1    **Quantifying and mapping topsoil inorganic carbon concentrations and stocks: approaches tested in**

2    **France.**

3    B.P. Marchant[1,2*], E.J. Villanneau[3], D. Arrouays[3], N.P.A. Saby[3] & B.G. Rawlins[1]

4    [1] British Geological Survey, Environmental Science Centre, Keyworth, Nottingham, NG12 5GG, UK.

5    [2]Rothamsted Research, West Common, Harpenden, AL5 2JQ, UK.

6    [3] INRA, US 1106 InfoSol, F-4075 Orléans, France.

7    [*]Corresponding author: Email benmarch@bgs.ac.uk; Tel. +44 1159 363100

8    **Abstract**

9    The potential for soils to act as a sink or a source of atmospheric carbon has long been recognised

10    and great efforts are made to monitor soil organic carbon stocks. Inorganic carbon is also exchanged

11    between soils and the atmosphere and is important for soil function but inorganic carbon stocks are

12    not measured in many national- and continental-scale soil monitoring networks.  Topsoil (0–30 cm)

13    inorganic carbon concentrations were measured at more than 2 000 sites on a regular 16-km grid as

14    part of the French National Soil Monitoring Network (RMQS: Réseau de Mesures de la Qualité des

15    Sols). We used design-based statistical methods to calculate unbiased estimates of the mean soil

16    inorganic carbon concentration and total stocks across France and we used model-based methods to

17    determine the uncertainty of these estimates and to predict the spatial distribution of these

18    quantities. The observations of inorganic carbon were highly skewed and did not conform to

19    standard statistical models. We therefore applied a non-parametric transform to normalise the data

20    and performed validation of the model that resulted. The estimates and predictions of inorganic

21    carbon are baselines against which the results of future phases of the network can be compared. We

22    found that the total topsoil inorganic carbon stocks in France amount to 1070 ±61 Tg (Tg = terragram

23    = $10^{12}$ g) which is approximately one third of the mass of the corresponding organic carbon stocks.

24    Their spatial distribution was strongly linked to the underlying geology. We note that in countries

25    where inorganic carbon is not measured within soil monitoring networks, its concentrations and

26    stocks might be estimated from other sources of soil legacy information such as databases of soil

27    tests requested by farmers. We tested the reliability of this approach by considering the French Soil

28    Test Database which contains the results of 280 000 soil analyses requested by farmers between

29    1990 and 2004. We found that these data led to a biased estimate of soil inorganic carbon

30    concentrations which was presumably the result of the locations of the soil samples being selected

31    according to the concerns of farmers rather than a statistical design.

32    **Introduction**

33    The global stocks of soil carbon exceed the combined stocks of carbon contained in the atmosphere

34    and above-ground biomass (Lal, 2004). The soil carbon reservoir is dynamic and the potential for it

35    to act as a sink or a source of atmospheric carbon dioxide has been long recognised. Lal (2004)

36    estimated that the global potential of soil organic carbon sequestration was 3.3 Pg C/year (Pg =

37    petagram = $10^{15}$ g).  Soil carbon stocks must be monitored to determine whether this sequestration

38    potential is being realized or alternatively whether soil carbon is being lost to the atmosphere. This is

39    one of the reasons why soil organic carbon has become the primary focus of many broad-scale soil

40    monitoring networks (SMNs; Black *et al.*, 2008).

41    Batjes (1996) estimated that one third of the global soil carbon stocks contained in the upper metre

42    of soil are in an inorganic form. These stocks can also act as either a sink or a source of atmospheric

43    carbon. The reaction of calcium and magnesium with atmospheric carbon dioxide and water in the

44    upper soil horizons can lead to the formation of secondary carbonates and the sequestration of

45    atmospheric carbon (Sahrawat, 2003). Manning (2008) and Washbourne *et al.* (2012) have

46    suggested that further stocks of inorganic carbon could be sequestered through the incorporation

47    into the soil of waste calcium silicate minerals from quarrying, demolition and steel manufacture.

48    Suarez (2006) noted that land management practices such as irrigation and use of acidifying

49  fertilizers can cause losses of soil inorganic carbon although inorganic carbon can be added to the

50  soil upon liming. There is a further need to monitor inorganic carbon where it supports soil function.

51  For example, in many soil types the dissolution of soil carbonate is the dominant buffering

52  mechanism which limits the soil acidification which can otherwise occur when nitrogen fertilisers are

53  added to the soil.


54  Inorganic carbon is excluded from many broad-scale SMNs such as the FOREGS geochemical survey

55  (Salminen et al., 2005) and the Soil Profile Analytical Database of Europe (Hannam *et al.*, 2009).

56  According to the ENVASSO European survey (Arrouays *et al.*, 2008) inorganic carbon was monitored

57  in only six of the 27 members of the European Community. Instead, SMNs tend to focus on soil

58  properties that are related to soil fertility and are expected to evolve rapidly (e.g. pH, organic

59  carbon, and soil nutrients) or on soil properties that are of environmental concern (e.g. heavy metals

60  and organic pollutants). However, in a review of field evidence and the results of mathematical

61  models, Sanderman (2012) found that inorganic carbon stocks in Australian agricultural soils could

62  change by as much as 1 t/ha/year. Therefore, measurements of inorganic carbon were included in

63  the protocols for the Australian National Soil Carbon Research Project (Sanderman *et al.*, 2011).


64  Previously reported broad-scale estimates of soil inorganic carbon stocks and concentrations have

65  been based on existing soil databases and information systems that were not constructed according

66  to a statistical design or with quantitative soil monitoring in mind. Expert judgement has been used

67  in the establishment of these databases to divide the study region into different soil classes and to

68  locate representative soil pits within these classes. For example, Wu *et al.* (2009) used 2 553 soil

69  profiles from the second national Chinese soil survey to determine inorganic carbon stocks in the A,

70  B and C horizons for each subgroup of the Chinese Soil Taxonomy. They upscaled these results to a

71  national stock of 55.3±10.7 Pg or 6.3±1.2 kg/m$^2$. Similarly, Guo *et al.* (2006) used the State Soil

72  Geographic Database to estimate the stock of inorganic carbon in the top two metres of soil in the

73  conterminous USA to be between 22.6 and 93.7 Pg. Lettens *et al.* (2004) divided Belgium into 492

74      landscape units based upon land cover and soil association and estimated mean inorganic carbon

75      stocks for each landscape unit using 13 000 geo-referenced soil profile descriptions. They found that

76      the inorganic stock in the top 30 cm was 4 Tg or 0.54 kg/m$^3$. The uncertainty of the estimate was not

77      reported.      The maps and estimates which result from these databases are informative but it is

78      challenging to account for the expert judgements when the uncertainty of the outputs is quantified.

79      Other studies have inferred inorganic carbon estimates by fitting simple relationships with other soil

80      properties and environmental covariates. In England, Rawlins *et al*. (2011) used a regression model

81      of calcium and aluminium concentrations to estimate inorganic carbon stocks in the top 30 cm of

82      soil. They found that the total inorganic stocks contained in soils over two groups of primary,

83      carbonate-bearing parent materials across parts of southern and eastern England amounted to 186

84      Tg (Tg = terragram = $10^{12}$ g) or 15% of the total (inorganic plus organic) topsoil carbon stocks in

85      England. The regression models were calibrated upon 100 measurements of inorganic carbon

86      concentrations in the top 15 cm of soil. These measurements ranged from 7 to 70 g/kg (mean 44

87      g/kg) on a Cretaceous chalk deposit and 1 to 60 g/kg (mean of 36 g/kg) on a Jurassic limestone

88      deposit. Given the relative complexity of their statistical procedure, Rawlins *et al.* (2011) did not

89      quantify the uncertainty of their estimates. In China, Na *et al*. (2008) estimated relationships

90      between inorganic carbon stocks, climatic parameters and land use information. The total stock of

91      inorganic carbon in China to a depth of 2m was estimated to be 53.3±6.3 Pg. Such an approach can

92      make very efficient use of the available data but it does rely on the assumption that the same simple

93      relationships hold across the study region.

94      In contrast, purpose-built SMNs use a statistical design to ensure unbiased estimates of both soil

95      status and soil change. The French national SMN (RMQS – Réseau de Mesures de la Qualité des Sols)

96      included over 2 000 observations of the concentration of soil carbonates and stocks of soil inorganic

97      carbon in the top 30 cm of soil across France (Fig. 1). We used geostatistical techniques to map the

98      inorganic carbon stocks across France and to determine the total mass of inorganic carbon stored in

99      the top 30 cm of soil. We used knowledge of the parent material across France (Fig. 2) to improve

100     our predictions. Such geostatistical techniques require that a valid model of the spatial variation of

101     inorganic carbon is fitted to the spatial data. We performed a design-based analysis (Brus & De

102     Gruijter, 1997) to validate our prediction of the total stocks. Design-based analyses require much

103     less stringent assumptions about the statistical distribution of the data. We also explored whether

104     the soil inorganic carbon concentrations could have been estimated from sources of soils data that

105     might be available in other countries. In particular, we considered the results of 268 000 soil

106     analyses that have been requested by farmers in France between 1990 and 2004.

107     **Statistical Theory**

108     *Design of soil monitoring networks*

109     Arrouays *et al*. (2012) reported that purpose-built SMNs tend to either employ a systematic design

110     such as a grid or to use a probabilistic design. In probabilistic designs, sampling locations are selected

111     independently so there is no need to account for correlations between observations. Mean values of

112     soil properties across a region and corresponding estimation variances can be estimated by classical

113     design-based statistical methods that require few assumptions about the variation of the property.

114     When a systematic design is applied, design-based methods can be used to estimate the mean of the

115     property but no unbiased design-based estimator of the variance is available. Instead a model-based

116     analysis is required to account for the correlation between observations when the estimation

117     variance is determined. Model-based analyses can also be used to predict maps of properties. The

118     predictions and prediction variances that result from these analyses are only valid if the model

119     appropriately represents the spatial correlation of the property.

120     Mean values and maps of properties can be determined from legacy datasets that were not

121     collected for the purpose of monitoring. For example, Orton *et al*. (2012) have estimated changes in

122     soil carbon concentrations in French soils using measurements requested by farmers to assess the

5

123    fertility of their soils. Generally, the locations of these measurements are not selected according to a

124    statistical design. Design-based analyses can only be applied if the locations are selected

125    probabilistically. Model-based methods can be applied if the sample selection is not biased

126    according to the expected value of the measurement. However, biases often occur in such surveys.

127    For example, a farmer might bias their measurements towards areas where they are concerned

128    about soil fertility. Such preferential sampling must be accounted for when using the measurements

129    to predict soil properties.

130    *Model-based analyses*

131    A model-based analysis of a survey assumes that the observed data are a realization of a random

132    function. A statistical model that describes the random function, including any spatial correlation,

133    must be fitted to the data prior to prediction and the production of maps. The statistical model is a

134    simplification of reality and its use requires that assumptions are made about the random function

135    from which the observed data are realized. For example, the random function is often assumed to

136    have a multivariate Gaussian distribution and to be second order stationary (Webster & Oliver,

137    2007).

138    In some cases the assumptions are implausible and must be relaxed. For example, the histogram of

139    inorganic carbon stocks observed in RMQS (Fig. 3) is highly skewed. Therefore, the histogram or

140    marginal distribution is inconsistent with a multivariate Gaussian distribution and a transformation

141    must be applied to the data prior to analysis. Once the observations have been transformed to an

142    approximate multivariate Gaussian distribution they can be represented by a linear mixed model

143    (LMM; Lark *et al.*, 2006). This model assumes that the transformed data $z^*$ are realizations of a

144    random function $Z^*$. The model splits the variation into two components or effects. Fixed effects are

145    linear relationships between the variable of interest and relevant covariates. Random effects are

146    spatially correlated residual terms. The spatial correlation is described by a parametric variogram

147    function, the parameters of which are fitted to the data by either maximum likelihood (ML) or

6

148    residual maximum likelihood (REML; see Lark *et al.*, 2006). The Matérn model is a flexible variogram

149    function that is often advocated in studies of soil properties (*e.g.* Marchant & Lark, 2007).

150    The appropriateness of fitted models with different fixed effects can be compared by calculating the

151    Akaike information criterion (AIC; Akaike, 1973):

$$\text{AIC} = -2L + 2q, \tag{1}$$

152    for each model where $L$ is the ML log-likelihood and $q$ is the number of parameters in the model.

153    The model with the smallest AIC best manages the trade-off between quality of fit and model

154    complexity (Webster & Oliver, 2007).

155    There is a small bias in the variance parameters of an LMM which are estimated by ML and therefore

156    REML is often advocated (*e.g.* Lark *et al.*, 2006) since this estimator adjusts the expression for the

157    likelihood to minimize this bias. However, the AIC cannot be calculated from these adjusted

158    likelihoods. Once the LMM has been estimated it is possible to krige (Webster & Oliver, 2007)

159    predictions of the mean ($m_j$) and the kriging variance ($\sigma_j^2$) of $Z^*$ at each node, $j$, of a grid where

160    predictions are required. The predictions of the transformed property must then be back-

161    transformed to the units of the measured observations.

162    Standard bootstrapping or resampling methods (Efron & Tibshirani, 1993) cannot be used to validate

163    a spatial LMM because these methods do not account for the spatial correlation amongst the data.

164    An LMM can be validated by leave-one-out cross validation. Here each observation, $z^*(\mathbf{x}_i)$, is

165    removed in turn from the dataset and the remaining observations are used to predict the

166    (transformed) property at the site of the removed observation. The standardized prediction errors

$$\theta_i = \frac{\{z^*(\mathbf{x}_i) - m_i\}^2}{\sigma_i^2}, \tag{2}$$

167    are calculated. If the LMM is accurate, the expected square error should be equal to the kriging

168    variance, and the mean of $\boldsymbol{\theta}$ should be 1 and the median equal to 0.45.

169     The mean of a property across the entire prediction grid can be estimated by using the multivariate

170     LU simulation method (Deutsch & Journel, 1998) to produce a large number (*e.g.* 1000) of

171     realizations of the transformed property, conditional on the transformed observed data, at all of the

172     nodes of the prediction grid. Each simulated value is then back-transformed and the mean of each

173     realization is calculated. The predicted mean is equal to the mean of the realization means. The

174     prediction variance is equal to the variance of the prediction means.

175     *Design-based analyses*

176     The model-based methods described above regard the observations of a property as realizations of a

177     random function whereas the sampling locations are treated as fixed. The model-based uncertainty

178     analysis considers the variation that will arise from sampling different realizations of the random

179     function. In contrast, design-based statistical methods regard the values of the property of interest

180     across the study region as fixed and the sampling locations are treated as random. Design-based

181     uncertainty analysis considers the variation that will arise from repeatedly estimating the mean

182     value of the property across the study region from different randomly selected sets of sampling

183     locations. If the $n$ sampling locations $\mathbf{x}$ are selected purely at random such that there is an equal

184     probability of each site being included then the mean of $z$ across the study region is estimated by

$$\hat{\bar{z}} = \frac{1}{n} \sum_{i=1}^{n} z(\mathbf{x}_i). \tag{3}$$

185     This estimate is said to be *p*-unbiased because

$$\mathrm{E}_p[\hat{\bar{z}}] = \bar{z}, \tag{4}$$

186     where $\mathrm{E}_p$ is the statistical expectation over repeated sampling under design $p$ and $\bar{z}$ is the actual

187     mean of $z$. The expected squared estimation error is

$$r = \mathrm{E}_p[\hat{\bar{z}} - \bar{z}]^2 = \frac{\sigma^2}{n} \approx \frac{\hat{s}^2}{n}, \tag{5}$$

188    where

$$\hat{s}^2 = \frac{1}{n-1} \sum_{i=1}^{n} \{z(\mathbf{x}_i) - \hat{\bar{z}}\}^2, \tag{6}$$

189    is the estimated variance of $z$. A major advantage of design-based inference over model-based is

190    that the mean and the expected error can be calculated by such formulae without assuming a

191    particular model of variation. The only required assumption is that $n$ is sufficiently large such that

192    the Central Limit Theorem can be invoked and the distribution of the repeated estimates of $\hat{\bar{z}}$ can be

193    treated as Gaussian (Brus & De Gruijter, 1997).

194    Design-based analyses have been extended to consider systematic random designs. