

Airborne radiometric survey data and a DTM as covariates for regional scale mapping of soil organic carbon across Northern Ireland.

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1 Summary

2 Soil scientists require cost-effective methods to make accurate regional predictions of
3 soil organic carbon (SOC) content. We assess the suitability of airborne radiometric
4 data and digital elevation data as covariates to improve the precision of predictions of
5 SOC from an intensive survey in Northern Ireland. Radiometric data (K band) and, to
6 a lesser extent, altitude are shown to increase the precision of SOC predictions when
7 they are included in linear mixed models of SOC variation. However the statistical
8 distribution of SOC in Northern Ireland is bimodal and therefore unsuitable for geo-
9 statistical analysis unless the two peaks can be accounted for by the fixed effects in
10 the linear mixed models. The upper peak in the distribution is due to areas of peat
11 soils. This problem may be partly countered if soil maps are used to classify areas of
12 Northern Ireland according to their expected SOC content and then different models
13 are fitted to each of these classes. Here we divide the soil in Northern Ireland into three
14 classes, namely mineral, organo mineral and peat. This leads to a further increase in
15 the precision of SOC predictions and the median square error is 2.2 %². However a
16 substantial number of our observations appear to be mis-classified and therefore the
17 mean squared error in the predictions is larger (30.6 %²) since it is dominated by large
18 errors due to mis-classification. Further improvement in SOC prediction may therefore
19 be possible if better delineation between areas of large SOC (peat) and small SOC
20 (non-peat) could be achieved.

21 Introduction

22 Soil organic carbon (SOC) is one of the most important constituents of the soil im-
23 parting structural stability, increased water holding capacity, acting as a source of
24 nutrients, and as a store of terrestrial carbon. The quantity of organic carbon in the
25 top 30 cm of the soil profile typically reflects the interplay of several factors including
26 climate (annual rainfall and temperature), elevation, local topography and land use.
27 Soil scientists require cost-effective methods to make accurate estimates of SOC con-
28 tent, which could be used to estimate soil-related carbon-dioxide emissions under the
29 UNFCCC (United Nations Framework Convention on Climate Change).

30 Traditional, grid-based sampling, with laboratory measurement and univariate
31 interpolation of SOC is subject to large estimation uncertainties at unsampled points.
32 These can be significantly reduced if intensive, secondary covariates such as data from
33 remote sensors are used for prediction by cokriging (McBratney & Webster, 1983),
34 regression kriging (Odeh *et al.*, 1995), or the use of linear mixed models (Lark *et*
35 *al.*, 2006). A variety of covariates have been shown to improve prediction of SOC.
36 For example, terrain attributes and land use have been shown to be correlated with
37 SOC at multiple scales (Mueller & Pierce, 2003), whilst hyperspectral airborne data
38 (Selige *et al.*, 2006), surface reflectance (Chen *et al.*, 2000) and electrical conductivity
39 (Simbahan *et al.*, 2006) was shown to be correlated with SOC in arable soils over scales
40 from a few to tens of kilometres. These secondary covariates are likely to be more or
41 less applicable in various types of soil environment (e.g. vegetated and unvegetated),
42 and at differing scales.

43 Another potential covariate which can be used in both vegetated and unvege-
44 tated environments are measurements of gamma radiation from the decay of natural
45 radionuclides in the soil. This radiation can be measured using airborne sensors; the
46 data correspond to the top 50 cm of a mineral-dominated soil, and depths of up to
47 one metre in low density materials such as peat. Airborne radiometric survey has been
48 used extensively in Australia for digital soil mapping (Cook *et al.*, 1996). Typically

49 the data on emissions are processed to generate values from three spectral bands which
50 correspond to the decay of potassium (K), thorium (Th) and uranium (U). In a recent
51 study in Australia, Minasny *et al.* (2006) combined data on radiometric K, land use
52 and terrain attributes to develop a depth-based function for estimation of SOC.

53 There are two reasons why we might expect spatial correlation between gamma
54 emissions from the soil and its SOC content in the wetter landscape of north-western
55 Europe. First, the well-established spatial correlation between gamma-ray attenuation
56 and soil moisture (Carroll, 1981) extends to SOC because the latter accumulates in
57 soils which are wet or waterlogged for much of the year. Water reduces the intensity
58 of gamma-rays significantly more than air; a 10% increase in soil water leads to a
59 reduction in K gamma radiation by the same amount (Minty, 1979). Second, for soil
60 with a wide range of SOC contents, the mineral content (and gamma emission) will be
61 smaller where organic matter contents are larger for soils derived from the same parent
62 material (with similar mineral composition). As the organic matter content rises, the
63 mineral content declines in a simple, two-component composition. It may be possible
64 to use these relationships to improve SOC estimation in organic rich soils such as those
65 of the Arctic Tundra (Smith *et al.*, 2004) or temperate latitudes such as Scotland and
66 Wales (Scottish Executive, 2007), so this approach warrants further investigation.

67 There have been relatively few regional-scale, airborne radiometric surveys of
68 landscapes in which SOC contents represent significant terrestrial carbon stores – such
69 surveys have been undertaken in Finland (Lilja & Nevalainen, 2005) and Sweden (Lun-
70 den *et al.*, 2001). One example is the recently-completed Tellus survey of Northern
71 Ireland (13 550 km²), in which SOC measurements and airborne geophysical surveys
72 (including the detection of gamma emitting radiation) were undertaken at around the
73 same time. The aim of this paper is to determine to what extent airborne radiometric
74 survey data and terrain attributes can be used as secondary covariates to improve esti-
75 mates of SOC across the landscape of Northern Ireland. A second objective is to assess
76 whether improvements in SOC estimation based on these covariates differs markedly

77 for the three major soil types across this landscape. Also we explore whether the
78 inclusion of information on radiometric K means that the number of observations of
79 SOC required for adequate predictions is reduced. We discuss the implications of our
80 findings for improving the estimation of SOC in cognate landscapes and some potential
81 limitations to the application of airborne radiometric survey for this purpose.

82 **Methods**

83 *Study region and surveys*

84 The soils of Northern Ireland have been described by Cruickshank (1997) and comprise
85 poorly-drained gley soils (54%), peats and rankers (24%) and freely drained soils (16%)
86 – see Figure 1. In the soil surveys of Northern Ireland described by Cruickshank (1997)
87 soil inspection pits were dug to between 80 and 90 cm. The larger proportion of gley
88 soils by comparison to England, Wales and Scotland reflects the wetter environment
89 of Northern Ireland, where average annual rainfall for the vast majority of the region
90 is greater than 1 m, with a minimum of around 0.75 m. Large areas of the region
91 are more than 100 m above sea level, with a maximum attitude around 850 m, whilst
92 central and eastern areas have lower elevations (<40 m).

93 The airborne geophysical survey of the whole of Northern Ireland was flown in
94 the summers of 2005 and 2006. Radiometric data were collected with an Exploranium
95 GR820 256 channel gamma spectrometer system comprising 32 litres of downward
96 looking NaI(Tl) detectors and 8 litres of upward looking detectors. Data were collected
97 every second (approximately 70 m flight line distance). The gamma radiation measured
98 comes from a shallow surface layer of no more than about 30 cm in rock, although this
99 will increase for low-density unconsolidated materials, perhaps to a maximum of a few
100 metres in dry peat. The ground area or footprint, from which most of the contribution
101 of gamma radiation comes, has the form of an ellipse elongated in the flight direction.
102 For example, at 56 m altitude, 75% of the measured radiation will come from a width
103 of about 150 m, extending to around 220 m along the flight line (Pitkin & Duval, 1980).
104 Survey lines were spaced 200 m apart and orientated NNW or SSE (165 and 345 °), with

105 tie-lines 2000 m apart, and at right angles to the flight line directions, acquired only in
106 the early part of the survey. The flying height was 56 m above ground in rural areas.
107 Procedures for processing the airborne radiometric data were based on those described
108 in AGSO and IAEA reference manuals (Grasty & Minty, 1995; IAEA, 1991). The
109 processing included corrections for aircraft and cosmic background radiation, aircraft
110 altitude and spectral interactions. The corrected count rates were used to estimate
111 the concentration of the three radioelements across specific energy ranges (MeV): K
112 (1.37–1.57), U (1.66–1.86), Th (2.41 – 2.81). The survey yielded *ca.* 1.2 million values
113 for equivalent K(%) and Th (mg kg^{-1}), U (mg kg^{-1}) and man-made radionuclides,
114 predominantly ^{137}Cs , although we do not consider the latter in this paper.

