

8

9

10 This study quantitatively examines whether different levels of hydrogen peroxide treatment for

11 the removal of organic matter result in measurable differences in particle size distribution. To

12 this end, four levels of hydrogen peroxide treatment and an untreated control were tested on four

13 different alluvial sediments. Comparisons of grain size distributions produced from these

14 experiments were used to establish the level of treatment required to obtain the lithic particle

15 signature. Grain size distribution response to hydrogen peroxide treatment was then examined in

16 regard to the proportion of organic material present and the microscopic characterization of

17 coarse organics (≥ 150 μm sieve class), which classified the samples according to the most

18 prevalent form of organic particles. Conclusions based on these parameters lead to broad

19 treatment suggestions for a range of sediment types and study goals. To further inform these

20 recommendations, changes of internal texture ratios (clay:silt:sand) and modal position between

21 untreated and "fully treated" replicates were evaluated for sensitivity to the presence of organic

22 particles. In light of these findings, the choice of organic treatment and grain size distribution

23 metric for application to the sediment of interest can be more confidently approached.

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2

3 **Methods**

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6 *Test Sediments*

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9 Selection of sediment was conducted to establish a range of sediment texture ratios and organic

10 content levels that one may commonly encounter when sampling alluvium (Table 1, Fig. 1).

11 Initial selection was performed on the basis of qualitative assessments of these parameters, which

12 were later quantitatively refined by our laboratory techniques. Final sediment texture

13 characterization as reported here is based on grain size distributions obtained after treatment with

14 five heated 20ml aliquots of hydrogen peroxide, with one anomalous replicate excluded for

15 sample S4 (Cosumnes Riverbank). Four samples were tested and they all were obtained from

16 field sites on low-lying depositional landforms in California, U.S.A. All four sample sediments

17 were collected from approximately 10 to 20 cm depths from structureless sediments. All samples

18 possessed postdepositional roots with the exception of S4, Navarro River Floodplain. Three

19 samples were composed of only silt and clay from a lithic perspective, with ratios of about 1:1

20 silt to clay (S3: Suisun Marsh) and 2:1 (S1: Salinas River Lagoon; S4: Cosumnes Riverbank) and

21 bulk organic contents of 29.4, 8.4, 5.8 and 10.4 % by mass, respectively. One sample primarily

22 composed of sand was used, which contained about 3 times more sand than fines with a 4:1 silt

23 to clay ratio, and only 1.9 % organics (S2, Navarro River Floodplain).

1

2

3 All bulk samples were homogenized within plastic bags by hand due to their moist, clayey

4 nature, except for S2, which was carefully stirred on a plate to avoid grain size partitioning of

5 this sandy sample. Subsampling was conducted with truncated, plastic 2cc syringes to produce 5,

6 ¼ cc replicates for each treatment, which were extruded into 150 ml beakers for treatment with

7 hydrogen peroxide. The untreated control replicates were deposited directly into 20 ml

8 scintillation vials. No attempts were made to manually remove organic particles.

9

10

11 *Treatments*

12

13

14 Hydrogen peroxide (30% H_2O_2) was used for all treatments except the control (Table 2). In

15 treatment A, 20 ml of H_2O_2 was added to each beaker, then covered with watch glasses and

16 allowed to react for 24 hrs. To dilute the peroxide, 60 ml of de-ionized (DI) water was then

17 added and the samples were allowed to evaporate uncovered at ambient temperature until

18 reaching a volume of about 5 ml, a process that lasted up to a week for some samples.

19 Treatments B, C and D were all heated applications of H_2O_2 in 20 ml aliquots with one, two and

20 five applications respectively. These treatments were conducted under watch glasses on hotplates

21 at levels adjusted to produce solution temperatures of 70 ^{o}C. When bubbling ceased for one H_2O_2

22 application, the watch glass was removed to allow the solution to evaporate more readily to 5 ml,

23 otherwise the solution would remain under the watch glass until reaching the aforementioned

1 volume. Upon reaching the reduced volume the next aliquot of peroxide was added and the

2 process of reacting under the watch glass followed by evaporation repeated until the final aliquot

3 was processed to the reduced volume. At this stage 60 ml of DI water was added to dilute the

4 remaining H_2O_2 in solution and evaporated to ~5 ml.

5

6

7 The sediment and supernatant from completed treatments and the control, untreated subsamples

8 were transferred to 20 ml scintillation vials with 1.00 g of Sodium Metaphosphate (SMP) as a

9 dispersant. These vials were adjusted with DI water to a total volume of ~20 ml to create a

10 solution of approximately 5% SMP. Replicates were mixed momentarily on a test tube vortex to

11 aid initial dissolution of SMP, followed by agitation on a mechanical vibrator for 24 hours.

12

13

14 *Grain Size Analysis*

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17 Particle size analysis was performed with a Beckman-Coulter LS 230 (Beckman Coulter Inc.,

18 Fullterton, CA, USA) laser diffraction type granulometer with polarization intensity differential

19 scattering (PIDS). Each replicate was flushed through the machine in three 90 second runs, while

20 the reservoir was sonicated for 60 s before and during the entirety of each run. The average of

21 the three runs was then used as the grain size distribution for the replicate.

22

23

1   Our initial preference settings lead to volumetric grain size distributions reported with a

2   sensitivity range of 0.375 to 2000 μm in 94 bins. However, due to operator error in setting run

3   preferences, a sensitivity range of 0.0399 to 2000 μm was used for sample treatments D and F,

4   reporting an additional 23 finer bins. An incidental comparison of the two settings was possible

5   for a sample outside of this study, as replicates were run each way. Inclusion of the additional

6   fine bins raised the aggregate percent clay reported, but otherwise did not seem to affect the

7   distribution of the coarser materials' grain size spectra. Thus, for comparisons between

8   treatments, the additional fine bins were removed from D and F spectra and concomitant

9   modification of the remaining distribution by a multiplier to achieve a summed volume of 100%

10   was performed. Multipliers were also used on occasion for comparisons between portions of

11   grain size distributions to eliminate the effect of certain parts of the distribution, as these data

12   were in the form of percent volume. To compare portions of distributions while discounting

13   others, one must correct the remaining array of percent volumes with a multiplier calculated as

14                               $$M = (100)/(100-D)$$ (1)

15   where M is the multiplier and D is the percent volume that has been remove from the population.

16

17

18   *Data Analysis*

19

20

21   The resultant grain size distributions were examined under the hypothesis that effective treatment

22   would produce the same findings between replicates within a given treatment and across further,

23   more extensive treatments. Although the distribution of organic particles in a sample may be

1 uniform across subsamples if homogenization and subsample size were successful and

2 appropriate respectively, it is expected that the process of organic matter digestion with hydrogen

3 peroxide does not progress uniformly. Therefore, incomplete digestion of organic matter was

4 hypothesized to produce a higher level of variance across replicates for a given sample treatment

5 than those sample treatments where all organic matter was removed. Furthermore, invariance of

6 grain size distribution with increased levels of treatment should also indicate complete removal

7 of organics.

8

9

10 Assessment of repeatability of the results was approached by 1) comparing grain size frequency

11 distributions at the replicate level within treatments, 2) as average sample treatment distributions

12 for inter-treatment comparison and then 3) cross referencing these results with the mean

13 coefficient of variation value for each sample treatment. By sample treatment, reference is being

14 made to the group of replicates that went through a given treatment for a given sample, for

15 example sample S1 treatment D.

16

17

18 The coefficient of variation (v) is a non-dimensional measure of variance that is scaled to the

19 mean value, and is defined as

20 $$v = \sigma/\mu \qquad (2)$$

21 where σ is the standard deviation of the samples and μ is the mean. For a given sample treatment

22 the coefficient of variation was calculated for each grain size bin across replicates. The v values

23 obtained for all grain size bins within the distribution were then averaged to produce a

1   representation of variation (V_{avg}) for the entire sample treatment using the equation

2   $$V_{avg} = \sum \nu/n \qquad (3)$$

3   where n is the number of individual coefficients of variation produced. V_{avg} values were also

4   calculated for the size classes 0.375-1.83 μm (denoted as V_{clay}) to compare the effect of different

5   treatments on clay size particles.

6

7

8   This study does not establish a maximum V value that is used directly to identify successful

9   organic digestion. Rather, V is used comparatively between sample treatments as an indicator of

10   effective organic removal, with lower values of V indicating lower levels of variance between

11   replicates for a given treatment. On the other hand, distribution comparisons between replicates

12   and treatment averages are used to identify the lithic and organic particle size signatures through

13   the disappearance of organic distributions with treatment. The identified lithic signature is then

14   used to differentiate between replicates that are near complete organic removal and those that

15   contain residual organic distributions. The lithic distributions, modified using Eq. (1) to represent

16   a complete distribution, are also compared to their respective control distributions to assess the

17   overlap of these two sedimentary constituents.

18

19

20   *Organic Content, Particle Size and Characterization*

21

22

23   Characterization of organic particle size for each sample was approached via two methods. First,

1 the average grain size distribution of the untreated replicates was compared to the average lithic

2 grain size distribution obtained after effective treatment and the difference plotted. Second, 2.5

3 cc subsamples were dispersed in 5% SMP for 24 hrs of agitation and then washed through nested

4 850, 600, 300 and 150 μm sieves. The contents of each sieve were transferred to dissection

5 dishes where the organic particles were characterized qualitatively with the aid of a dissection

6 microscope under magnifications of 10 to 40 times.

7

8

9 Organic content was approximated through the loss-on-ignition method. Three, 1.2-cc

10 subsamples (1/4 teaspoon) were collected from each homogenized alluvium and then dried for

11 24 hours at 105 °C, weighed, combusted for four hours at 550 °C in a laboratory furnace, and re-

12 weighed. Calculations of organic content are reported as percent of dry weight.

13

14

15 **Results**

16

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18 Large changes, primarily reduction of the coarser portion of the grain size distributions, were

19 evident with hydrogen peroxide treatment for S1, S3 and S4 in comparison to control samples.

20 Examination of sample treatments at the replicate level showed repeated post treatment patterns

21 of complete coarse material loss of a constant range (by sample) for S1, S3 and S4.   Sample

22 distributions produced their lowest V values with treatments A and D in general, as these

23 treatments generally produced fewer replicates with persistent coarse distributions.

1

2

3   *Internal Texture Ratios, Mean Values and Organic Content*

4

5

6   Sediment response to treatments generally resulted in large changes in texture ratios and mean

7   values in sediments with higher levels of organic content (Fig. 1, Table 1). S2 experienced very

8   little change between all treatments and the control, while S3 shifted from primarily sand sized

9   particles to a clayey silt ratio that was very similar between all treatments. S1 changed from a

10   clayey, sandy silt to a clayey silt that varied more in clay:silt ratio between treatments, although

11   treatments A and D were very similar. The sand fraction in S4 was present in the control and

12   across all treatments, although it was much reduced in treatments C and D.

13

14

15   *S1- Salinas River Lagoon*

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17

18   The grain size frequency distribution for the Salinas River Lagoon sample showed a persistent

19   bimodal distribution in the clay to medium silt range across all treatments with hydrogen

20   peroxide (Fig. 2a). The primary mode varied in placement from 2.01-3.20 μm, while the

21   secondary, more leptokurtic peak showed up at 15.65 μm for all treatments and 17.18 μm for the

22   control (Table 3). Deviations from this consistent pattern appeared in replicates from the

23   untreated control, treatment B and treatment C (Fig. 3). The anomalous replicates from the

1   control and Treatment C contained multi or single modal, negatively (coarse) skewed

2   distributions of coarse sand size particles up to a maximum of about 1mm. A single anomalous

3   replicate from treatment B was the only replicate for all treatments of this sample which lacked

4   the bimodal silt distribution, exhibiting a strongly leptokurtic clay peak followed by a secondary

5   fine silt peak. This replicate shared no distributive characteristics in common with others from

6   this sample, and as such was discarded under suspicions of laboratory error. Comparison of V_{avg}

7   values showed the largest values calculated for the control and treatment C, reflecting the

8   presence of the coarse particle bearing replicates (Table 3). Treatment A produced the lowest

9   value of V_{avg} (0.10) in contrast to the heated treatments B and D which had values nearly twice

10 as large.

11

12

13 Examination of the Salinas sample with a dissection microscope after dispersion and sieving

14 revealed organic particles dominated by root pieces from all sieve sizes used; many of those

15 caught by the 850 μm sieve had lengths in excess of 1 mm. Experience during sub-sampling

16 indicated that the longest root pieces often did not make it into ¼ cc subsamples, as evidenced by

17 the fact that these particles showed up in only 2 of 5 control replicates. Plotting the difference in

18 grain size distribution between treatment D and the control revealed a poly modal range of

19 particles from 20.71 to 1142.8 μm with a major mode at 24 μm (Fig. 4a).

20

21

22 Amplification of the control distribution to bring the total percent volume up to 100% for the

23 section that overlaps with the treatment D distribution allowed for a comparison of the control

1 with what we will henceforth refer to as the fully treated or "lithic range" (Fig. 5a). The

2 distributions over this range were remarkably similar. The control shared the same general curve

3 shape with treatment D, but the primary mode was slightly depressed in intensity and both mode

4 placements shifted one grain size bin coarser, while the notch between the two modes was softer

5 than for the treated sample.

6

7

8 *S2 - Navarro River Floodplain*

9

10

11 Distribution analysis of the Navarro River Floodplain showed a unimodal, leptokurtic

12 distribution negatively skewed toward medium sand with a long platykurtic tail extending

13 through fine sand, silt and clay sizes (Fig. 2b). The mode was remarkably consistent at 339.9 μm

14 for 23 of 25 replicates across all treatments (Table 3, Fig. 3). The control exhibited a small

15 secondary peak (~ 2 orders of magnitude lower than the major mode) at 1254.4 μm for two

16 replicates, which is also evident in a Treatment C replicate and one from treatment D. Heated

17 treatments of these floodplain sediments produced larger average coefficient of variance values

18 than that calculated for the control, while the unheated treatment resulted in a value about half

19 that of the control (Table 4). Much of this variance again arose as a result of replicates that

20 contained small amounts of the larger particles that did not show up on the majority of

21 distributions.

22

23

1   The grain size frequency diagram of the average distribution obtained for each treatment

2   revealed two major zones of variability between treatments: 1) medium silt to fine sand and 2)

3   the major modal sand peak (Fig. 2b). Changes in total frequency within these two zones were

4   inversely related between treatments. The strength of the major mode generally decreased

5   through the progression of treatments from the control to treatment A, followed by the heated

6   treatments (B, C, D), while the silt/fine-sand region increased in frequency throughout this

7   progression.

