

1 **Compositional data analysis of Holocene sediments from the West Bengal**
2 **Sundarbans, India: geochemical proxies for grain-size variability in a delta**
3 **environment**

4

5 R.P. Flood^{1,2*}, M.R. Bloemsa³, G.J. Weltje⁴, S.M. O'Rourke⁵, I.D. Barr¹, J.N. Turner⁶,
6 J.D. Orford¹

7 ¹School of Geography, Archaeology, and Palaeoecology, Queen's University Belfast, BT7
8 1NN, Northern Ireland, UK

9 ²Present address: School of Natural Sciences, Trinity College Dublin, Dublin 2, Republic
10 of Ireland

11 ³Tata Steel - Netherlands Main Office, Postbus 10000, 1970 CA IJmuiden, The Netherlands

12 ⁴Department of Earth and Environmental Sciences, Geology Division, University of
13 Leuven, Celestijnenlaan 200E, 3001 Leuven-Heverlee, Belgium

14 ⁵School of Biosystems Engineering, University College Dublin, Belfield, Dublin 4,
15 Republic of Ireland

16 ⁶School of Geography & UCD Earth Institute, University College Dublin, Belfield, Dublin
17 4, Republic of Ireland

18

19 *Corresponding author. Email Address: rflood02@qub.ac.uk Phone number:
20 +442890973929

21

22 Keywords: XRF; core-scanner; compositional data; Ganges-Brahmaputra delta;
23 calibration; geochemistry; grain-size.

24

25 **ABSTRACT**

26 This paper is part of a special issue of Applied Geochemistry focusing on reliable
27 applications of compositional multivariate statistical methods. This study outlines the
28 application of compositional data analysis (CoDa) to calibration of geochemical data from
29 a set of Holocene sedimentary cores from the Ganges-Brahmaputra (G-B) delta. Over the
30 last two decades, understanding near-continuous records of sedimentary sequences has
31 required the use of core-scanning X-ray fluorescence (XRF) spectrometry, for both
32 terrestrial and marine sedimentary sequences. Initial XRF data are generally unusable in
33 'raw-format', requiring data processing in order to remove instrument bias, as well as
34 informed sequence interpretation. The applicability of these conventional calibration
35 equations to core-scanning XRF data are further limited by the constraints posed by
36 unknown measurement geometry and specimen homogeneity, as well as matrix effects.
37 Log-ratio based calibration schemes have been developed and applied to clastic
38 sedimentary sequences focusing mainly on energy dispersive-XRF (ED-XRF) core-
39 scanning. This study has applied high resolution core-scanning XRF to Holocene
40 sedimentary sequences from the tidal-dominated Indian Sundarbans, (Ganges-
41 Brahmaputra delta plain). The Log-Ratio Calibration Equation (LRCE) was applied to a
42 sub-set of core-scan and conventional ED-XRF data to quantify elemental composition.
43 This provides a robust calibration scheme using reduced major axis regression of log-ratio
44 transformed geochemical data. The application of these techniques to Holocene
45 sedimentary data offers an improved methodological framework for unravelling Holocene
46 sedimentation patterns.

47

48 **1. GEOCHEMISTRY OF HOLOCENE SEDIMENTARY ENVIRONMENTS**

49 The composition and physical properties of sediments and sedimentary rocks are for the
50 most part controlled by chemical processes taking place during weathering, transport, and
51 burial (diagenesis) (Bjørlykke, 2010). Thus, understanding the physical properties of
52 sediments and sedimentary rocks requires an understanding of the chemical processes
53 underlying sedimentary deposition. The formation of clastic sediments is a result of the
54 erosion and weathering of source parent rocks. The dissolved fraction of this clastic
55 sediment flows into seas or lakes, with subsequent precipitation as biological or chemical
56 sediments. During transport, grains continue to undergo weathering and abrasion, with
57 resultant sediments potentially undergoing repeated cycles of deposition and erosion prior
58 to final deposition. In order to establish the origin of these sediments, and to gain an
59 understanding of the processes that have operated prior to their deposition, there is a need
60 to analyse their geochemistry. For Holocene sediments (i.e., those deposited within the last
61 11.7 ka), environmental geochemistry offers a series of approaches to analyse sediment
62 geochemistry. For example, the identification of minerals in soils and sediments usually
63 involves high powered electron microscopy to image crystal forms, and diffraction and
64 vibrational spectroscopy to determine crystallographic structures (Ryan, 2014).
65 Understanding the elemental composition of sediment usually involves the analysis of
66 elemental absorbance, emission, fluorescence or mass (Ryan, 2014). These approaches to
67 elemental analysis fall into two groups: destructive and non-destructive. The former
68 involve the dissolution of minerals into an aqueous solution, whilst the latter are
69 characterised by the analysis of mineral powders (Ryan, 2014). These non-destructive

70 approaches include X-ray fluorescence (XRF) which this study will examine for the
71 purposes of the chemometric calibration of element geochemistry from the Sundarbans,
72 West Bengal, India. This paper provides a background to XRF, XRF core-scanning and
73 calibration through compositional data analysis (CoDa), with a focus on the sediments of
74 the Sundarbans, to demonstrate the usefulness of the techniques. Through the application
75 of CoDa, a number of calibration coefficients can be derived for key proxy geochemical
76 indicators and used to study sedimentary provenance and depositional processes. The
77 objective of the study is to investigate how the application of LRCE & PLS to Holocene
78 sediments of a Delta environment can improve interpretation of geochemical indicators of
79 grain-size variability.

80

81 **2. BACKGROUND TO THE INDIAN SUNDARBANS**

82 The Sundarbans is one of the largest coastal wetland sites in the world (~ 1 million hectares)
83 covering the western delta of the Ganges and Brahmaputra (G-B) rivers (Fig. 1). The
84 Sundarbans is a complex network of tidal creeks and deltaic islands with most sediment
85 arriving indirectly from the G-B river systems (which drain the Himalayas). The Indian
86 Sundarbans comprises just over 400,000 hectares in the western sector of the G-B delta,
87 and is cross-cut by a number of approximately north-south estuarine channels (Fig. 2).
88 Overall, the G-B delta is generally divided into two sub-systems of fluvially and non-
89 fluvially dominated depositional environments (Fig. 1) (Rogers et al., 2013). The eastern
90 sector of G-B delta comprises the fluvially dominated system, whilst the older abandoned
91 part of the delta, in the west, comprises the non-fluvially dominated environment that is no
92 longer directly linked to the G-B river sources (Fig. 1). This western part of the delta (which

93 underlies the present day Indian Sundarbans) was fluvially abandoned prior to c. 5000 cal
94 yr BP, as the Ganges River migrated eastward towards its present position (Goodbred and
95 Kuehl, 2000). Shoreline progradation in the eastern delta complex following the joining of
96 the Ganges and Brahmaputra rivers in the Meghna Estuary is considered to be fluvially-
97 dominated (Allison, 1998a).

98 The western extent of the G-B delta is now thought to be undergoing net delta front
99 erosion (Allison, 1998b; Allison et al., 2003), likely reflecting an eroding environment in
100 areas distal to areas of contemporary fluvial-deltaic deposition (Allison (1998b). As the
101 Ganges river shifted from its former western discharge channel (i.e., Hoogly River) to its
102 current position in the east, a series of palaeo-distributary channels were left abandoned
103 (Allison, 1998b). These channels reflect an almost exclusively tidal-driven
104 geomorphology, with sediments and discharge from the main G-B rivers no longer entering
105 the western delta front (Allison, 1998b; Bhattacharyya et al., 2013).

106 In order to fully explore the processes of sedimentation and the potential sources of
107 variance in sediment composition during the late-Holocene (post Ganges shift), high
108 resolution data analysis is required. Such analysis has never been performed on
109 sedimentary cores from the Sundarbans, and this study represents the first attempt at
110 characterising the sedimentary facies using high-resolution core-scan XRF and
111 establishing variation in sediment deposition.

112

113 **3. INTRODUCTION TO XRF CORE-SCANNING**

114 The application of X-ray fluorescence (XRF) to geological materials is well established,
115 and recognised as a conventional technique for deriving elemental composition (Ramsey

116 et al., 1995; Jenkins, 1999; De Vries and Vrebos, 2002; Weltje and Tjallingii, 2008). The
117 underlying principle of XRF analysis is that excitation of electrons by incident X-radiation
118 (X-rays) leads to the ejection of electrons from the inner ring of an atomic shell. This
119 ejection results in a vacancy, which is filled by cascading electrons from the outer shells,
120 which, in turn, leads to the emission of energy (Weltje and Tjallingii, 2008). The emitted
121 energy and wavelength spectra are atomically indicative of particular elements, allowing
122 relative abundances of elemental compositions to be derived (Weltje and Tjallingii, 2008).

123 In the 1990s, the development of a non-destructive core logging technique which
124 applies XRF for the determination of major-element concentrations in split sediment cores
125 was first utilised by the Royal Netherlands Institute for Sea Research (NIOZ) (Jansen et
126 al., 1998). The most advantageous surface for XRF sample determination is homogeneous,
127 dry, and smooth (Jansen et al., 1998). Using split-cores surfaces provides comparable
128 geochemical data to powder samples (Jansen et al., 1998). This is due to the response
129 depths that vary between elements. However, it has been found problematic that larger
130 particles tend to attenuate the fluorescent radiation of elements more than fine particles
131 (Jansen et al., 1998). The ‘ideal’ homogeneity of a sample occurs when the majority of the
132 material can pass through a 70-mm sieve (Potts, 1987; Jansen et al., 1998), with ‘ideal’
133 results derived from silts and clays, rather than from sands (which require careful
134 interpretation of results) (Jansen et al., 1998). The key advantages of XRF core-scanning
135 over conventional geochemical analysis of discrete specimens is that element intensities
136 are obtained directly at the surface of a split sediment core (allowing for the extraction of
137 near-continuous records of element intensities), and the spatial resolution of ED-XRF core-
138 scanning is much higher than conventional discrete sampling destructive methods (Weltje

139 and Tjallingii, 2008). However, one of the main drawbacks of the approach has been the
140 conversion of element intensities measured by ED-XRF core-scanners to element
141 concentrations (Weltje and Tjallingii, 2008). Thus, the results obtained by ED-XRF core-
142 scanning are generally presented in the form of count rates (counts per unit time per unit
143 area), or as ratios of counts, count rates, or intensities of elements (Richter et al., 2006;
144 Rothwell et al., 2006; Thomson et al., 2006; Weltje and Tjallingii, 2008). Within regular
145 calibration schemes, measurement geometry and specimen homogeneity is very poorly
146 constrained due to the inhomogeneity of samples and the irregular surface of a split-core
147 (Weltje and Tjallingii, 2008; Weltje et al., 2015). In addition, in some instances, spatial
148 variations in the thickness of an adhesive pore-water film which forms directly below a
149 protective polyester film covering the split core surface should be considered a further
150 constraining factor on measurement geometry values in the calibration equation (Weltje
151 and Tjallingii, 2008). Due to these poorly constrained and uncontrollable variations in the
152 experimental setup, the measurement geometry becomes an ‘unknown’ in the calibration
153 equation and renders its solution intractable within reasonable limits of uncertainty (Weltje
154 and Tjallingii, 2008). As a result of this uncontrollable variable in the calibration equation,
155 the experimental setup of quantitative XRF core-scanning must incorporate control
156 specimens of known intensities (Weltje and Tjallingii, 2008). However, such calibration
157 approaches often possess inherent intractability which can make the exercise inappropriate
158 for fully quantifying core-scan ED-XRF intensities. As a result, calibration requires an
159 alternative approach within the scope of CoDa in the form of the Log-Ratio Calibration
160 Equation (LRCE): a univariate log-ratio calibration (ULC) approach that combines
161 conventional calibration approaches in ratio form (Weltje et al., 2015).

162 The primary justification for the application of the LRCE and calibration in this
163 study is outlined by Bloemsma (2015) in terms of deriving meaningful data. As discussed
164 by Bloemsma (2015) calibration can be considered going from a not very meaningful data
165 set illustrated as 'X' to a meaningful data set 'Y', shown in the Venn diagram Fig. 1a, with
166 a parametric model used to capture this overlap. With calibration, $X \setminus Y$ may be interpreted
167 as noise and $Y \setminus X$ indicates the unpredictable variability in Y which may be interpreted as
168 a shortcoming of X (Bloemsma, 2015). Since the main goal of such a multivariate
169 calibration exercise, in the case of this study that of calibrating geochemistry and using
170 calibrated geochemistry to examine grain-size variability, this is understood through the
171 prediction of Y from X and $Y \setminus X$ has a different significance than $X \setminus Y$, since calibration is
172 an asymmetric exercise (Bloemsma, 2015). Also when both X and Y are meaningful
173 measures (i.e., quantitatively & compositionally meaningful, and this is illustrated with the
174 LRCE), then it may be possible to parameterise the overlap between X and Y in order to
175 gain more insight into their relationship (Bloemsma, 2015). Thus in the case of Fig. 1a, the
176 unique information (i.e., $X \setminus Y$ and $Y \setminus X$) is of potential value as both data sets are
177 quantitatively & compositionally meaningful, which is not the case with XRF intensity
178 data (Weltje and Tjallingii, 2008; Bloemsma, 2015).

179

180 **4. METHODOLOGY**

181 4.1. Quantification of core-scan derived XRF through the LRCE

182 The LRCE works by using the relationship between elements derived from core-scan and
183 conventional ED-XRF. Core-scan ED-XRF cannot be calibrated in standard equations due
184 to unknown coefficients of such models, as it is not possible to correct for grain-size, water

185 content etc., on a split core log without altering the sample. In principle, calibration of
186 conventional ED-XRF faces the problems of being a closed dataset (i.e., appropriate data
187 for compositional data analysis), but still representative of relative quantities of elements
188 in a sample. However, although core-scan ED-XRF is semi-quantitative (i.e., data are in
189 form of counts per second) there are also relative abundances of elements (i.e., core-scan
190 ED-XRF counts are relative to the sum-total of counts that are present between each
191 element). If a series of points is measured using core-scan ED-XRF and subsequently sub-
192 sampled and processed with conventional ED-XRF, then there are two datasets for the
193 same sample: conventional ED-XRF and core-scan ED-XRF.

194 The two datasets that are modelled in the LRCE are the core-scan ED-XRF counts
195 (i.e., intensity data) for which the concentration is unknown, and the concentration values
196 (e.g., %, ppm, etc.) dataset from the same set of samples as the intensity data, that form the
197 reference dataset in the calibration procedure. The way in which the LRCE works is that
198 the empirical model coefficients α and β are the log-ratio equivalents of the matrix effect
199 and detection efficiency (this is true in the case of single-element XRF spectrometry),
200 respectively (Weltje and Tjallingii, 2008). The LRCE uses a number of independent
201 models for the binary sub-compositions of a given set of elements to the spectrum of
202 relative XRF intensity data by using major axis regression based on singular value
203 decomposition (SVD) (Weltje and Tjallingii, 2008).

204 The LRCE can be considered a form of additive log-ratio transformation (alr)
205 (Aitchison, 1982; 1986), whereby the transformation is performed on every linear
206 combination of the sub-compositions examined (Weltje and Tjallingii, 2008). The key
207 principle however is that the calibration functions in log-ratio space and that these are

208 linear. After which, inverse log-ratio transformation and closure, the same data can be
209 expressed in relative intensities against concentrations in binary composition (Weltje and
210 Tjallingii, 2008). Predictions of the most optimum log-ratio denominator are allowed for
211 in this approach which reduces any non-linearity introduced by matrix effects (Weltje and
212 Tjallingii, 2008). Although the calibration process is carried out in log-ratio space it is
213 possible to inverse-transform the results using the inverse-alr function, giving
214 compositional data as output (Weltje and Tjallingii, 2008; Bloemsmma, 2010). The LRCE
215 derives multiple element composition estimates from XRF core-scanner output by fitting a
216 series of mutually independent models for binary sub-compositions of elements to the
217 spectrum of (relative) intensities (Weltje and Tjallingii, 2008). The variables are only
218 considered in the form of dimensionless log-ratios, which implies that normalisation prior
219 to analysis is not relevant, and this is consistent with the key tenets of the CoDa approach
220 (Weltje and Tjallingii, 2008). With this in mind, the model is unconstrained from the unit-
221 sum and non-negativity problems imposed by a closed dataset (Weltje and Tjallingii, 2008).
222 A full derivation of the LRCE is given in Weltje and Tjallingii (2008) and Weltje et al.
223 (2015).

224 In this study the prediction of the ED-XRF core-scan sub-composition was carried out
225 according to the following scheme:

- 226 • The core-scan intensity ED-XRF data and the percentage (%) concentration PXRF
227 data are examined for the α and β model parameters through major axis regression
228 by SVD (Press et al., 1994).
- 229 • Binary sub-compositions between intensity ED-XRF (core-scan) and %
230 concentration PXRF are plotted (i.e., the optimum log-ratio denominator that gives

231 the best linear fit is derived and a series of alr-transformations are used employing
232 this optimum log-ratio denominator, to derive a linear relationship between %
233 concentration data and intensity data).

234 • The best fit model for intensity ED-XRF – the ED-XRF data from both the %
235 concentration and predicted concentration are permuted and calculated for each
236 log-ratio pair of linear distances, which derives the best fit for the intensity ED-
237 XRF sub-composition (Weltje and Tjallingii, 2008). This is empirically quantified
238 by taking the median of the squared discrepancies between the predicted and the %
239 concentration geochemical composition with discrepancies calculated through the
240 use of a ‘leave-one-out-cross-validation’ (LOOCV) (Bloemsma et al., 2012).

241 • The Aitchison distance between predicted and reference composition is used as the
242 determinant for the optimal denominator element in the sub-composition (i.e., the
243 residual variance between measurements in both the regression and predicted
244 models) (Bloemsma et al., 2012).

245 • The goodness-of-fit of the optimum log-ratio denominator is derived from the
246 residual variance and the total variance (Weltje and Tjallingii, 2008).

247 • The relative abundance of each element in the sub-composition from the predicted
248 weights is determined through an inverse alr-transformation, with data expressed
249 in a conventional (closed) form (Weltje and Tjallingii, 2008).

250 Data from core-scan derived ED-XRF are now calculated based on the relative
251 abundances of the sub-composition. However, to perform any further statistical analysis of
252 the data, they are required to be subjected to further log-ratio transformation (e.g., alr-,
253 centred log-ratio (clr), or isometric log-ratio (ilr) transformation). As the LRCE is founded

254 on the CoDa principles, the use of a common log-ratio denominator is unrestricted and
255 functions as a normalisation approach (Weltje and Tjallingii, 2008). The use of a common
256 log-ratio denominator in the calibration model is generally independent of any
257 environmental or sedimentological considerations (i.e., the log-ratio denominator is
258 independent of any physical reasoning for use in the calibration model) (Weltje and
259 Tjallingii, 2008).

260

261 4.3 Joint geochemical and grain-size modelling

262 Grain-size and geochemical composition of clastic sediments have been found to be highly
263 correlated as a result of the processes that control the generation of sediment from
264 crystalline rocks (Bloemsma et al., 2012). The composition of modern sediments and their
265 grain-size variation is due to four key factors: (i) contributions of mineralogically and
266 texturally distinct grains from a number of divergent sources (ii) rock fragments being
267 mechanically weathered into a finer composition, (iii) labile grains being more susceptible
268 to chemical weathering and (iv) transport associated sorting of compositionally distinct
269 grains (Whitmore et al., 2004).

270 Bloemsma et al. (2012) have expanded on this relationship between geochemical
271 and modal grain-size variation, as geochemical variation is generally considered to reflect
272 the pervading environmental conditions of sediment genesis. In terms of relating grain-size
273 variation to bulk geochemical composition, it may be postulated in terms of the chemical
274 weathering of crystalline rocks, in which the release of unstable elements as solutes takes
275 place, whereas elements such as Al remain in the solid phase (Nesbitt and Young, 1984;
276 Bloemsma et al., 2012).

277 The development of the PLS modelling approach for joint geochemical and grain-
278 size relationships is premised on whether in a series of sediment samples derived from a
279 source area that, over time the extent of chemical weathering was static, then the bulk
280 geochemical variation may be attributed to; selective entrainment, transport, and deposition
281 (Bloemsma et al., 2012). In a sedimentological context, such a one-to-one relationship
282 between grain-size and geochemistry is rare with geochemical variability being a function
283 of: chemical weathering; hydraulic/aerodynamic sorting; mixing; and diagenesis
284 (Bloemsma et al., 2012). In these regards, the variability between grain-size and
285 geochemistry is considered as being what is shared and what is unshared, in which case if
286 the former is removed from the data and the residuals calculated, then unknown trends such
287 as provenance may be distinguished as a result (Bloemsma et al., 2012).

288 The Partial Least Squares (PLS) modelling approach was developed by Bloemsma
289 et al. (2012) and has two key assumptions: (1) that there is a monotonic relationship
290 between grain-size and geochemical composition, and; (2) grain-size distributions and
291 geochemical compositions are both compositional in nature, necessitating the use of
292 models in log-ratio space (Bloemsma et al., 2012).

293 Effectively, geochemical data are considered to contain two parts, with one part
294 that is correlated with grain-size, and a second part which varies independently from grain-
295 size (Bloemsma et al., 2012). The model is carried out by finding a basis for which
296 maximizes the geochemical variance explained by the grain-size (Bloemsma et al., 2012).
297 If then, the mean is subtracted from these geochemical and grain-size data matrices, the
298 values of the residuals are provided (Bloemsma et al., 2012). If there is significantly high
299 correlation found in the projection of both datasets onto the basis vectors, then these are

300 considered to be the ‘shared signals’ (Bloemsma et al., 2012). The residual signal are then
301 calculated by subtraction of the shared signals from the raw data, giving the variability
302 unique to each dataset (Bloemsma et al., 2012). The number of uncorrelated (i.e.,
303 orthogonal) components is a hyperparameter that may vary between zero and N-1, with N
304 being the minimum number of variables (e.g., grain-size bins or chemical elements)
305 (Bloemsma et al., 2012). The implementation of the PLS modelling approach follows on
306 from the work of Bloemsma et al. (2012) in which:

- 307 • clr-transformation of both the geochemical and grain-size data.
- 308 • Detection of replicate samples using the depth attribute.
- 309 • Derive the basis Q in \mathbb{R}^D that can maximise the geochemical variance explained by
310 the grain size through the Partial Least Squares (PLS) (Wold et al., 1982).
- 311 • Fit a model onto data matrices X^* (where $X = L$ grain size classes) and Y^* (where
312 $Y = D$ variables).
- 313 • Subtract the mean from the X^* and Y^* to derive X_c^* and Y_c^* through the SIMPLS
314 algorithm (de Jong, 1993) and calculate the PLS matrix decomposition.
- 315 • Orthogonalise the bases (i.e., the loadings) through SVD with the score matrices
316 recalculated.
- 317 • Test the significance of correlation between geochemistry and grain-size
318 distribution scores on the k-th basis vector using the Kendall and Stuart (1973) test.
- 319 • Derive r for any order of k, where r is the Pearson’s correlation coefficient between
320 the k-th column and the previously orthogonalised bases.
- 321 • With a confidence level of α and $p = 1 - \alpha$, the first k of shared signals is removed
322 if for the k the Kendall and Stuart (1973) criterion is established.

- 323 • The model is applied to all grain-size and geochemical data as the transpose of the
324 bases are orthonormal, thus the scores of all observed grain-size distributions and
325 geochemical compositions may then be derived by the matrix product.
- 326 • Reduced-rank approximation is used to derive the shared signal in both the grain-
327 size distributions (GSDs) and geochemistry datasets.
- 328 • The residuals are calculated and subtracted from the common variability for both
329 the GSDs and geochemistry input data.
- 330 • The mean is added such that the residual signals centre around the mean of their
331 corresponding raw data matrix as result (Bloemsma et al., 2012).

332 Thus, through this algorithm implementation it may be possible to derive the grain-
333 size dependent and independent geochemical components from the dataset. It is not the
334 objective of this study to outline the PLS modelling approach and the reader is referred to
335 Bloemsma (2010), Bloemsma et al. (2012), and Bloemsma (2015) publications for a more
336 exhaustive discussion. However, it is only through utilising the calibrated geochemical data
337 presented here that proxy information for environmental change may be derived, in this
338 case for grain-size variability and the depositional environment for the Dhanchi Island site.
339 Grain-size data was gathered from the Dhanchi Island core samples prior to PXRF analysis,
340 following the methodology of Flood et al. (2015).

341

342 4.3. Data acquisition: Grain-size analysis

343 GSDs were analysed following Flood et al. (2015) using a MalvernMastersizer 2000
344 instrument. Data were aggregated into quarter phi intervals (ϕ scale) over the range of 0.02
345 – 2000 μm , following collection of measurements from the instrument. The centred log-

346 ratio transformation (clr-transformation) was implemented on all grain-size classes with
347 any zero-valued bins of quarter phi intervals removed (i.e., where entire column vectors
348 consisted of 0 row values). Classes of the grain-size distribution containing a zero in any
349 of the observations (i.e., columns where only some of the row values are > 0), were
350 amalgamated and the arithmetic mean calculated (cf. Bloemsa et al., 2012). This process
351 was carried out on the 62.50 μm to 2000 μm fraction (i.e., 4.00 ϕ to -1.00ϕ) for the
352 Dhanchi Island GSD data.

353

354 4.3. Data acquisition: ITRAXTM core-scanning

355 Coring was carried out at Dhanchi, Bonnie Camp, and Sajnekhali in November 2011 (sites
356 shown in Fig. 2). Three cores (one from each site) were extracted using a motor driven
357 percussion coring device. These cores were analysed using the ITRAXTM core-scanner
358 (Cox Analytical Systems, Mölndal, Sweden) housed at the School of Geography,
359 University College Dublin. This is a non-destructive analytical approach which provides
360 ED-XRF elemental profiles along with optical imagery and micro-density (X-radiography)
361 information (Croudace et al., 2006). The geochemical data were acquired through an ED-
362 XRF spectrometer consisting of a molybdenum cathode (Croudace et al., 2006). The
363 voltage and current of the X-ray source was the 3kW Mo tube set to 30 kV and 50 mA
364 respectively, with a measurement step-size of 300 μm and exposure time of 16 seconds.
365 The latter setting was employed for expedience, to provide high-resolution scanning of all
366 the cores (c. 25 m of material length). The element data (table of elements shown in Table
367 1) were processed using fitting procedures in the Q-Spec spectral analysis package in order
368 to extract the individual elemental intensities from the spectra output (Croudace et al.,

369 2006). Operation of the software involved selecting elements to be extracted from the XRF
370 spectra, with any spurious or unnecessary elemental choices or incorrect fitting parameters
371 adjusted post hoc through a batch-controlled post-processing of the spectra (Croudace et
372 al., 2006). Invalid readings were noted and not employed in any post-hoc processing (i.e.,
373 invalid readings were not used in the LRCE). The scan-lengths from each of the cores were
374 666 cm for Dhanchi-2 (hole-depth of 728 cm), 923.2 cm for Bonnie Camp (hole-depth of
375 1022 cm), and 639.4 cm for Sajnekhali Island (hole-depth of 791 cm). The total number of
376 readings from each core were Dhanchi-2 with $n = 22,129$ valid readings from a total output
377 of 22,201 readings (72 invalid readings), Bonnie Camp with $n = 30,517$ valid readings from
378 a total output of 30,773 readings (256 invalid readings), and Sajnekhali with $n = 23,822$
379 valid readings from a total output of 24,201 (379 invalid readings).

380 The LRCE was applied to the global discrete sampling dataset collected ($n=568$)
381 with the model then unfolded onto the elemental data from the high-resolution ITRAX™
382 ED-XRF ($n=76,468$). The alpha (α) and beta (β) slope and intercept regression parameters
383 derived from the LRCE were used to predict the relative concentration of a sub-
384 composition of elements (see 5 Results of this study), for this higher resolution dataset.

385

386 4.4. Data acquisition for calibration: portable X-ray fluorescence spectrometry of reference
387 samples

388 Data acquisition using ED-XRF was undertaken using a Bruker S1 TURBO SD portable
389 X-ray fluorescence (PXRF) spectrometer (Bruker Corporation, Massachusetts, USA)
390 consisting of a 10 mm X-Flash® SDD Peltier-cooled detector with a 4-watt (W) X-ray tube
391 consisting of an Ag target and a maximum voltage of 40kV. Analysis was carried out on

392 discrete samples collected from the Dhanchi-2, Bonnie Camp and Sajnekhali Island cores.
393 In order to ascertain major and trace element composition, the elemental suite was
394 generated using two analytical settings for each sample analysed. Major elements were
395 acquired using a vacuum-pumped, low-energy and high current setting of 15kV and 55 μ A
396 instrument setting with no filter. The vacuum-pump was used to remove air from between
397 the sampling window and the detector and allowed for improved analysis of the material,
398 in particular increased sensitivity to light major elements, below and including iron (Fe).
399 The other analytical setting was used for trace element analysis and acquired without a
400 vacuum-pump and employed a yellow filter (Ti and Al), high-energy instrument setting of
401 40kV and 19.60 μ A. With these instrument settings, elemental data are acquired for heavier
402 elements with little sensitivity for those elements below calcium (Ca). The filter used
403 consists of a 0.001” Ti and 0.012” Al and is already present in the instrument. Using the
404 portable XRF, high and low energy data were acquired for each sample. Unknown samples
405 from the Sundarbans were each measured for 16 seconds, with a set of 22 international
406 geochemical reference standards (shown in Table 1) measured for 120 seconds, this was
407 carried out so as to develop a robust calibration line for the PXRF instrument specific
408 calibration. Since the Bruker software is proprietary, a full disclosure and discussion of the
409 calibration routine is not possible in this study (cf. Rowe et al., 2012).

410 The calibration models used in this research depend on the estimation of error of
411 the covariance matrices, where the magnitude of the uncertainty in the measured variables
412 is accounted for (Bloemsma 2015; Weltje et al., 2015). With this in mind, due to lack of *a*
413 *priori* knowledge concerning these uncertainties, replicated analysis is required in order to
414 estimate these uncertainties (Bloemsma 2015). Repeated measurements were carried out

415 on a total of 9 samples (3 per core) with 30 additional measurements on each of these
416 samples (n = 270 repeated measurements in total) using the portable ED-XRF.

417

418 4.5. Data acquisition – portable ED-XRF spectra calibration

419 The raw spectra obtained from the Bruker S1 TURBO SD portable ED-XRF require a
420 calibration to convert the data into quantitative weight percentages. The calibration for the
421 portable ED-XRF unit is matrix-specific, so a calibration for major and trace elements of
422 sediments and soils was developed using a suite of 22 reference materials. The calibration
423 of the ED-XRF spectra was carried out using the Bruker AXS calibration software
424 S1CalProcess Version 2.2.32 with the reference concentrations for the low and high energy
425 calibrations produced for each element being evaluated against the concentration of the
426 element as derived from the slope and baseline corrected peak heights. Linear regression
427 analysis of the elemental concentrations quoted by the manufacturers for the international
428 geochemical reference standards are examined along with elemental composition derived
429 from the Bruker AXS S1CalProcess.

430

431 **5. RESULTS**

432 The results presented in this section reflect the data processing and outline how the LRCE
433 was applied to the integrated core-scan ED-XRF data along with the discrete samples
434 analyzed using conventional ED-XRF and grain-size analysis. The LRCE model depends
435 on comparability of the intensity measured elemental composition (i.e., data from the core-
436 scan ITRAX™ data) along with the % elemental composition (i.e., conventional XRF data)
437 a sub-composition of the elements were examined for these modelling purposes.

438 The LRCE model was applied to all of the integrated core-scan samples from the
439 cores. These input data consisted of the total sample population from the three cores
440 (Dhanchi, n = 163; Bonnie Camp, n = 228; Sajnekhali, n = 176; with a total sample
441 population, n = 567) with fifteen outliers removed. These outliers were removed as they
442 deviated substantially from the general spread of data points and would bias the prediction
443 of the model. Fig. 3 shows the cross plot of results from the closed, inverse transformed
444 sub-composition of elements with calcium (Ca), iron (Fe), and potassium (K) depicted in
445 the top row (a-c) and rubidium (Rb), titanium (Ti), and zirconium (Zr) shown in the bottom
446 row (d-f). The conventional weighted (reference) ED-XRF composition is on the x-axis
447 with the integrated ITRAX™ derived intensity (predicted) ED-XRF on the y-axis.

448 The lack of a full suite of elemental output is due to the fact that the majority of
449 these elements correspond to the lower energy, and thus atomically lighter, end of the
450 spectrum with poorer excitation efficiency and detection. Data derived from these lighter
451 elements are more difficult to calibrate as there tend to be more peak-overlaps. Finally, as
452 the penetration depth of ED-XRF for the light elements (e.g., Si, Al etc.) tends to be ~
453 hundreds of μm , there is a risk of not actually measuring sediment (i.e., with core scan
454 derived ED-XRF, it is possible to measure water pooled under the Mylar® polyester film).
455 The efficacy of the LRCE is illustrated in Fig. 3, where data appears to be well spread along
456 the model, with calcium, iron and titanium representing the best spread of data points.
457 There appears to be some bias in the potassium modelled output where a number of sample
458 points deviate from the model. This bias may be attributed to the measurement of potassium
459 in ED-XRF (both core-scan and conventionally derived ED-XRF), where potassium
460 appears close to calcium and in some cases there may be some peak overlap if the count

461 time is low (Bloemsma 2015). However, given that the potassium is spread along the x-
462 axis of the known weighted elemental composition, such an artefact of analysis may be
463 attributed to the conventional ED-XRF. Rubidium data points appear to be spread across
464 the regression and derive a reduced correlation. There is also a clustering of the data points
465 from the regression model applied to zirconium.

466 The calibration coefficients, α and β , for the LRCE model are shown in Table 2 and
467 Table 3, respectively. These coefficients can be considered to reflect the matrix effect (i.e.,
468 scattering, absorption and enhancement effects introduced during measurement, caused by
469 the presence of other elements) and detection efficiency (i.e., sensitivity of the ED-XRF
470 data after pre-processing) in a single-element from ED-XRF derived output (Weltje and
471 Tjallingii, 2008). The LRCE removes the specimen effects, which relate to the deviations
472 of measurement from ideal conditions, however not all of these effects are fully removed
473 (Weltje and Tjallingii, 2008). The α and β regression parameters reflect physical
474 parameters such as grain-size, core-surface elevation, and water content (Weltje and
475 Tjallingii, 2008), and are the main criteria used in the LRCE for calculating the best model
476 fit for each of the elements (i.e., what is the 'best' log-ratio denominator for each of the
477 elements in the dataset) (Weltje and Tjallingii, 2008).

478 In Table 4 and Table 5 the residual variances of the regression and prediction of the
479 dataset used in the LRCE are shown. The residual variance refers to noise as it does not
480 correlate with the compositional variations in a specimen (Bloemsma, 2010). This variance
481 is quantified by taking a clr-transformation of a set of measurements from the same core-
482 locations (i.e., replicate measurements) with the Euclidean distance between the
483 observations measured in order to calculate error estimation (Bloemsma, 2010). Thus, the

484 residual variance effectively quantifies the level of relative ‘noise’ that may be derived
485 from the regression and prediction. The residual variance for both the regression and
486 prediction reveal that calcium accounts for the most consistent variance.

487 The α and β parameters from the log-ratio transformed dataset shown in Fig. 4 (a-
488 e) with Ca found to be the best fitting denominator for Fe, K, Rb, Ti, and Zr. The R^2 values
489 of goodness-of-fit in the LRCE denominator are shown in Table 6. The non-linearity found
490 in the original back-transformed data (Fig. 3, Rb and Zr) along with bias (Fig. 3, K) is now
491 removed. Ca is found to be the optimal denominator using the Aitchison distance between
492 the predicted and reference composition. Table 4 shows the median variances and Table 5
493 depicts the 95% confidence limits corresponding to these residual variances. The non-
494 linearity introduced by the matrix effects has been greatly reduced with log-ratio intensities
495 now distributed linearly with the log-ratio relative concentration (cf. Weltje and Tjallingii,
496 2008). As a consequence, the elemental concentration can now be derived from any of the
497 intensity observations based on the linear model (black line intersecting the point clouds in
498 Fig. 4) (cf. Weltje and Tjallingii, 2008).

499 Using the residual variance of the prediction and the regression (Table 4 and Table
500 5), the sub-composition closure of the high-resolution dataset from the ITRAX™ ED-XRF
501 has been estimated from the lower resolution calibration dataset. As a result, it is now
502 possible, through the calibrated intensity derived ED-XRF with the weighted ED-XRF, to
503 interpolate the high resolution intensity ED-XRF.

504 Shown in Fig. 5a is the PLS model output for the Dhanchi Island core with the PLS-
505 coefficients of c. 0.3 for grain-size depicted by negative values corresponding to the coarse-
506 clay to coarse-silt size fractions. Positive PLS coefficients of c. +0.3 are indicated by

507 coarse-silt to sand sized. The PLS-scores for grain-size indicate positive score fluctuations
508 appear to correspond to coarser sediment coefficients with negative scores found to
509 correspond to that of finer sediment coefficients. The PLS-coefficients for geochemistry
510 (Fig. 5b) show positive values for zirconium and calcium, with the highest negative values
511 found for iron, potassium, rubidium, and titanium. Calcium and zirconium indicate the
512 highest PLS coefficients at c. 0.4 and 0.3 respectively. In contrast, iron, potassium,
513 rubidium and titanium are negatively correlated with PLS-coefficient values of between -
514 0.3 and -0.4. The PLS-scores show a decline in grain-size with a concomitant decline in
515 PLS-scores for geochemistry (calcium and zirconium) (Fig. 5c & d). Furthermore there is
516 an apparent trend found in the PLS-scores for grain-size, firstly a trend consisting of a form
517 of oscillation taking place from c. 787 cm to 491 cm that is superseded by a second trend
518 of PLS-score decline. These trends in light of the PLS-scores may be interpreted as a form
519 of grain-size variability, in which oscillations in grain-size appear to correlate with
520 oscillation in zirconium, while a decline in zirconium is reflected in a decline in grain-size.
521 When the PLS-data are considered along with the PC1-scores and PC1-coefficients for
522 residual geochemistry (Fig. 5e & f), it is evident that throughout the Dhanchi Island core
523 there is a consistent decline of calcium taking place. This can be discerned through the
524 PC1-coefficients for residual geochemistry which depict positive values driven most
525 strongly by calcium at c. 0.7 with negative values being concomitantly driven by zirconium
526 at just over -0.6. Furthermore, negative PC1-coefficient values may be discerned for the
527 rubidium and titanium compositions, with potassium and iron represented by positive
528 coefficient values.
529

530 **6. DISCUSSION**

531 6.1 Reconstructing Late Holocene environmental change from sediments in the West
532 Bengal Sundarbans, India

533 The objective of the study is to investigate how the application of LRCE & PLS to
534 Holocene sediments of a Delta environment can improve interpretation of geochemical
535 indicators of grain-size variability. The geochemistry derived from the application of the
536 LRCE to Holocene sediments in the present study illustrates the efficacy of these subset of
537 elements as useful indicators of environmental change. The LRCE shows that, in the case
538 of the Sundarbans, K, Rb, Fe, Ti, Zr, and Ca can be calibrated, with Ca found to be the
539 best-fit denominator. The utility of these elements for interpreting environmental change
540 within the Sundarbans can be explored by examining the Dhanchi Island core and how
541 these calibrated data may be employed in order to interpret the depositional environment
542 through grain-size variability. However, in order to understand the data generated in this
543 study, there is a requirement to place into the context the key aspects of deltaic
544 environments and how these aid in the interpretation of facies variability derived through
545 the LRCE & PLS models for the case study of the Dhanchi Island core. The role of this
546 discussion is to outline a potential set of circumstances that may characterise a depositional
547 model for this particular site in the Sundarbans.

548

549 6.2 Contextualising deltaic environments: implications for understanding the Sundarbans

550 In order to develop any interpretation of facies variability through geochemistry and grain-
551 size analysis, illustrated in this study, an exposition is required on generalised 'boundary
552 conditions' in deltaic environments. This is not an exhaustive discussion on every aspect

553 of deltaic environments, but rather the principal aspects of these boundary conditions for
554 understanding the Sundarbans and the results from the Dhanchi Island core.

555 Through high sediment availability with variability in ocean hydrodynamics and
556 localised coastal progradation, river deltas develop as coastal features characterised as
557 ‘protuberances’ (cf. Elliott, 1986; Wright, 1978; Hanebuth et al. 2012). Attempts to classify
558 deltas into a ternary diagram representing endmembers of fluvial, tidal, and wave
559 dominances have failed to capture the variability represented by the fact that many deltas
560 do not fall into a singular regime classification (Hanebuth et al., 2012). There is a rather
561 dynamic relationship in terms of laterally graded intensity between sediment discharge
562 along defined channels counterbalanced with the influence of tides, waves and longshore
563 currents (Hanebuth et al., 2012). In these regards, the differentiation of external forces in
564 this manner leads to more diverse organisation of deltaic environments that are more
565 locally segmented and temporally complex (Hanebuth et al., 2012). With this, the focus of
566 deltaic research should consider the individual segments of a delta as opposed to the entire
567 delta which transitions through different classification schemes (Ta et al., 2005; Yoshida
568 et al., 2007; Hanebuth et al., 2012). This study attempts to apply this approach to
569 considering the Sundarbans in this manner of localised variability in terms of sedimentary
570 deposition as opposed to applying a generalised model over the entirety of the Ganges-
571 Brahmaputra delta. Modern Holocene delta development has been demonstrated to have
572 commenced between 9 and 7.5 cal ka BP associated with the deceleration of sea-level rise
573 approximately 1 ka prior to the mid-Holocene sea level maximum (Stanley and Warne,
574 1994). It has been proposed however, that during this initial stage of delta growth deposits
575 are, with the exception of the sedimentary facies succession filling central fluvial valley,

576 not of a deltaic character but have formed under a strong tidal influence, comprised mainly
577 of tidal flats, mangrove swamps and salt marshes (e.g., Tanabe et al., 2006) (Hanebuth et
578 al., 2012). Although this proposition stands in contrast to the generally held concept of
579 supply-dominated, progradational environments, the observation does hold some potential
580 insight into the conditions that characterise the late Holocene (< c. 4,000 cal yr BP)
581 environment of the Sundarbans.

582 In order to better understand geochemical and grain-size variability, and the
583 implications that these have for teasing-out aspects of environmental change in the
584 Sundarbans, some general aspects of sediment supply need to be considered. As discussed
585 by Gao and Collins (2014) it has been found that the occurrence of coastal-shelf deposits
586 are indicative of the provenance of sediment supply. In their argument, it is put forward
587 that if the supply of sediment is ‘small’, then the seabed may consist only of bedrock, relict
588 sediment or reworked materials (Gao and Collins, 2014). This condition is known as being
589 “sediment starved” (Gao and Collins, 2014, pp. 270). If there is an abundant supply of
590 sediment, then thick Holocene deposits with a large areal coverage may occur (Gao and
591 Collins, 2014). Sediment supply is principally provided by rivers, derived from catchment
592 erosion with the amount of available sediment dependent on the catchment characteristics
593 (Milliman and Syvitski, 1992; Syvitski et al., 2003; Gao and Collins, 2014). Sediment
594 supply, in terms of rivers at least, is dependent upon geographical variability at the global
595 scale (Milliman and Farnsworth, 2011). An example of this can be seen in monsoon-
596 controlled southeastern Asia, where the warm climate favours physical and chemical
597 weathering and, therefore, generates a high sediment yield with intense rainfall that results
598 in high river discharges (Liu et al., 2000; Gao and Collins, 2014). Thus, as a result of these

599 conditions, southeastern Asia in these regards has the highest terrestrial denudation rates
600 in the world with the majority of sediment input into oceans derived from this region
601 (Milliman and Farnsworth, 2011; Gao and Collins, 2014). In terms of erosion at the coastal
602 zone, more than half of all coastlines are undergoing erosion with sediments deposited in
603 areas adjacent to the shoreline & littoral zone with the transport offshore of the remaining
604 sediments (Bird, 1984; Gao and Collins, 2014). Combining these general aspects of
605 sediment supply to understanding deltaic environments may be best considered when
606 looking at grain-size variability.

607 Grain-size compositions examined with an experimental microdelta by Endo et al.
608 (1996) have found that these compositions are strongly controlled by the textural
609 composition of source sand, analogous to a real-world river system. These results indicate
610 that textural composition of a depositional system is primarily determined by the textural
611 composition of sediment input (Swift et al., 1971; Liu et al., 2000). With this the observed
612 grain-size variability are a result of the transport and deposition processes of sediment
613 delivery to a system, with subsequent reworking of sediments already deposited (Liu et al.,
614 2000). Thus, the nature and amount of sediment input can therefore determine the textural
615 characteristics of a depositional system in receipt of these sediments (Liu et al., 2000).
616 Therefore, the textural characteristics of a marine depositional system, its sources, and
617 processes by which delivery of sediments takes place and is deposited, may be understood
618 as being highly connected (Liu et al., 2000). An example of this connected nature of
619 sediments in depositional environments may be seen with the distributional patterns of
620 individual grain-sizes on a wave-dominated shoreface by Liu and Zarillo (1990). It was
621 found that both influence of source and the influence of hydrodynamics that have reworked

622 and redistributed sediments during transport were discerned (Liu and Zarillo, 1990). Such
623 unique grain-size distributions therefore highlight the different responses to processes of
624 hydrodynamics on the shoreface and how these may be utilised in order to examine how
625 sediments respond to hydrodynamic processes (Liu and Zarillo, 1989). It is therefore now
626 possible to fully consider the data from the Dhanchi Island core and what may be gleaned
627 from the geochemical and grain size variability found and how these fit into the present
628 understanding of deltaic environments.

629

630 6.3 Use of Sundarbans elemental log-ratios as environmental proxies

631 The calcium variability in the Dhanchi Island sediments may therefore be understood as
632 declining from a depth of approximately 500 cm to the core surface. This decline in calcium
633 with the subsequent increase in zirconium, titanium, potassium, and rubidium composition
634 may be interpreted as terrestrial sediment flux with diminished marine deposition. This
635 calcium signal is pervasive in the four log-ratio pairs and does not appear to lend to the
636 interpretation of grain size variability per se in the depositional characteristics of the
637 Dhanchi Island site. It may be discernible that terrestrial sediment flux appears to be
638 uncorrelated with calcium, thus, sediment provenance for the fine and coarse sediment
639 appears to be independent of a marine or a tidally driven source.

640 In this context, the Dhanchi Island sediments exhibit a predisposition to terrigenous
641 sediments, in agreement with Rogers et al. (2013) that geographical distance is not
642 necessarily a limiting factor on sedimentation taking place (assuming the predominance of
643 terrigenous sediment in the Dhanchi Island sediments). One of the key trends in all of these
644 log-ratio pairs with calcium as the denominator, is that there appears to be a non-

645 stationarity signal present, in which although the variability between log-ratio values
646 appears to indicate some form of oscillation throughout the sequence, in each log-ratio pair
647 however the overall behaviour as noted is an increase in the numerator value at the expense
648 of the calcium denominator (Fig. 6). Non-stationary signals, in the case of these log-ratio
649 pairs, implies that the depositional processes taking place are drifting in time, in particular
650 the increase in zirconium relative to calcium may be derived from the aggradation of the
651 island surface.

652 Grain size variation delivered by rivers has also been found to become finer in the
653 seaward direction and this is more pronounced in an aggradational environment
654 (Dalrymple and Choi, 2007). However, given that this part of the Sundarbans is an
655 ‘abandoned’ deltaic-estuarine site, it may be classed as being part of the ‘middle estuary’
656 which occupies effectively the same environmental location within an estuary as active
657 delta-plain distributary channels within a delta (Dalrymple and Choi, 2007). In terms of a
658 deltaic system such an abandoned set of distributary channels are thought of as estuarine
659 due to the fact that they do not carry as much river discharge and also experience reworking
660 by tidal currents (Dalrymple, 2006; Dalrymple and Choi, 2007). These areas experience
661 net landward transportation of sediment from the seaward margin, which is contrast to that
662 of active delta channels that experience a reverse (Dalrymple and Choi, 2007). It has also
663 been noted that in terms of evidence for river action in the physical structures present, there
664 tends to be almost no evidence for seasonality in fluvial discharge (Dalrymple and Choi,
665 2007). Along with this, there tends to be a case in abandoned channels of such delta plain
666 estuaries that sediments from somewhat older distributary-mouth-bar deposits experience

667 reworking within these systems (Dalrymple and Choi, 2007). The overarching presence of
668 silt and clay would suggest a muddy depositional environment.

669 As identified by Goodbred and Saito (2011) such environments are generally made
670 of what are termed ‘sand-mud alterations’ consisting of flaser, lenticular and wavy
671 laminations or bedding. Furthermore, such tidal flat environments are composed of
672 bidirectional sedimentary structures such as sand-layer stacking, cross-laminations, mud-
673 drapes, and potentially, double mud-drapes (Goodbred and Saito, 2011). These
674 depositional features are usually indicative of tidal depositional constraints on a
675 sedimentary system (Goodbred and Saito, 2011). In this regard, although such sedimentary
676 structures are difficult to discern from a discrete number of grain size samples, it is possible
677 to elucidate such a depositional environment, potentially through high-resolution core-
678 scanning as shown in Fig. 6. However, without having a robust chronology, it is still
679 difficult to discern such tidal sedimentary structures. In a study of grain size characteristics
680 of tidal-bore deposition in the Qiantang Estuary by Fan et al. (2014), GSDs are found to be
681 composed of a principal coarse and secondary fine component. The modal size, sorting,
682 and proportions found in these coarse and fine components are ascribed to different
683 depositional processes on the tidal flats (Fan et al., 2014). Sandy laminae were found to be
684 well sorted compared to those of muddy laminae, reflecting disparate depositional stages
685 of waning flow and slack tides (Fan et al., 2014).

686 The dominant, upward-fining in GSDs as shown in Fig. 5 & 6 may be attributed to
687 what Dalrymple et al. (1992) refer to as ‘lateral shifting of channel bedforms’. Such lateral
688 shifting leads to this trend in grain size as currents tend to be higher at greater depths and
689 weaker when over bar crests (Dalrymple et al., 1992). These fining-up sequences

690 comprising muddy tidal flats may actually cap subtidal sand ridges (Wells, 1995). A similar
691 model of facies succession has been proposed by Goodbred and Saito (2011), where the
692 migration of tidal channels and creeks across tidal flats, contribute to this fining up facies
693 succession. The clay fraction elucidated from the first and second principal components
694 may represent the mud-drapes and fluid-muds which may be attributed to slack water or
695 poor water flows (cf. Wells, 1995).

696 Sediment that may have terrigenous origins may also be indicative of a fining-up,
697 when considered with the Ca decline throughout the sequence. The element profile of Ca
698 in sedimentary depositional environments is generally considered to reflect the
699 predominant abundance of biogenic carbonates (CaCO_3) in marine sediments (Arz et al.,
700 1998; Tjallingii, 2007; Tjallingii et al., 2010). There is known to be poor preservation of
701 of CaCO_3 in the Sundarbans especially in the progradational lower delta plain sequence
702 relative to the marsh and mangrove deposits of other deltaic systems around the world (see
703 Allison et al., 2003). In the case of the Sundarbans however, the presence of Ca may be
704 interpreted as indicative of the solubility of Ca in water. Since Ca has a low ionic potential
705 it is unable to break the bonds in the water molecule and remains in solution as a hydrated
706 cation (Bjørlykke, 2010). The result of this is that the Ca ion is surrounded by water
707 molecules with the negative dipole towards the Ca cation (Bjørlykke, 2010). As water
708 molecules have a strong dipole this causes them to be attracted to cations with the resulting
709 cation, in this case, Ca becoming hydrated (Bjørlykke, 2010). This small cation is therefore
710 less likely to be adsorbed to clay minerals that are negatively charged (Bjørlykke, 2010).
711 Finally, Al has been known to replace Ca as the dominant exchangeable cation where the
712 acidity of soil increases, thus, high Al concentrations are usually correlated with reduced

713 Ca concentrations (Salminen et al., 2005). In this regard, Ca may be interpreted as a proxy
714 for marine flux in the Sundarbans sedimentary environment; given the ionic potential and
715 physical properties outlined.

716 There appears to be greater agreement found between sediment provenance
717 proposed by Rogers et al. (2013) and sediment depositional model outlined here in terms
718 of distal sediment transport from fluvial sources, reflected in the log-ratio pairs discussed.
719 The non-stationary signals found in elemental log-ratio pairs may be attributed to tidal
720 processes in the manner described by Dalrymple and Choi (2007). However, what is further
721 elucidated through the joint geochemical and grain-size analysis approach is that the
722 Sundarbans, through the Dhanchi Island example presented in this study reflects a locally
723 segmented & temporally complex system that does not fall into a singular regime
724 classification given the complex relationship that is exhibited by tidal variability (Hanebuth
725 et al., 2012). Furthermore, although sediments may undergo reworking, what has been
726 found is a predominantly terrestrial source for sediments present in the Sundarbans; this
727 does not fit closely with the implication that the Sundarbans are ‘sediment starved’ as
728 outlined by Gao and Collins (2014). Rather, geographically (Milliman and Farnsworth,
729 2011) and climatically (Liu et al., 2000; Gao and Collins, 2014) variable processes operate
730 in producing a complex depositional environment. Sedimentary facies variability in the
731 form of tidal processes can only be inferred in this study by the diminished calcium
732 variability found. These tidal processes do not appear to operate in isolation and may be
733 coupled to some form of monsoonal variability in the manner proposed by Liu et al. (2000)
734 for Asia and by Rogers et al. (2013) more specifically applied to the Sundarbans.

735 The utility of these calibrated geochemical proxies from the Sundarbans is
736 illustrated in Fig. 6 from the Dhanchi Island core. Through plotting the log-ratio pairs there
737 appears to be some oscillating trend throughout the core, in particular with log-transformed
738 Zr and Rb (see Fig. 5). There is a steady decline in Zr nearer to the top of the core (from a
739 depth of 450 cm to the core surface). This indicates a decline in zirconium, and potentially
740 an increase in rubidium. It is only through CoDa however that such a trend can be
741 illustrated in the first place as ratios by themselves possess the undesirable property of
742 asymmetry, meaning that conclusions based on evaluation of the ratio of two elements
743 (e.g., A/B), cannot be directly translated into equivalent statements about B/A (Weltje,
744 2012; Weltje et al., 2015). Taking this approach further, the Rb and K log-transformed data
745 shown in Fig. 5, appear to reflect the trend found in rubidium and zirconium; with an
746 oscillating trend throughout the core. However, there does not appear to be any discernible
747 increase or decrease in rubidium up core, with the log-ratio data remaining somewhat
748 unvarying.

749 The overarching trend would suggest a strong relationship between zirconium and
750 coarse grained sediment, as these sites are considered to reflect upward fining sequences
751 (e.g., Allison et al., 2003; Flood et al., 2015). In particular the trend consists of coarse/very
752 coarse-silt and sand with a concomitant relationship between coarse clay and
753 medium/coarse-silt for rubidium. Furthermore, the variability of rubidium with potassium
754 would suggest an unvarying relationship between the fine-grained sediments. This might
755 indicate that fine-grained provenance is tied to rubidium and potassium, with coarse
756 grained sediment provenance strongly linked to zirconium. Ca geochemistry (shown in Fig.
757 5) may be linked to some external environmental control, such as sea-level or tidal

758 inundation as calcium is generally only present in liquid form in the marine environment.
759 Ca appears to correlate negatively with Zr, Ti, K, and Rb in the Dhanchi Island core. This
760 decline in calcium with concomitant increases in Zr, Ti, K, and Rb (Fig. 5) may be
761 interpreted as reflecting terrestrial derived sediment flux with diminished marine or
762 carbonate deposition (or at least a marine source of variability). Terrestrial sediment flux
763 therefore appears to be uncorrelated with Ca, implying that sediment provenance is
764 independent of a marine or tidally driven source.

765

766 **7. CONCLUSION**

767 Through CoDa it has been possible to calibrate core-scan derived XRF data, and produce
768 useful elemental proxies for analysing a clastic sedimentary environment. When using the
769 LRCE calibration model coefficients to examine such clastic sedimentary environments in
770 the Indian Sundarbans quantified data outputs are possible, and combined with grain-size
771 data a broader understanding of the depositional environment is possible. The lack of a full
772 elemental suite, attributed to a poorer linear fit between weighted concentration and
773 intensity data, does not detract from the approach to XRF core-scan calibration. The
774 elements that have been calibrated through the LRCE in this study may be used to
775 demonstrate provenance (e.g., Zr, Rb, Ti, etc.) and processes of sedimentation (e.g., Ca) in
776 this area of the G-B delta. Ca has been found to be the optimum log-ratio denominator, and
777 when examined in a log-ratio framework, it may be used to distinguish between marine-
778 terrestrial sediment fluxes in a high-resolution XRF dataset. Future research should focus
779 on building a more constrained calibration model for the G-B delta, with more sedimentary
780 cores from different facies sequences and employing other geochemical analyses tools

781 (e.g., ICP-OES/MS). The LRCE & PLS approaches applied in this study for calibration of
782 sediments represent a robust application of the principles of CoDa, and it is recommended
783 that future studies in the G-B delta and other delta environments should seek to refine core-
784 scanning XRF and grain-size analysis in light of the approaches outlined in this study.

785

786 **ACKNOWLEDGEMENTS**

787 RPF acknowledges the support provided by a Research Studentship from the Department
788 for Employment and Learning (Northern Ireland) and the Department of Education and
789 Science's Higher Education Grant Scheme (ROI) provided through Laois County Council
790 (ROI). RPF also acknowledges the School of Geography, Archaeology and Palaeoecology
791 (GAP), Queen's University, Belfast (QUB) for the fieldwork support provided by their
792 Soulby Research Fund. RPF acknowledges the assistance and technical support provided
793 by Mike Dobby (formerly of Bruker Instruments UK Ltd.), John Meneely and Patricia
794 Warke (QUB), Ciara Fleming, Clare Ní Cholmáin, and David Colgan (UCD). The authors
795 would like to thank the three anonymous reviewers for the constructive comments and help
796 in improving the quality of this manuscript.

797

798 **Reference list**

799 Aitchison, J., 1982. The statistical analysis of compositional data (with discussion). *J. R.*
800 *Stat. Soc. Ser. B* 44, 139–177.

801 Aitchison, J., 1986. *The Statistical Analysis of Compositional Data*. Chapman and Hall,
802 London. 416 pp.

803 Allison, M.A. 1998a. Geologic framework and environmental status of the Ganges-
804 Brahmaputra delta. *Journal of Coastal Research* 14, 826–836.

805 Allison, M.A., 1998b. Historical changes in the Ganges-Brahmaputra delta. *Journal of*
806 *Coastal Research* 14, 1269–1275.

807 Allison, M.A., Khan, S.R., Goodbred Jr., S.L., Kuehl, S.A., 2003. Stratigraphic evolution
808 of the late Holocene Ganges-Brahmaputra lower delta plain. *Sedimentary Geology*
809 155, 317–342.

810 Bhattacharyya, S., Pethick, J., Sensarma, K. 2013. Managerial response to sea level rise in
811 the tidal estuaries of the Indian Sundarban: a geomorphological approach. In Xun,
812 W., Whittington, D. (Eds.) *Water Policy Journal: Special Edition: The Ganges. Basin*
813 *Water Policy* 15, pp. 51–74.

814 Bjørlykke, K., 2010. Chapter 3 Sedimentary Geochemistry: How Sediments are Produced.
815 In Bjørlykke, K. (ed.). *Petroleum geoscience: From sedimentary environments to*
816 *rock physics*. Heidelberg, Springer, 508 pp.

817 Bloemsma, M.R. (2010) *Semi-Automatic Core Characterisation based on Geochemical*
818 *Logging Data*, Unpublished M.Sc. Thesis: Delft University of Technology.

819 Bloemsma, M.R. (2015) *Development of a Modelling Framework for Core Data*
820 *Integration using XRF Scanning*, Unpublished Ph.D. Thesis: Delft University of
821 Technology.

822 Bloemsma, M.R., Zabel, M., Stuut, J.B.W., Tjallingii, R., Collins, J.A., Weltje, G.J. (2012)
823 'Modelling the joint variability of grain-size and chemical composition in sediments',
824 *Sedimentary Geology*, 280, pp. 135-148.

825 Croudace, I.W., Rindby, A., Rothwell, R.G., 2006. ITRAX: description and evaluation of
826 a new multi-function X-ray core scanner. In: Rothwell, R.G. (Ed.), *New Techniques*
827 *in Sediment Core Analysis*. Special Publication, vol. 267. Geological Society,
828 London, pp. 51–63.

829 Dalrymple, R.W. and Choi, K., 2007. Morphologic and facies trends through the fluvial–
830 marine transition in tide-dominated depositional systems: a schematic framework for
831 environmental and sequence-stratigraphic interpretation. *Earth-Science Reviews*,
832 81(3), pp. 135-174.

833 De Vries, J.L., Vrebos, B.A.R., 2002. Quantification of infinitely thick specimens by XRF
834 analysis. In van Grieken, R.E., Markovicz, A.A. (Eds.), *Handbook of X-Ray*
835 *Spectrometry*, Second Edition. Marcel Dekker, New York, pp. 341–405.

836 Flood, R.P., Orford, J.D., McKinley, J.M., Roberson, S., 2015. Effective grain-size
837 distribution analysis for interpretation of tidal–deltaic facies: West Bengal
838 Sundarbans. *Sedimentary Geology*, 318, 58-74.

839 Goodbred Jr., S.L., Kuehl, S.A., 2000. The significance of large sediment supply, active
840 tectonism and eustasy on margin sequence development: Late Quaternary
841 stratigraphy and evolution of the Ganges-Brahmaputra delta. *Sedimentary Geology*
842 133, 227–248.

843 Jansen, J.H.F., Van der Gaast, S.J., Koster, B., Vaars, A.J., 1998. CORTEX, a shipboard
844 XRF scanner for element analyses in split sediment cores. *Quat. Res.* 151, 143–153.

845 Jenkins, R., 1999. *X-Ray Fluorescence Spectroscopy*, Second Edition. Wiley & Sons, New
846 York. 207 pp.

847 Nesbitt, H.W., Young, G.M., 1984. Prediction of some weathering trends of plutonic and
848 volcanic rocks based on thermodynamic and kinetic considerations. *Geochimica et*
849 *Cosmochimica Acta* 48, 1523-1548.

850 Potts, P.J., 1987. *Handbook of Silicate Rock Analysis*. Blackie, Glasgow. 622 pp.

851 Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P., 1994. *Numerical Recipes*
852 *in FORTRAN: The Art of Scientific Computing*, Second Edition. University Press,
853 Cambridge. 963 pp.

854 Ramsey, M.H., Potts, P.J., Webb, P.C., Watkins, P., Watson, J.S., Coles, B.J., 1995. An
855 objective assessment of analytical method precision: comparison of ICP-AES and
856 XRF for the analysis of silicate rocks. *Chem. Geol.* 124, 1–19.

857 Richter, T.O., Van der Gaast, S., Koster, B., Vaars, A., Gieles, R., De Stigter, H., De Haas,
858 H., van Weering, T.C.E., 2006. The Avaatech XRF core scanner: technical
859 description and applications to NE Atlantic sediments. In: Rothwell, R.G. (Ed.), *New*
860 *Techniques in Sediment Core Analysis*. Special Publication, vol. 267. Geological
861 Society, London, pp. 39–50.

862 Rogers, K.G., Goodbred Jr., S.L., Mondal, D.R., 2013. Monsoon sedimentation on the
863 ‘abandoned’ tide-influenced Ganges-Brahmaputra delta plain. *Estuarine, Coastal and*
864 *Shelf Science* 131, 297–309.

865 Rothwell, R.G., Hoogakker, B., Thomson, J., Croudace, I.W., Frenz, M., 2006. Turbidite
866 emplacement on the southern Balearic Abyssal Plain (western Mediterranean Sea)
867 during Marine Isotope Stages 1-3: an application of ITRAX XRF scanning of
868 sediment cores to lithostratigraphic analysis. In: Rothwell, R.G. (Ed.), *New*

869 Techniques in Sediment Core Analysis. Special Publication, vol. 267. Geological
870 Society, London, pp. 79–98.

871 Rowe, H., Hughes, N., Robinson, K., 2012. The quantification and application of handheld
872 energy-dispersive x-ray fluorescence (ED-XRF) in mudrock chemostratigraphy and
873 geochemistry. *Chemical Geology* 324–325, 122–131.

874 Ryan, P., 2014. Environmental and low temperature geochemistry. New York, John Wiley
875 & Sons, 416 pp.

876 Thomson, J., Croudace, I.W., Rothwell, R.G., 2006. A geochemical application of the
877 ITRAX scanner to a sediment core containing eastern Mediterranean sapropel units.
878 In: Rothwell, R.G. (Ed.), *New Techniques in Sediment Core Analysis*. Special
879 Publication, vol. 267. Geological Society, London, pp. 65–77.

880 Weltje, G.J., Bloemsa, M.R., Tjallingii, R., Heslop, D., Röhl, U., Croudace, I.W., 2015.
881 Prediction of geochemical composition from XRF-core-scanner data: A new
882 multivariate approach including automatic selection of calibration samples and
883 quantification of uncertainties. In Croudace, I.W., and Rothwell, R.G., (eds.) *Micro-
884 XRF Studies of Sediment Cores: Applications of a non-destructive tool for the
885 environmental sciences*. Dordrecht, NL, Springer, 507-534. (Developments in
886 *Paleoenvironmental Research*, 17).

887 Weltje, G.J., Tjallingii, R., 2008. Calibration of XRF core scanners for quantitative
888 geochemical logging of sediment cores: theory and application. *Earth and Planetary
889 Science Letters*, 274(3), 423-438.

890 Weltje, G.J., 2012. Quantitative models of sediment generation and provenance: State of
891 the art and future developments. *Sedimentary Geology*, 280, 4-20.

892

893 **List of Tables**

894 Table 1: Tally of reported values, minimum values, and maximum values of elemental
895 concentrations (%) for the suite of calibration international geochemical reference
896 standards used in the Bruker AXS S1CalProcess calibration software and subsequent
897 LRCE

898 Table 2: Alpha (α) LRCE model parameters

899 Table 3: Beta (β) LRCE model parameters

900 Table 4: Residual variance of regression of Sundarbans dataset

901 Table 5: Residual variance of predicted of Sundarbans dataset

902 Table 6: R^2 values of LRCE (Ca R^2 values highlighted in bold, representative of optimum
903 log-ratio denominator) of Sundarbans dataset

904

905 **List of Figures**

906

907 Fig. 1a Graphical representation of the rationale behind the calibration approach. Further
908 details are provided in the text (adapted from Bloemsmma et al., 2012)

909 Fig. 1 Extent of the G-B tidal delta complex, (a) West Bengal Sundarbans (India), (b) East
910 Bengal Sundarbans (Bangladesh), and (c) Kuakata Peninsula (Bangladesh) (adapted from
911 Rogers et al., 2013)

912 Fig. 2 Sites cored in the West Bengal Sundarbans, India (November 2010) (after Flood et
913 al., 2015)

914 Fig. 3 Results of the calibration of the ED-XRF data, with the reference bulk composition
915 (x-axis) and predicted bulk chemistry (y-axis) of discrete samples from the Dhanchi-2,
916 Bonnie Camp, and Sajnekhali Island cores. Calcium (Ca) is shown in (a), iron (Fe) is shown
917 in (b), potassium is shown in (c), rubidium is shown in (d), titanium is shown in (e), and
918 zirconium (Zr) is shown in (f)

919 Fig. 4 Linear fit between log-ratio measured intensities and log-ratio of the reference bulk
920 chemistry with Ca as the optimum log-ratio denominator from the discrete samples of the
921 Dhanchi-2, Bonnie Camp, and Sajnekhali Island cores. Fit of iron and calcium shown in
922 (a), fit of potassium and calcium shown in (b), fit of rubidium and calcium shown in (c),
923 fit of titanium and calcium shown in (d), and fit of zirconium and calcium shown in (e)

924 Fig. 5 Partial least squares (PLS) model of grain-size and calibrated geochemistry for the
925 Dhanchi Island core

926 Fig. 6 log-ratio elemental logs from the Dhanchi Island core