115 To assess whether temporal fluctuations in soil moisture status during the pe-
116 riod of the airborne surveys was broadly representative of the long-term average, we
117 extracted from the MIDAS database (UK Meteorological Office) monthly rainfall data
118 (mm) throughout 2005 and 2006, along with average monthly rainfall between 1961
119 and 1990 for meteorological stations across Northern Ireland.

120 The soil geochemical survey was undertaken between July 2004 and March 2006.
121 A sample of topsoil was collected from a site in every other square kilometre of the Irish
122 National Grid, by simple random selection within each square, subject to the avoidance
123 of roads, tracks, railways, urban areas and other seriously disturbed ground. There were
124 6862 sample sites in total. At each site soil was taken with a hand auger from between
125 depths of 5 and 20 cm from five holes at the corners and centre of a square with a side of
126 length 20 m and combined to form a bulked sample. All samples of soil were air-dried
127 in a dedicated temperature controlled oven at 30°C for 2–3 days and disaggregated.
128 From each a 50-g sub-sample was ground in an agate planetary ball mill. The total
129 concentrations of 55 major and trace elements were determined in each sample by
130 wavelength and energy dispersive XRFS (X-Ray Fluorescence Spectrometry), although
131 we only consider K (%), Th (mg kg^{-1}) and U (mg kg^{-1}) in this study. Soil organic
132 carbon was estimated in each sample using loss-on-ignition analysis by heating a sub-

133 sample 450 °C for eight hours and multiplying the mass difference by 0.58 (Broadbent,
134 1953). The coefficient of variation for this method for 174 replicate analyses of a sample
135 standard was 3.6%.

136 The topographic data were a series of 50-m spaced observations for elevation
137 (m) covering Northern Ireland (Ordnance Survey of Northern Irelands data) based
138 on airborne, photogrammetric acquisition; 65% of the data are accurate to ± 1 metre.
139 Simple linear interpolators are often used to create continuous Digital Elevation Models
140 (DEMs; Moore *et al.*, 1991) from stereo, aerial photo-derived point elevation data. We
141 used inverse distance weighted (IDW) interpolation to form a DEM surface in ESRI
142 ArcMapTM.

143 We used the DEM to estimate Compound Topographic Index (CTI) in ArcInfo
144 WorkStationTM which has been shown to be correlated with SOC content (Moore *et al.*,
145 1993). We extracted values for elevation (m) and CTI for the soil sampling locations
146 by point intersection.

147 We used a spatial join procedure to associate each soil sampling observation with
148 its nearest radiometric survey observation. The median distance between the sample
149 sites and the corresponding radiometric measurement was 52 m, with an interquartile
150 range of 47 m showing that the soil sampling locations fall entirely within the support of
151 the airborne detector. We used digital versions of the (1:50,000) soil maps of Northern
152 Ireland to form a three-fold classification of the soil sampling locations (see Figure 1):
153 *organic soils* (SOC > 20 % and > 50 cm in thickness; peats), *organo mineral soils*
154 (with an organic surface horizon overlying mineral subsoil; peaty podzols, rankers and
155 humic-gleays) and *mineral soils* (no organic horizon and SOC < 10 %; brown-earths,
156 podzols, gleys and rankers).

157 *Exploratory analysis*

158 The appropriateness of using the airborne measurements of K, Th and U as auxiliary
159 information in a regional survey of SOC was initially explored by (i) comparing the
160 summary statistics with those of the corresponding ground based variables (Table 1)

161 and (ii) by calculating the correlation coefficients between the airborne and ground
 162 based variables and the estimates of SOC based upon LOI analysis (Table 2). Sim-
 163 ilarly we also explored the correlation of SOC with the two terrain variables. These
 164 exploratory analyses were the basis for deciding on the variables to include in our
 165 models of SOC variation.

166 We calculated total annual rainfall for a subset of 20 meteorological stations
 167 across Northern Ireland for both 2005 and 2006, the years in which the airborne surveys
 168 were flown. A comparison of these data with the long-term, average annual rainfall
 169 (1961-1990) indicated that they were of a similar magnitude. We also plotted monthly
 170 rainfall totals for observations from several meteorological stations during 2005 and
 171 2006 and compared these to the long-term monthly averages (1961-1990). There was no
 172 compelling evidence that rainfall throughout 2005 or 2006 was spatially or temporally
 173 anomalous and so we feel justified in assuming that the soil moisture regime over the
 174 period of the airborne survey was representative of its long-term variation.

175 *Spatial analysis: linear mixed models*

176 A prediction set of 3000 observations was randomly extracted from the SOC data set
 177 and the remaining observations were used as a validation set. We considered linear
 178 mixed models of the form

$$\mathbf{z} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\eta}, \quad (1)$$

179 where \mathbf{X} is an $n \times p$ design matrix containing values of p auxiliary variables or fixed
 180 effects, $\boldsymbol{\beta}$ is the length p vector containing the coefficients of the fixed effects and
 181 $\boldsymbol{\eta} \sim \mathcal{N}(0, \mathbf{V})$ is a vector of spatially correlated random residuals with a Gaussian
 182 distribution and covariance matrix \mathbf{V} . We assume that the spatial correlation of $\boldsymbol{\eta}$ can
 183 be represented by an isotropic nested nugget and Matérn variogram model

$$\begin{aligned} \gamma(h) &= c_0 + c_1 \left\{ 1 - \frac{1}{2^{\nu-1}} \Gamma(\nu) \left(\frac{h}{a}\right)^{\nu} K_{\nu}\left(\frac{h}{a}\right) \right\} \text{ for } h > 0, \\ \gamma(h) &= 0 \text{ for } h = 0, \end{aligned} \quad (2)$$

184 where h is the lag distance separating observation pairs, ν is a smoothing parameter,

185 K_ν a modified Bessel function of the second kind of order ν (Abramowitz & Stegun,
 186 1972) and Γ is the gamma function. Bessel and gamma functions may be calculated by
 187 many standard numerical packages such as IMSL (1994). The smoothness parameter
 188 gives the Matérn function greater flexibility for modelling the spatial covariance than
 189 more commonly-used models such as the exponential and spherical models (Webster
 190 & Oliver, 2007). For each fixed effects matrix we calculated $\hat{\beta}$, the estimate of β , by
 191 ordinary least squares, subtracted $\mathbf{X}\hat{\beta}$ from the data and used the method of moments
 192 (Matheron, 1962) to fit the vector of variogram parameters $\alpha = (c_0, c_1, a, \nu)$. Following
 193 Cressie (1985), when fitting the variogram model to the experimental variogram by least
 194 squares we applied weights

$$w_i = \frac{N(h_i)}{\hat{\gamma}(h_i)^2}, \quad (3)$$

195 where $N(h_i)$ is the number of observation pairs within the bin centred on lag h_i and
 196 $\hat{\gamma}(h_i)$ is the experimental variogram for h_i . Generally the REML estimator is recom-
 197 mended for fitting linear mixed models (Lark *et al.*, 2006) because there is known to be
 198 some bias when the method of moments is applied. However for 3000 observations this
 199 bias will be very small and does not justify the prohibitive computation time required
 200 by REML.

201 We fitted a number of linear mixed models with different fixed effects to the
 202 prediction data to compare (i) the effectiveness of including different auxiliary variables
 203 as fixed effects (ii) the effectiveness of fitting a single model for all soil types with the
 204 effectiveness of fitting different models for each of our three broad soil classes and (iii)
 205 how the precision of the different linear mixed models varies with the intensity of SOC
 206 observations. The variables to be included as fixed effects were selected according to
 207 the findings of our exploratory analyses.

208 Each linear mixed model was fitted first to all the prediction data. The linear
 209 mixed models assume that the random effects are Gaussian and therefore we log trans-
 210 form the data if the skew is greater than 1 and this assumption is implausible (Webster
 211 & Oliver, 2007). We note that strictly we should test the skew once we have subtracted

212 the fixed effects from the data. However this could lead to the data being transformed
213 for some but not all of the models so in order to make fair comparisons between the
214 different models we decide whether to transform based upon the skew of the raw data.
215 The entire prediction set had skew equal to 2.03. Therefore a log transform was ap-
216 plied and the skew was reduced to 0.92. The empirical best linear unbiased predictor
217 (E-BLUP) was used to predict SOC content at the validation sites (Lark *et al.*, 2006).
218 To calculate the mean prediction in the original units – and the mean squared error
219 MSE between the predictions and observed SOC values at the validation sites – an
220 unbiased inverse log transform (Cressie, 2004) was performed.

221 The prediction and validation data were then divided into the three soil classes
222 according to our three-fold classification and separate models were fitted to the predic-
223 tion data from each class and the appropriate soil class model was used to predict SOC
224 content at each validation location by the E-BLUP. The skew for the SOC in mineral
225 soil was 3.94 which was reduced to 0.80 by applying a log transform. No transform was
226 applied to data from the organo mineral and peat soil classes because they had skew
227 of 0.86 and -0.53 respectively.

228 The values of SOC are substantially larger on peat soils than mineral soils and
229 sites at which the soil is mis-classified are likely to have large prediction errors which
230 will dominate the MSE. We therefore also record the median square error (MdSE) and
231 the MdSE based upon the back transform to the median prediction in the original
232 units.

233 This test was then repeated using random subsets of n_s of the prediction data
234 where $n_s = 100, 200, \dots, 2900$, to explore how the quality of the predictions at the
235 validation sites varies with the number of SOC observations.

236 Results

237 *Exploratory analysis*

238 The airborne radiometric estimates of K and Th were strongly correlated with their
239 measurements in the soil survey ($r=0.86$ and 0.80 respectively; Table 2) which demon-

240 strates that the airborne survey is an effective method for estimating these elements.
241 Airborne radiometric estimates of K exhibited a strong negative correlation with ground-
242 based estimates of SOC ($r = -0.51$); this correlation was stronger than for Th, U and
243 total counts. We therefore chose to include radiometric K as a fixed effect in a linear
244 mixed model of SOC. Furthermore, plots of radiometric K against SOC (not shown)
245 suggested that this relationship may be nonlinear and therefore the square of radio-
246 metric K (K^2) was also included as a fixed effect.

247 We also explored the correlation of SOC with the two terrain parameters: altitude
248 and compound topographic index (CTI). First we transformed the SOC data to a
249 more Gaussian distribution by taking natural logarithms; the transformed variable
250 had a skewness coefficient of 0.94. The correlation coefficients (r) between log SOC
251 and altitude and CTI were, respectively: 0.6 and -0.03. Given the strong positive
252 correlation between SOC and altitude we chose to include the latter as a fixed effect
253 in the estimation of SOC.

254 The histogram of the SOC observations across all soil types in Northern Ireland
255 is shown in Figure 2a. The distribution of SOC is bimodal. The main peak occurs
256 between 0 and 10 % and there is a secondary peak around 50 %, which corresponds to
257 peat soils. Bimodal distributions are not suited to geostatistical analyses and therefore
258 this histogram vindicates our decision to analyse mineral, organo mineral and peat
259 soils separately. We expect that mineral soils will have SOC less than 20 % and peat
260 soils will have SOC greater than 20 %; this is the threshold adopted in Northern
261 Ireland. According to the (1:50,000) soil map of Northern Ireland, 5552 (81.0 %) of
262 the observations are from mineral soils, 382 (5.6 %) are from organo mineral soils and
263 915 (13.4 %) are from peat soils. Figures 2 b, c and d show the distribution of SOC
264 for mineral, organo mineral and peat soils.

265 The largest peak in the organo mineral soils is for SOC less than 10 % but there is
266 a secondary peak greater than 50 %. Thus a substantial proportion of our observations
267 appear to be misclassified by the soil map. This is likely to be because the soil map

268 is unsuitable for recognising very local variations in soil type. The soil classification is
269 partially successful in separating the observations with large and small SOC and the
270 secondary peak is not evident in the mineral soil distribution. However, some larger
271 than expected SOC values remain in the mineral soil set (4 % of mineral soils have
272 SOC greater than 20 %). The majority of peat soil observations have SOC greater
273 than 40 % although 26 % of observations have SOC less than 20 %.

274 *Spatial analysis: linear mixed models*

275 The effectiveness of six different linear mixed models of SOC variation were compared.

276 The fixed effects for these models were:

277 Model 1 Constant (i. e. the mean),

278 Model 2 Constant and altitude,

279 Model 3 Constant and K,

280 Model 4 Constant, K and K^2 ,

281 Model 5 Constant, altitude and K,

282 Model 6 Constant, altitude, K and K^2 .

283 Figures 3-6 show the variograms fitted to residuals of all soils, mineral soils, organo
284 mineral soils and peat soils respectively. On the all soils variogram the sill variance is
285 largest when the fixed effects consist of a constant (the overall mean). The sill variance
286 is reduced when altitude is also included in the fixed effects and further reductions
287 are achieved by including radiometric K. The smallest variances are seen for Model 6.
288 A similar pattern is seen on the mineral soils variogram although the semi-variances
289 are substantially smaller for each model than the all soils variograms. For the organo
290 mineral and peat variograms the sill variances are again largest with constant fixed
291 effects and a greater reduction in these variances is achieved by including radiometric
292 K rather than altitude. There is some evidence of spatial correlation in the Model 1
293 (constant mean) variograms on organo mineral and peat soils but the proportion of
294 spatially correlated variation becomes smaller as other variables are added to the fixed
295 effects. This indicates that the spatial correlation has been resolved by the inclusion

296 of other variables in the fixed effects.

297 Figures 7-9 illustrate the different components of a single Model 6 linear mixed
298 model fitted on all soils types. The log SOC observations are presented in Figure 7, the
299 contributions from the fixed effects are presented in Figure 8 and the residuals between
300 the observations and fixed effect contributions are presented in Figure 9. The fixed
301 effects contain many of the large scale features of the observations such as large SOC
302 values in the NE, SE, SW and a cluster slightly NW of centre. The residuals show
303 less spatial structure, as would be expected from the almost all nugget variogram for
304 Model 6 in Figure 3.

305 The MSEs between the observations and predictions at the validation sites are
306 shown in Table 3 and the MdSEs in Table 4. We indicate the number of soil classes into
307 which the prediction set is divided for fitting of the linear mixed model. The first two
308 rows of each table show the errors upon predicting SOC over the entire validation set.
309 In the remaining six rows the validation set is divided according to the soil classification
310 and the errors for each classification are shown.

311 As variables are added to the fixed effects the MSEs and MdSEs generally decrease
312 in the same pattern as the semi-variances in Figures 3-6 with the largest decreases
313 occurring when radiometric K is added to the fixed effects. This illustrates that SOC
314 is correlated with altitude but more effective information comes from radiometric K.

315 The MSEs and MdSEs are smaller when separate models are fitted to each soil
316 class than when the soil classes are combined. For example the smallest MSE for
317 the model fitted to the entire prediction set is 41.08 %² whereas the smallest MSE
318 when three separate models are fitted is 30.38 %². The greatest improvement for three
319 models over one model is seen for peat, particularly when the fixed effects include
320 radiometric K. The MSEs for mineral soils when three models are fitted are slightly
321 larger than those from a single model. We suspect that this is an artefact due to
322 the large squared differences between predictions and observations which have been
323 mis-classified as mineral. To illustrate this Table 5 contains the MSEs for mineral

324 soils when only observations with SOC less than 20 % are included in the validation
325 set. Removing the observations from mineral soils which we assume are mis-classified
326 reduces the MSEs, and the MSEs for three models are now substantially less than those
327 for one model. The MdSEs are consistently smaller than the MSEs further illustrating
328 that the MSEs are dominated by classification errors.

329 Figure 9 compares root MSEs for SOC from Model 6 (the model which generally
330 had the smallest MSE), Model 2 (the model with the smallest MSE of those models
331 which did not include radiometric K as a fixed effect) and Model 1 (the model with no
332 auxiliary information) against n . In each of these plots, separate models are fitted for
333 each soil class. The results are combined to give the MSE across Northern Ireland in (a)
334 and plots (b), (c) and (d) show the absolute differences over mineral, organo mineral
335 and peat soils respectively. In each plot a substantial improvement upon including
336 radiometric K in the fixed effects is evident. We also note that the precision of our
337 predictions decreases very slowly as n decreases.