8

9

10 Microscopic characterization revealed that the organic particle assemblage was primarily

11 composed of charcoal. Only a few pieces of plant debris showed up on the 600 and 300 μm

12 sieves. Charcoal abundance increased between the 800, 600 and 300 μm sieves, and then

13 decreased on the 150 μm sieve relative to quartz grains present. This assessment agreed with the

14 difference between the average control distribution and the treatment that differed most from it

15 (treatment D). The plot of this difference showed a range of particle sizes from 213 to 1821 μm

16 with a lepidokuritic mode at 373.13 μm, similar in shape to the grain size distribution obtained

17 for all treatments of this sample (Fig. 4b).

18

19

20 *S3 - Suisun Marsh*

21

22

23 The Suisun Marsh sample showed large difference in grain size distribution between the control

1 and all treatments (Fig. 2c). The control distribution was polymodal, bearing a 449.66 μm

2 primary mode, negatively skewed with a platykurtic shoulder in the medium silt to fine sand

3 range and has an extensive fine tail (Table 3). Treated subsamples had a broad major modality at

4 2.2072 μm and a secondary peak at 15.651 μm. Only two replicates (both from treatment D)

5 varied slightly from the major mode, while the minor mode showed more variance in size and

6 placement within and between treatments (Fig.3c). Average treatment mode placement spanned

7 three grain size bins from 13.00 to 15.65 μm and strengths of 1.118 to 1.797 percent volume.

8

9

10 A high level of repeatability (V_{avg} = 0.10) was found for the control replicates (Table 3). In fact,

11 there was a high level of repeatability within and between all peroxide treatments, in contrast to

12 the large difference in grain size distribution between treated samples and the control (Table 3,

13 Fig. 2c & 3). The unheated treatment had a very low V_{avg} (0.03), while heated treatments

14 experienced higher values with increased treatment.

15

16

17 Organic particles were abundant for all sieve classes. Microscopic characterization revealed a

18 suite of plant detritus dominated organics composed primarily of stem pieces with only minor

19 amounts of root pieces and seeds and very little charcoal across all sieve sizes. The difference

20 plot between the control and treatment D showed a poly modal distribution of medium silt to

21 sand sized material, ranging from 15.7-1821.9 μm with a primary mode at 449.66 μm (Fig. 4c).

22 Comparison of overlapping portions of the distributions for treatment D and the control

23 (corrected for the removed coarse section) showed large differences in the lithic range, as the two

1   distributions did not resemble each other (Fig. 5b).

2

3

4   *S4 – Cosumnes Riverbank*

5

6

7   All Cosumnes Riverbank treatments and the control shared the same polymodal characteristics

8   for the fine portion of the grain size distribution (Fig. 2d, 3). A major, leptokuric peak at 17.181

9   μm was flanked by a platykurtic, shoulder- like minor mode around 4.24 to 5.61 μm and a notch

10   at 27.4 μm followed by a small peak 30.1-33.0 μm peak (Table 3). More variation was visible in

11   the coarse portion of the spectra across treatments, although there were resilient peaks in this

12   region for the control around 73-80 μm and 213-234 μm (Fig 3). This coherence between

13   distributions led to a lower V_{avg} for the control than any treatment; the lowest treatment value

14   was for D at nearly twice that of the control (Table 3). Across treatments a reduction in the

15   number of replicates that exhibited the presence of any sand size particles was apparent as one

16   progressed from the control (4 replicates) to treatments A and B (three replicates each), and

17   finally the more extensive heated treatments C and D (one replicate each) (Fig 3).

18

19

20   The bulk of organic particles produced by sieving was charcoal, with some plant debris present

21   in the form of stem and root pieces. Organic material showed up in low amounts relative to S1

22   and S3 on each sieve. The grain size spectra of sand sized particles were heavily affected by

23   peroxide treatment for this sample. Removal of the one replicate of treatment D that continued to

1   display particles above 43.667 μm was performed for the calculation of the average lithic

2   distribution as it was assumed to bear organics. The plot of the difference in grain size

3   distribution between the control and treatment D showed a broad, multimodal distribution of

4   medium silt to medium sand size particles ranging from 33 to 450 um (Fig 4d). The modified

5   control and Treatment D lithic range comparison revealed similar distributions, although the

6   control exhibited a depressed mode and elevated % volume on the coarse end of the distribution

7   relative to treatment D (Fig. 5c).

8

9

10   **Discussion**

11

12

13   Reduction of the coarse range of material with H_2O_2 treatment in S1, S3 and S4 indicates that the

14   abundance of larger particle sizes in these sediments was due to the presence of organics. This

15   finding is supported by the observation of distinct organic particles in the sand sized sieve

16   fractions with microscopy. Changes in grain size distribution due to the removal of organics are

17   also noticeable in S2, though muted due to the lower amount of organics in this sample and the

18   overlapping distribution of the inorganic and primarily co-depositional charcoal particles.

19

20

21   The major modes of all samples, except S3, which also contained the highest level of organics

22   (29.3%), were very resilient to organic particle presence. Although control replicates from these

23   samples also deviated from the mineralogic major mode, the concomitant average distributions

1   either agreed with this mode (S2 and S4) or deviated from it by only one grain size bin (S1).

2   Examination of the control distribution ranges that overlap with treatment D distributions in S1,

3   S3 and S4 shows salient characteristics in S1 and S4 that do not change much with treatment,

4   while sample S3 fines are heavily influenced by organic particles in the control (Fig. 5).

5

6

7   The four samples in this study therefore exemplify three different results of organic interference

8   with inorganic particle size determination. In the cases of S1 and S4, the inorganic and organic

9   distributions are disparate to a degree in which the organic distribution primarily has a

10   dampening effect due to the occupation of % volume; reducing the intensity of the inorganic

11   distribution but causing little distortion in its morphology. For such distributions, measurements

12   of central tendency that rely upon summed distribution calculations (mean, median) and internal

13   texture ratios are highly skewed by the presence of organics, while modal analysis may be little

14   affected. The overlap of organic and inorganic particle size distribution in S2 and S3 bore very

15   different results. Low amount of organics present and their nearly identical distribution to that of

16   the inorganic fraction in S2 lead to very little change in texture ratios and central tendency

17   metrics. Conversely, in S3 the overlap of the inorganic clayey silt distribution with the fine tail of

18   the primarily coarse organic distribution served to blot out all of the inorganic characteristics,

19   destroying any chance to describe this fraction without pretreatment.

20

21

22   Thus, we recommend that all analyses utilizing total distribution metrics such as textural ratios or

23   mean grain size for alluvial sediments take into account sensitivity to the effect of organic

1   particle presence, even at more moderate organic levels such as those found in the S1 and S4

2   samples (8.35 and 5.80 % respectively). Moreover, modal analyses are not significantly affected

3   by the presence of moderate amounts of organics only in cases where organic and inorganic

4   distributions either do not overlap significantly or overlap almost precisely. Therefore, even

5   when utilizing modal characterization of grain size distribution one must be cautious in the

6   presence of organics. Although analyses focusing solely on modal trends in terms of grain size

7   distribution may simply elect to deflocculate samples rather than pursue treatment for organic

8   removal, which has been suggested for clayey silts with little organic content (Allen and

9   Thornley, 2004), we recommend that hydrogen peroxide treatment should be employed for

10   samples with moderate to large amounts of organics.

11

12

13   Sample response to H_2O_2 treatment appears to be contingent upon organic particle size and

14   characterization rather the proportion of organic to lithic particles. Those samples with organic

15   assemblages comprised primarily of plant roots and detritus at moderate and high organic levels

16   (S1 and S3) responded well to all forms of peroxide treatment, with the exception of replicates

17   which are assumed to have contained large residual root fragments. In contrast, samples

18   characterized by charcoal were more recalcitrant in terms of organic digestion. Charcoal pieces

19   in excess of 800 μm were present in very low amounts in S2, and may have persisted when

20   present across all treatments, although the small subsamples required for laser diffraction

21   analysis may have also only occasionally captured the coarsest mineral grains present. Coarse

22   charcoal was present in S4 at higher levels than in S2 and also showed resilience to peroxide

23   digestion, with more complete removal arising from extensive heated treatments.

1

2

3   The large size of the organic particles in S1 and S4 may have lead to the inability to homogenize

4   the organics in these samples in regard to our subsampling methods, as evidenced by the lack of

5   these distributions in several control replicates. Homogenization/sub-sampling of the organic

6   constituents was more successful for S3 than all other samples as reflected in the coefficient of

7   variation value for this sample treatment. In such cases where very large particles contribute

8   much of the organic distribution interference, the time and effort necessary to conduct manual

9   removal is probably warranted.

10

11

12   Yet, there may be other options for large organic particle removal. A sample outside of this study

13   was collected near S4 and bore nearly the same lithic distribution and organic characterization

14   (charcoal) with almost twice as much organic content (>10%). However, this copious coarse

15   fraction did not show up on particle size distributions even without treatment. The high occlusion

16   produced by fine lithics and humic/fulvic acids required a large amount of sample dilution within

17   the LS-230 sample chamber before running the sample. It seems that dilution through successive

18   bleeding/filling cycles in the sample chamber may provide a method for drawing off low-density

19   organic material.

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22   In light of the sensitivity of some sediments to degradation due to H_2O_2 exposure, particularly

23   weathered micas (Drosdoff, 1938), the clay fraction of sample replicates were examined for this

1   effect. Assuming that the breakdown process would not be uniform, one would expect to find

2   increased variability with increased levels of treatment. Comparison of V_{clay} between treatments

3   for each sample did not indicate a single treatment that consistently produces the lowest values,

4   nor are there indications of an increase in V_{clay} with increased levels of heated treatment (Table

5   3). The control displayed the largest values for S1 and S3, but had the lowest values for S2.

6   Taking only H_2O_2 treatments into consideration, treatment A resulted in the lowest V_{clay} for S1

7   and S2, however the second lowest value was reported from treatment D for both samples. Also,

8   V_{clay} values decreased with increased heated treatment (B-C-D) in both S2 and S4. Thus, this

9   study found no evidence for inorganic particle degradation in regard to alterations in grain size

10 distributions. However, further studies that include the full range of clay size analysis available

11 to the LS-230 would tackle this issue in more depth.

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13

14 **Conclusions**

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17 A uniform approach to peroxide treatment that yields complete organic removal is desirable for

18 comparisons between samples that are meant to reflect differences in parameters other than

19 sample pretreatment. When a large range of organic constituents may be encountered, down the

20 length of a sediment core for example, the necessary uniform treatment must be tailored toward

21 the most recalcitrant of samples. Unless in-depth characterization of organic particles is

22 conducted before grain size analysis, one should assume the presence of both large plant material

23 and charcoal. Based on the results from this study, textural ratios and measures of the central

1   tendency of particle size distributions, including modal analysis, can be heavily impacted by the

2   presence of organic particles. Thus, a protocol for the removal of organic constituents requires

3   the application of long duration, unheated dispersions in 30% H_2O_2 for a standard amount of

4   time, followed by a fixed amount of further heated aliquots in combination with the removal of

5   large particles by manual methods.

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8   **Acknowledgements**

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19   **References**

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Table 1. Sediment samples

Sample	Provinence	Organics (% mass)*	character
S1	Salinas River Lagoon	8.4	roots
S2	Navarro River Floodplain	1.9	charcoal
S3	Suisun Marsh	29.4	stems
S4	Consumnes Riverbank	5.8	charcoal

*Estimate from loss on ignition

Table 2. Pre-treatment for grain size analysis

Treatment	Method
A	20 ml unheated H_2O_2
B	1 X 20 ml heated H_2O_2
C	2 X 20 ml heated H_2O_2
D	5 X 20 ml heated H_2O_2
F	no treatment

Table 3. Mean, average primary mode and modal intensity for all sample treatments. Treatment D $_{mod.}$ has been modified to remove grain size detectors below 0.375 µm.

Sample	Mean (um)	Intensity (% vol)	Mode (µm)
S1F	42.11	2.41	3.21
S1A	6.02	3.15	2.92
S1B	5.14	4.20	2.01
S1C	61.12	2.73	3.21
S1D	5.82	3.04	2.92
S1D$_{mod.}$		3.19	2.92
S2F	276.78	7.02	339.9
S2A	262.23	6.63	339.9
S2B	250.14	6.25	339.9
S2C	253.52	6.33	339.9
S2D	244.46	6.14	339.9
S2D$_{mod.}$		6.18	339.9
S3F	368.03	2.63	449.7
S3A	4.00	3.92	2.21
S3B	3.73	3.99	2.21
S3C	3.87	3.96	2.21
S3D	3.36	3.75	2.21
S3D$_{mod.}$		4.07	2.21
S4F	33.10	2.34	17.18
S4A	40.55	2.65	17.18
S4B	112.43	2.62	17.18
S4C	15.03	3.46	17.18
S4D	12.20	3.34	17.18
S4D$_{mod.}$		3.65	17.18

Figure legends.

Figure 1. Internal texture ratios for averaged sample treatments. Sample number shows sample location (1 = Salinas River Lagoon, 2 = Navarro River floodplain, 3 = Suisun Marsh, 4 = Consumnes River floodplain), letter indicates level of treatment (F = no treatment, A = 20 ml unheated H_2O_2, B = 20 ml heated H_2O_2, C = 2 x 20 ml heated H_2O_2, D = 5 x 20 ml heated H_2O_2).

Figure 2. Average grain size distribution for each treatment. Sample number shows sample location (1 = Salinas River Lagoon, 2 = Navarro River floodplain, 3 = Suisun Marsh, 4 = Consumnes River floodplain), letter indicates level of treatment (F = no treatment, A = 20 ml unheated H_2O_2, B = 20 ml heated H_2O_2, C = 2 x 20 ml heated H_2O_2, D = 5 x 20 ml heated H_2O_2).

Figure 3. Grain size distribution of all sample treatment replicates.

Figure 4. Difference in grain size distribution between the control and treatment with five aliquots of heated peroxide.

Figure 5. The average grain size distribution over the lithic range of samples 1,3 and 4 subjected to treatment D plotted with each respective control rescaled to 100%.
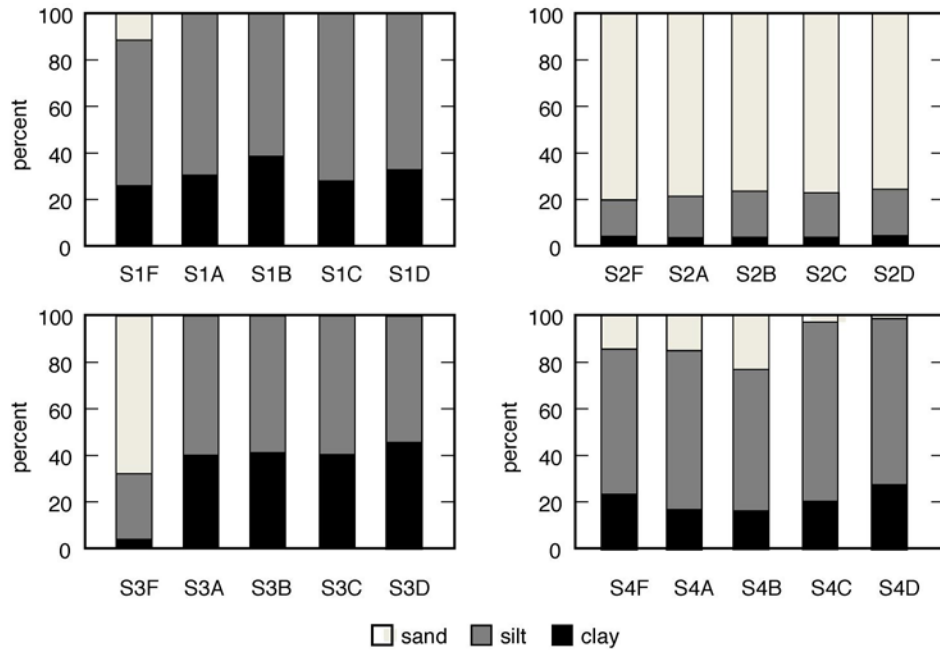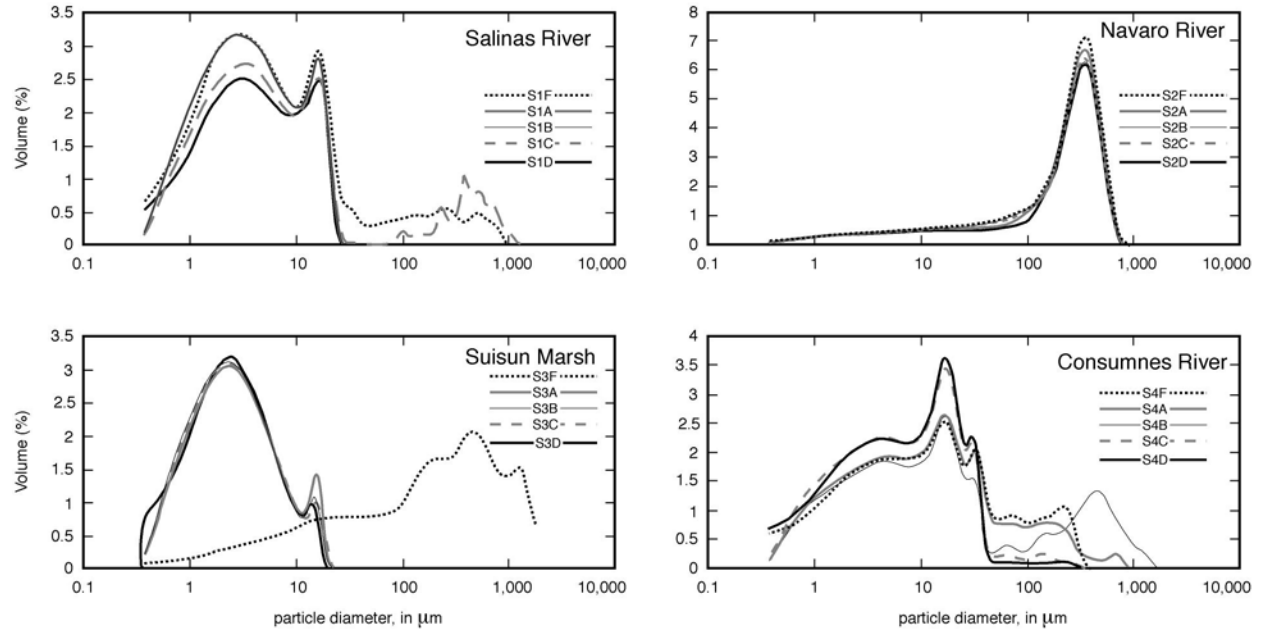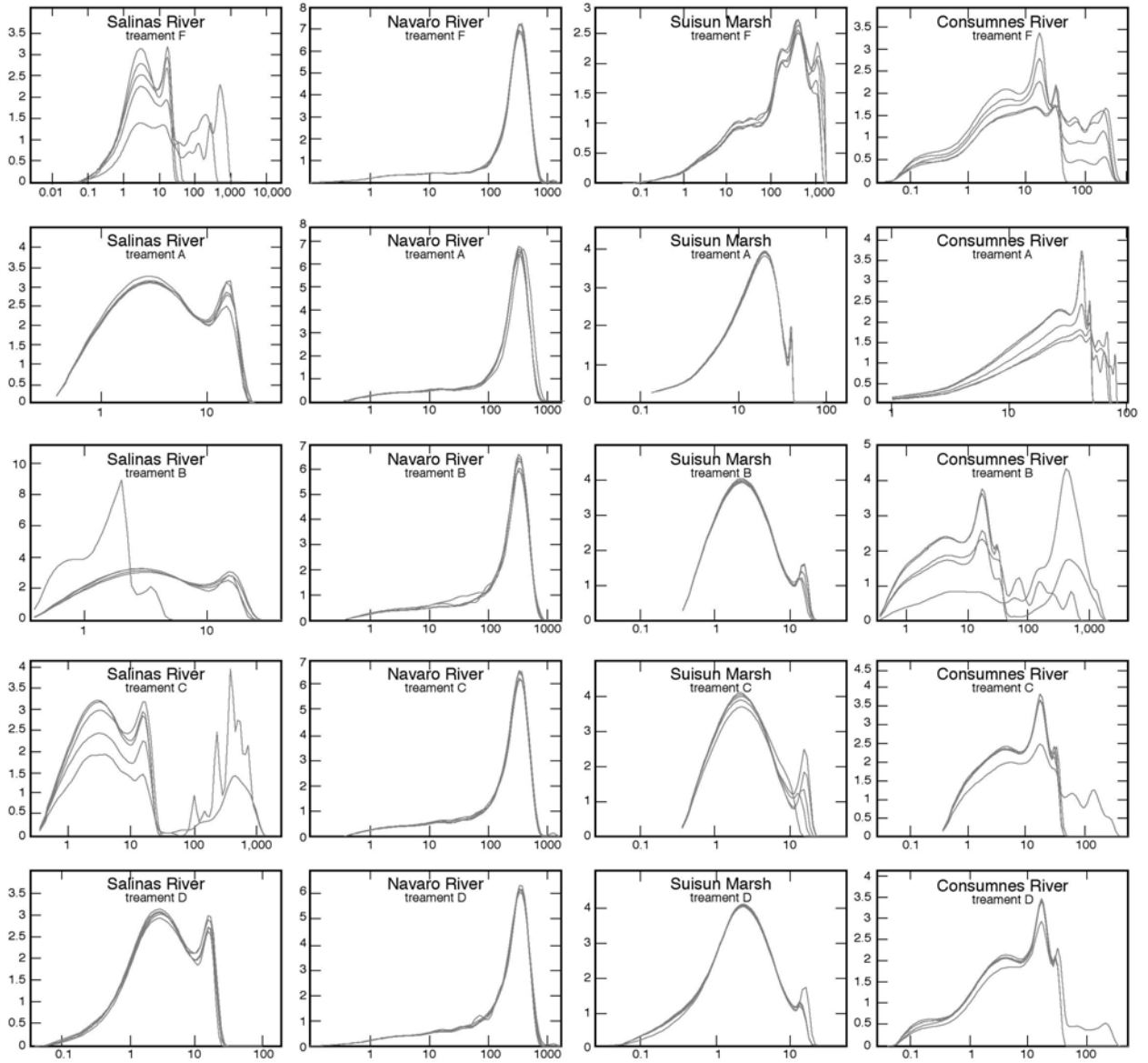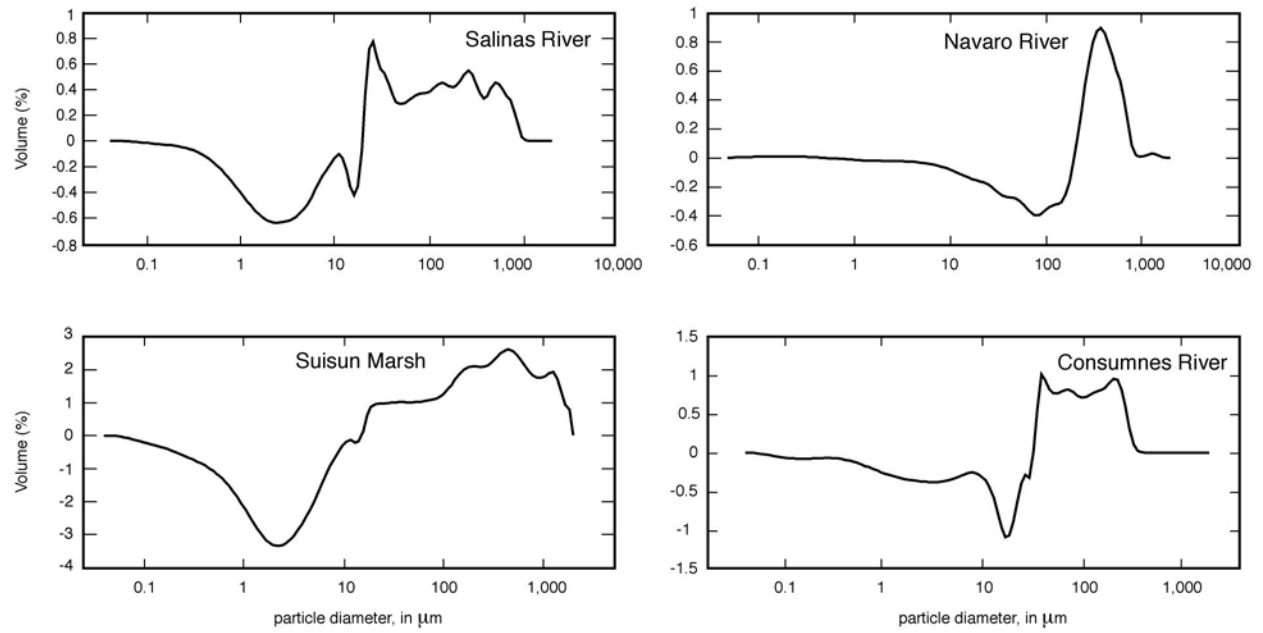
Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.