338 Discussion

339 The distribution of SOC will be bimodal over any study region which contains both
340 organic and mineral soils. Thus if we wish to map SOC over such a region we must
341 address the problem of applying geostatistics to bimodal distributions. By dividing the
342 study region into three soil classes based on a (1:50,000) soil map of Northern Ireland
343 we substantially improved the precision of SOC predictions across Northern Ireland.
344 However a proportion of soils appeared to be mis-classified. The errors at these sites
345 dominate the MSEs which are much larger than the corresponding MdSEs which are
346 more robust to a proportion of large errors due to mis-classification. Therefore further
347 improvements in regional predictions should be based upon improving our ability to
348 differentiate peat and non peat soils. Some mis-classification may be inevitable because
349 it is not practical to create soil maps which resolve very small scale deposits of organic
350 or mineral soil. This classification may be significantly improved by using airborne
351 hyperspectral data (McMorrow *et al.*, 2004) or satellite data (e.g. ASTER or Landsat).

352 Even without such improvements, the approach we describe could be applied to the
353 data from the Tellus survey in combination with data on soil bulk density to improve
354 current estimates of carbon pools across Northern Ireland, in which peat soils are
355 estimated to account for more than 50% of the total (Cruickshank *et al.*, 1998).

356 Further work is required to elucidate the factors influencing the airborne esti-
357 mates of radiometric K and its spatial correlation with SOC for each of the three soil
358 types. The two dominant factors which influence this are: i) the variation in mineral-K
359 content; this decreases with increasing quantities of soil organic matter, and ii) increas-
360 ing soil-moisture resulting in greater attenuation of the gamma signal from the soil.
361 This would require contemporaneous measurements of soil moisture content which we
362 do not have from the original survey.

363 There are likely to be limitations to the widespread application of airborne radio-
364 metric data as a covariate for mapping SOC. First, it relies upon a spatial correlation
365 between SOC and long-term (i.e. annual) soil moisture content which is only likely
366 to occur in certain combinations of climate, topography and land use where SOC has
367 accumulated above some minimum threshold. The soils of northern Europe include sig-
368 nificant areas with soils common to those in northern Ireland, particularly the Gleysols
369 and Histosols of northern Scandinavia, the Baltic States and Russia. Further work is
370 required to establish the utility of airborne radiometric data as a covariate for map-
371 ping SOC, particularly for the large area of Podzols across northern Europe (European
372 Soil Bureau Network, 2005). Second, patterns of antecedent rainfall conditions and the
373 quantity of precipitation during the airborne survey may cause unusually large temporal
374 and spatial variations in soil moisture contents across the study area. This may reduce
375 the degree of spatial correlation between SOC and the gamma radiation which is due to
376 greater attenuation of the latter where the ground is wetter and where carbon accumu-
377 lates. To address this potential limitation, it may be possible to ensure surveys are not
378 flown when significantly atypical soil moisture conditions occur, based on antecedent
379 rainfall data and medium-term precipitation forecasts. In addition, laboratory-based

380 soil column experiments, in which in-situ measurements of gamma radiation are made
381 under controlled soil moisture conditions for soils with range of SOC contents, could be
382 used to calibrate the relationship between airborne radiometric data and SOC based
383 on antecedent rainfall data. Finally, where the soil parent material contains very little
384 K (0.5 %), such as quartzite, the accuracy of airborne radiometric estimation of soil-K
385 may be insufficient. However, 90 % of European soils contain more than 0.83 % K (or
386 1 % K_2O ; Salminen, 2005) suggesting that for the vast majority of soils, accuracy near
387 the limit of detection is unlikely to be problematic.

388 One of the main applications of SOC maps is the estimation of carbon stocks.
389 Where soil carbon is concentrated in the upper horizons, radiometry may be partic-
390 ularly useful as a covariate as it measures gamma radiation from the upper 35 cm of
391 the solum. However, in deep organic-rich soils or areas of Arctic tundra where SOC
392 may be transported to depth by cryoturbation (Ping *et al.*, 1997), the utility of gamma
393 radiometry will be diminished because no information is provided for the deeper parts
394 of the soil profile.

395 **Conclusions**

396 Our results show that the precision of regional predictions of SOC across Northern
397 Ireland are substantially improved by including auxiliary information on radiometric
398 K from airborne surveys as fixed effects in a linear mixed model of SOC variation. To
399 a lesser extent the precision is also improved by including altitude in the linear mixed
400 model. We have also seen that the number of observations of SOC may be substantially
401 reduced with little cost in terms of the precision of the predictions. However the
402 MSEs between predictions and observations are still large even when radiometric K
403 and altitude are included in the linear mixed model. This is because SOC in Northern
404 Ireland has a bimodal distribution which is not suited to geostatistical analyses. After
405 separating the soil into three main classes (mineral, organo mineral and organic), the
406 MSEs are substantially reduced. However, large independent validation errors occur
407 at certain mis-classified sites where, for example, the soil map shows a mineral soil but

408 its SOC content indicates it is organic. Improvements in our ability to differentiate
409 between mineral and organic-rich soils are required to make better predictions of the
410 SOC at the regional scale.

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For Peer Review

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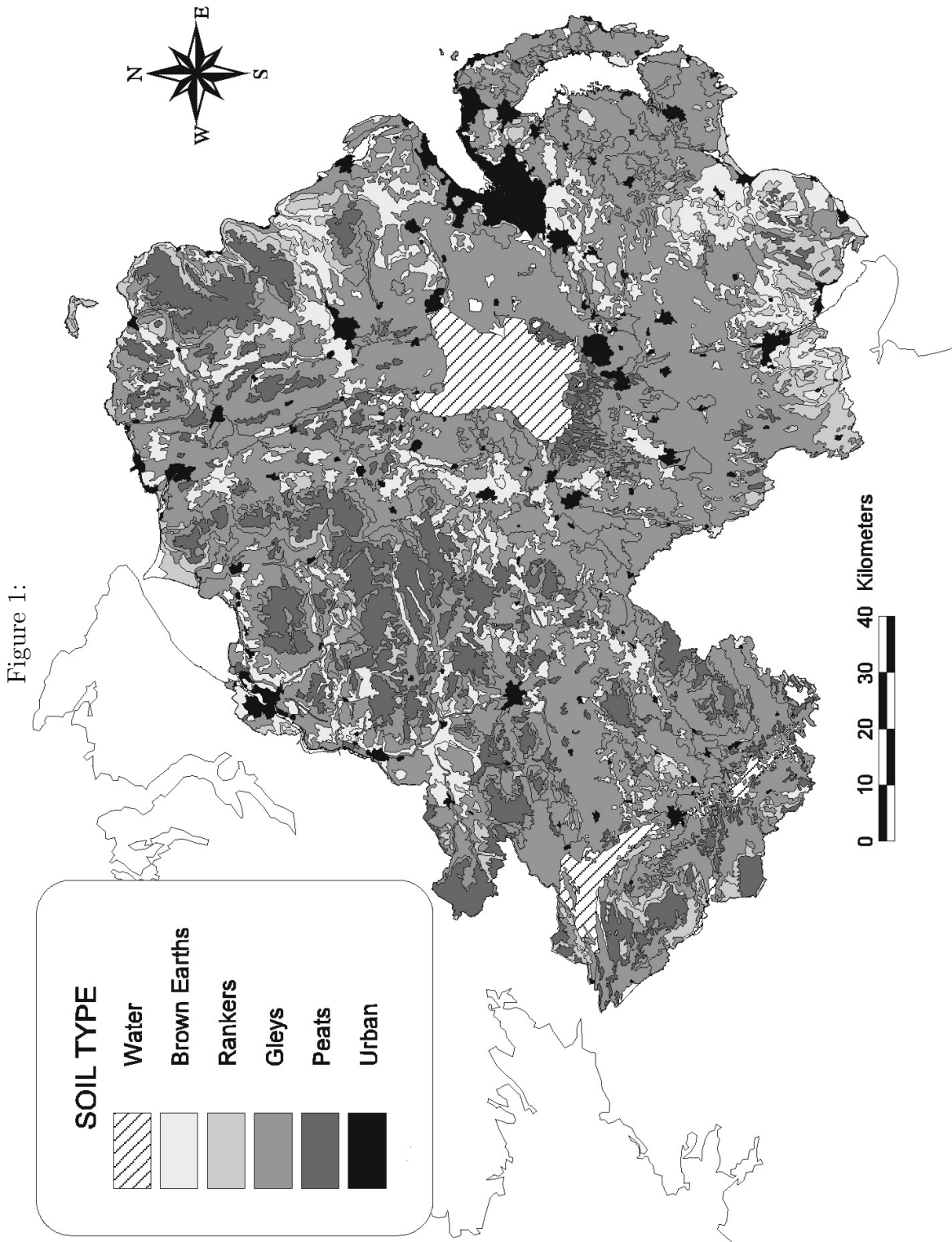


Figure 1:

Figure 2:

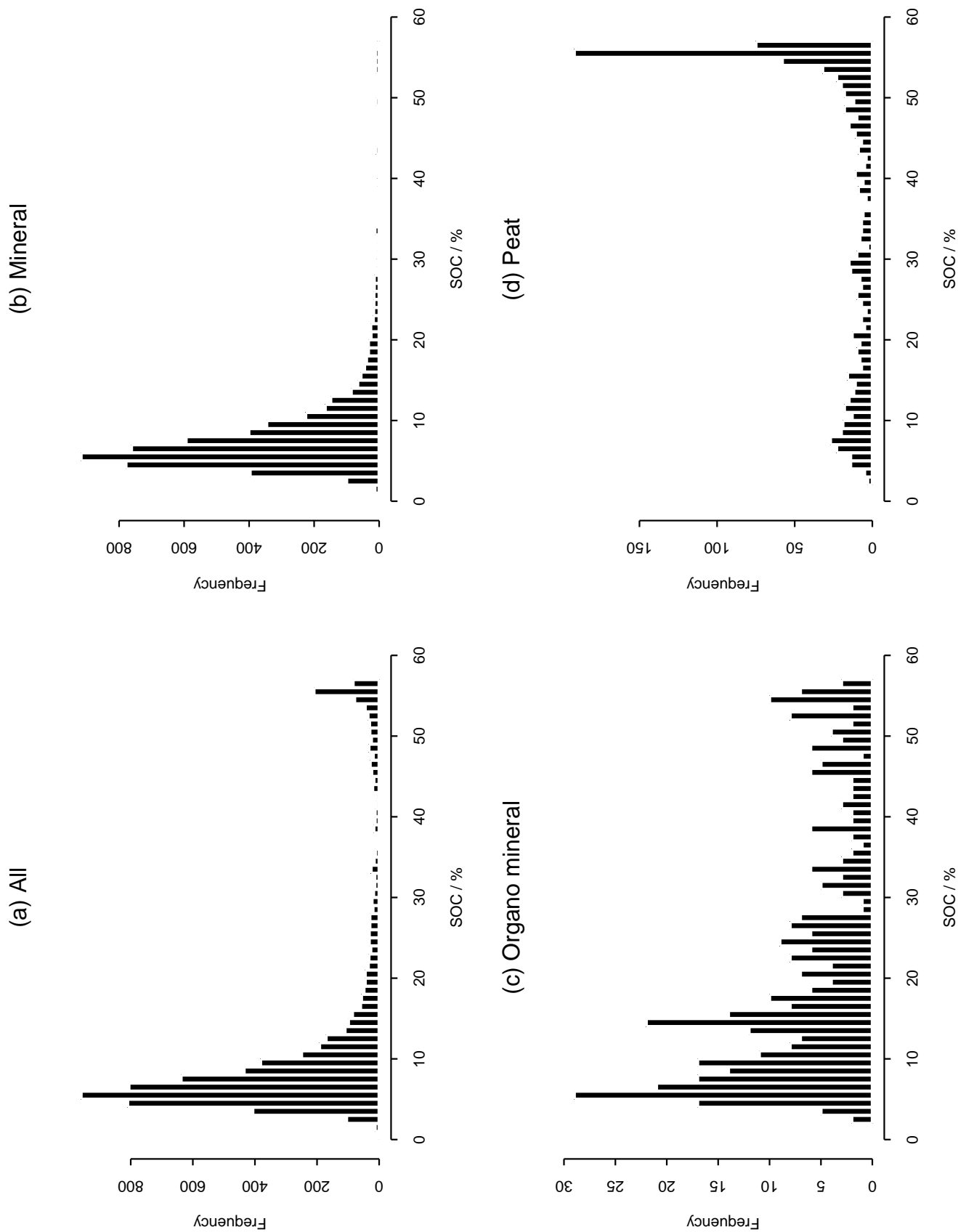


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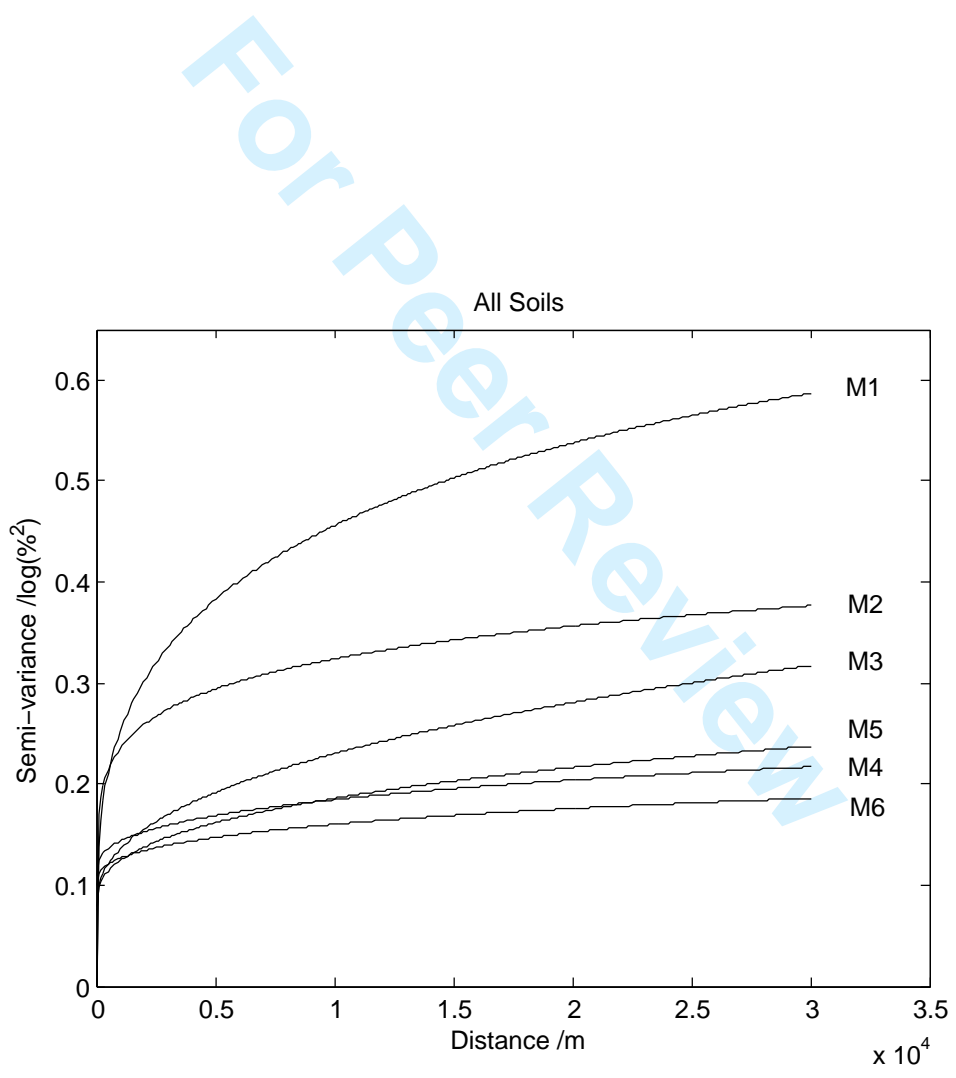


Figure 4:

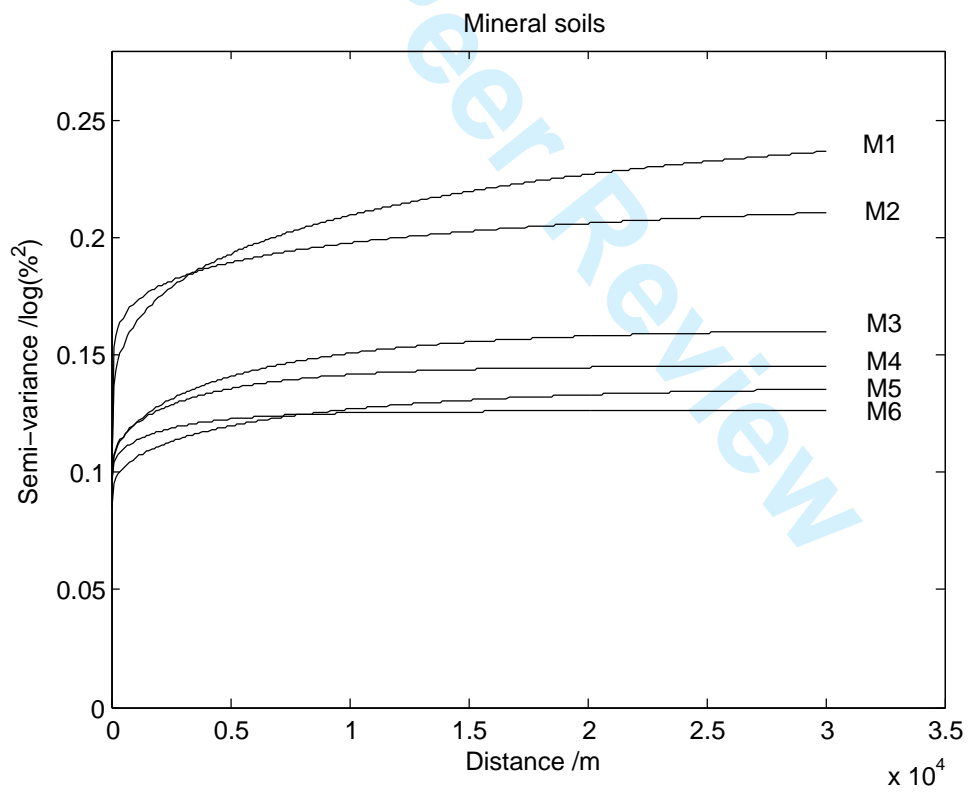


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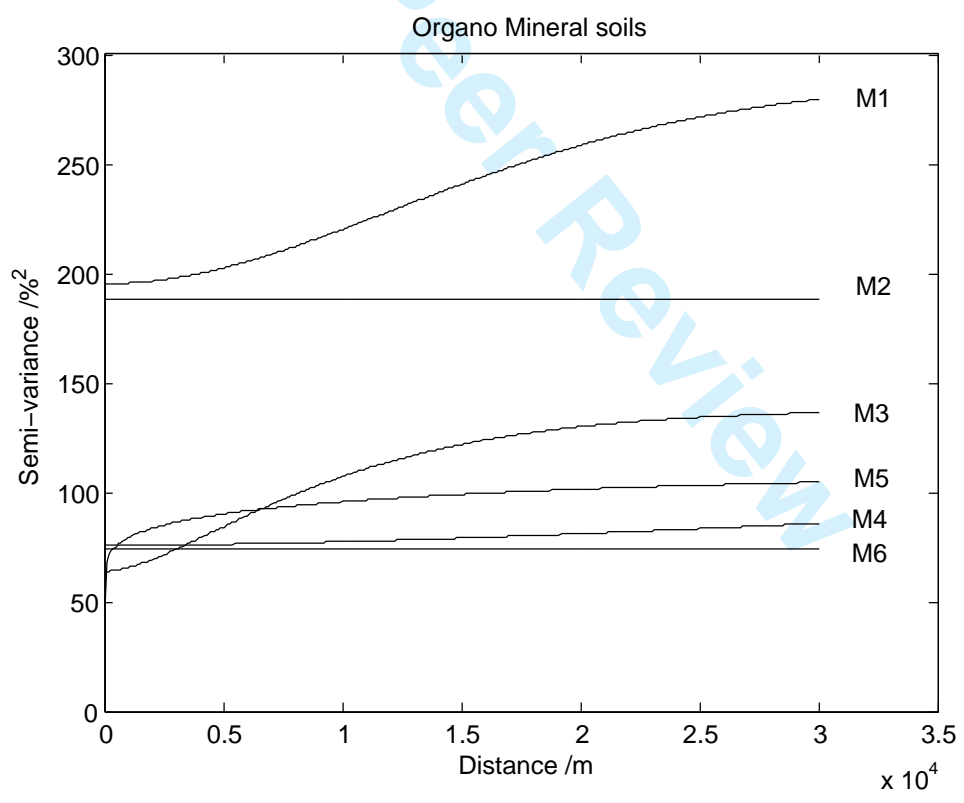
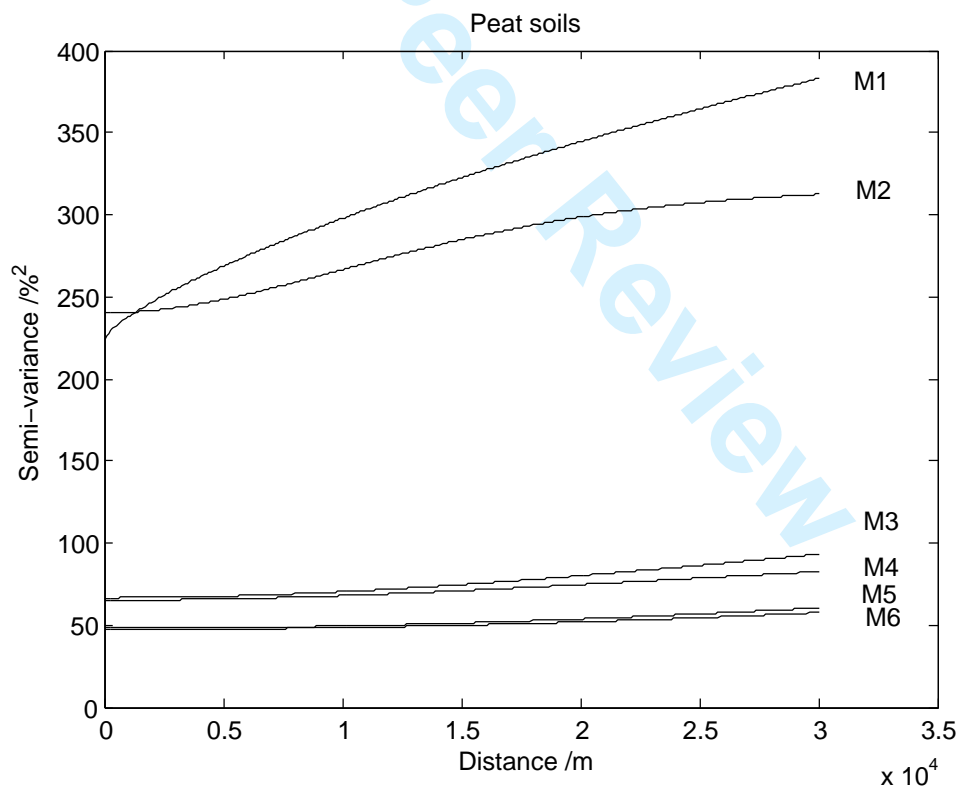
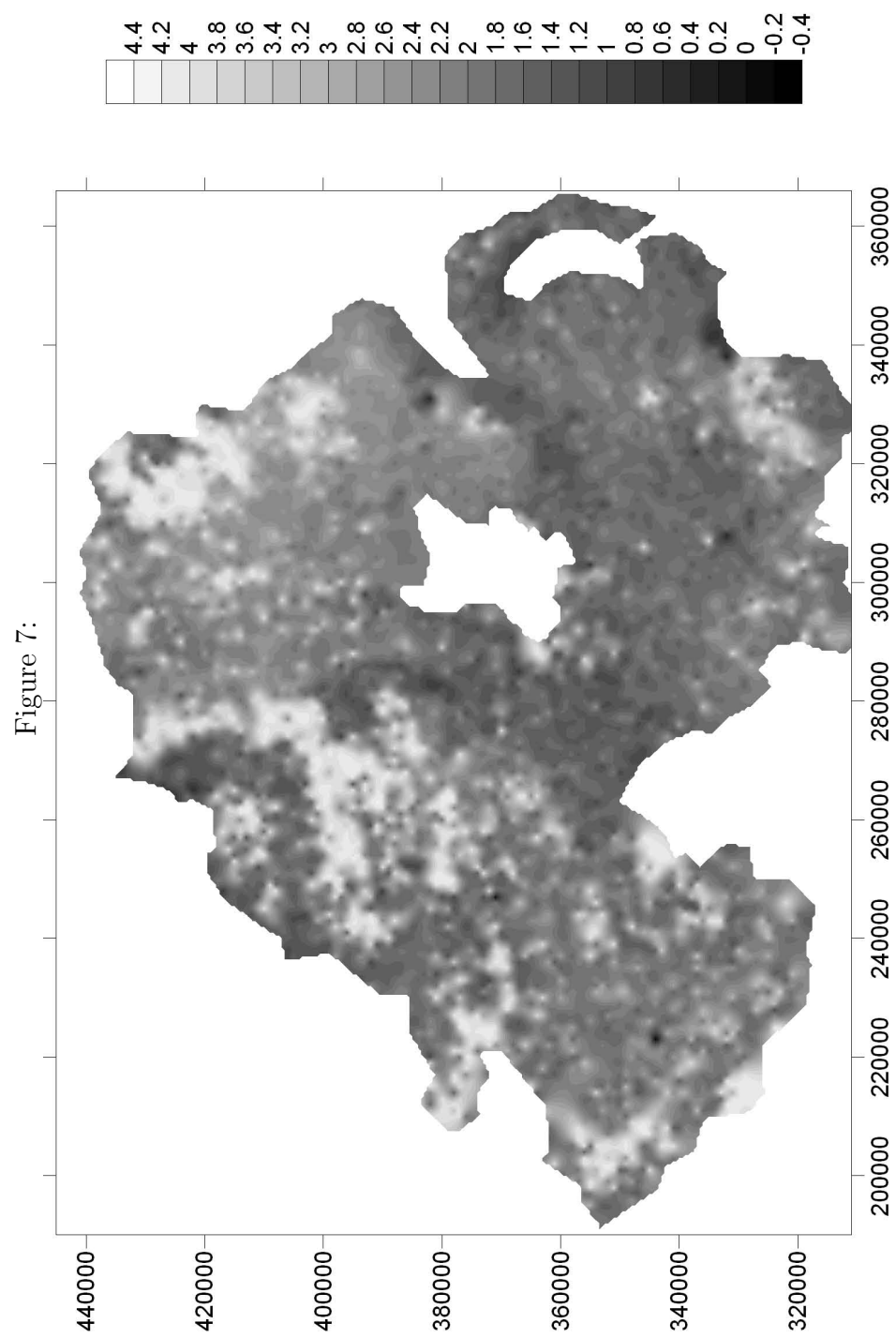
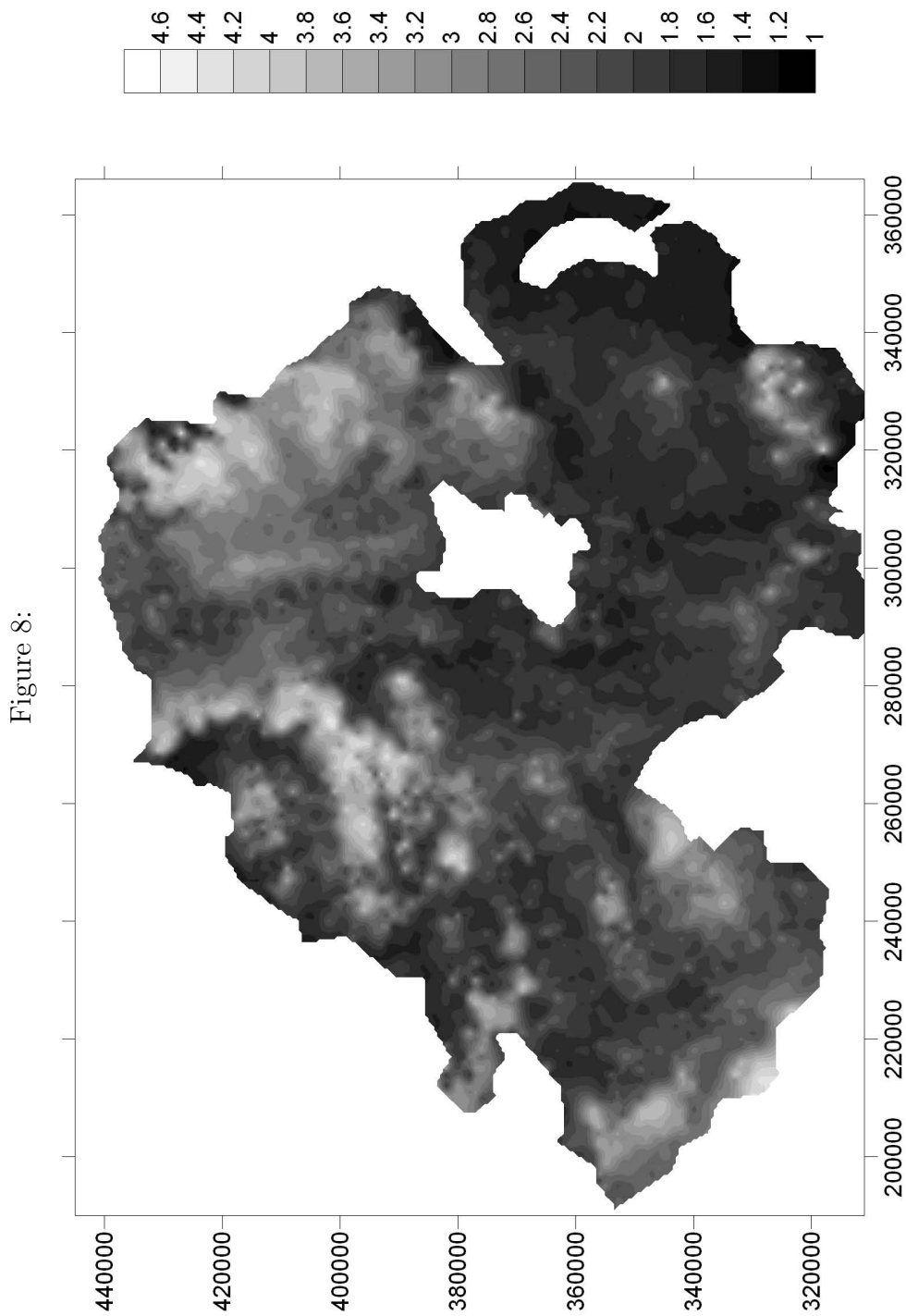


Figure 6:







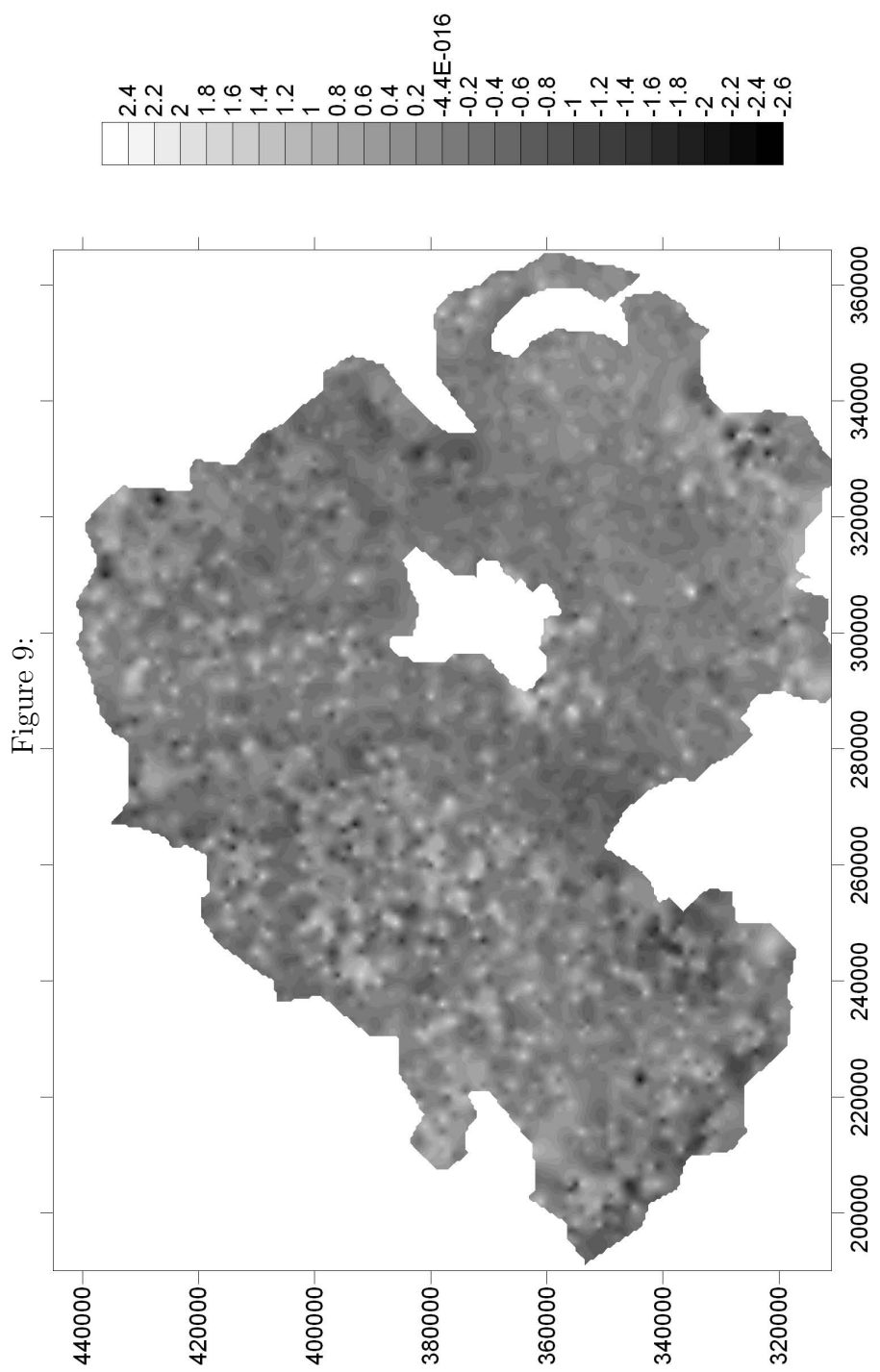


Figure 10:

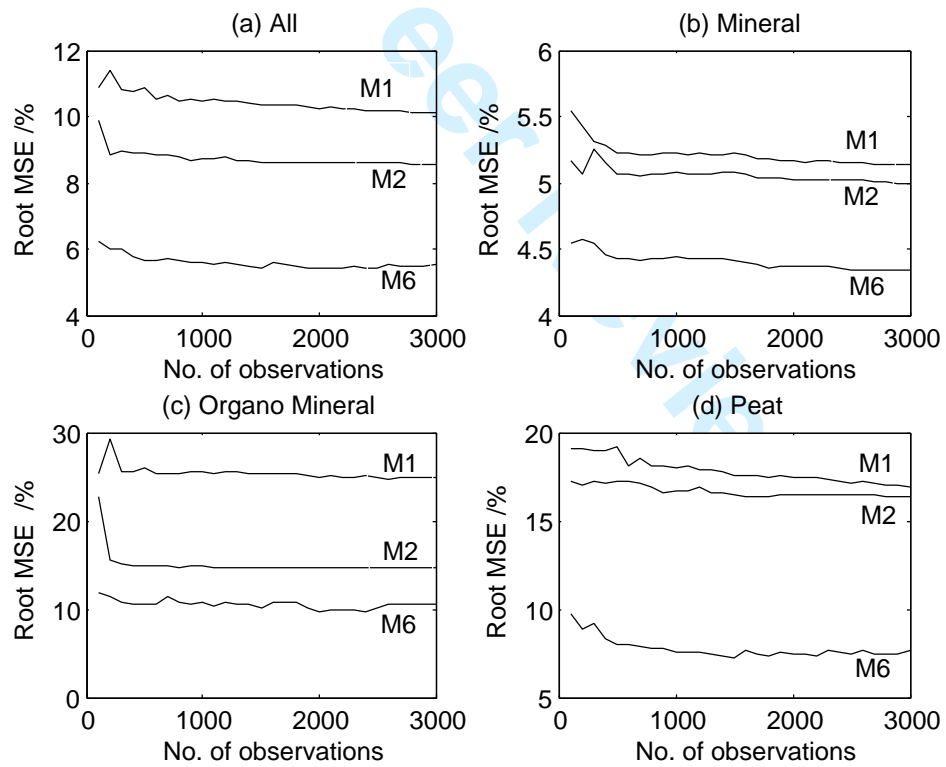


Table 1 Summary statistics for the soil and the nearest radiometric survey location (n=6862). Units are % for K and soil organic carbon (SOC), mg kg⁻¹ for Th and U. By SS we denote the soil geochemical survey data, and by Rad the radiometric data.

Element Dataset	K		Th		U		SS-SOC
	SS-K	Rad-K	SS-Th	Rad-Th	SS-U	Rad-U	
Mean	1.38	0.91	5.04	3.44	2.48	0.79	13.57
Median	1.47	0.89	5.00	3.19	2.30	0.68	7.49
Variance	0.52	0.38	8.10	7.96	8.10	0.64	212
Standard deviation	0.72	0.61	3.00	2.82	2.85	0.80	14.6
Skewness	0.07	0.50	2.48	2.52	29.2	2.82	1.99
Log _e skewness							0.94

Table 2 Correlation matrix for K, Th, U and soil organic carbon (SOC) for the soil survey (SS) data and the nearest neighbouring radiometric data (Rad).

	Dataset and element						
	SS-K	SS-Th	SS-U	SS-SOC	Rad-K	Rad-Th	Rad-U
SS-K	1						
SS-Th	0.75	1					
SS-U	0.18	0.45	1				
SS-SOC	-0.63	-0.45	-0.03	1			
Rad-K	0.86	0.71	0.25	-0.51	1		
Rad-Th	0.67	0.80	0.39	-0.36	0.79	1	
Rad-U	0.51	0.66	0.36	-0.29	0.60	0.70	1

Table 3 MSEs for SOC predictions from Models 1-6 (M1- M6) at all validation sites and at validation sites classified as mineral, organo mineral (O M) and peat soils. Units are %².

Soils	Soil classes ^a	M1	M2	M3	M4	M5	M6
All	1	119.42	116.67	60.18	41.08	67.69	49.37
	3	78.70	73.14	36.92	30.60	34.24	30.38
Mineral	1	34.45	30.11	17.74	14.95	17.89	15.44
	3	26.34	24.95	20.97	19.57	19.79	18.85
O M	1	215.24	319.65	107.04	93.01	139.65	108.08
	3	238.53	216.96	127.05	102.98	112.88	110.74
Peat	1	523.05	485.37	262.17	156.18	298.53	202.27
	3	286.82	265.99	83.69	58.82	77.79	58.04

^a The number of soil classes into which the prediction set is divided when fitting the linear mixed model.

Table 4 MdSDs for SOC predictions from Models 1-6 (M1-M6) at all validation sites and at validation sites classified as mineral, organo mineral (O M) and peat soils. Units are %².

Soils	Soil classes ^a	M1	M2	M3	M4	M5	M6
All	1	4.77	4.69	3.37	2.99	3.41	3.01
	3	3.22	3.03	2.45	2.20	2.38	2.26
Mineral	1	2.79	2.84	1.96	1.91	2.01	1.97
	3	1.94	1.83	1.65	1.53	1.51	1.51
O M	1	51.00	40.13	22.83	22.85	21.07	18.71
	3	102.37	93.12	49.17	37.81	39.57	45.14
Peat	1	406.92	282.18	169.17	101.81	130.21	99.70
	3	192.38	190.50	27.70	12.07	26.33	10.06

^a The number of soil classes into which the prediction set is divided when fitting the linear mixed model.

Table 5 MSEs for SOC predictions from Models 1-6 (M1- M6) on validation sites classified as mineral soils when observations greater than 20 % are removed from the validation set. Units are %².

Soils	Soil classes ^a	M1	M2	M3	M4	M5	M6
Mineral	1	21.85	15.73	10.60	8.94	8.81	8.00
	3	6.93	6.71	5.87	5.83	5.69	5.76

^a The number of soil classes into which the prediction set is divided when fitting the linear mixed model.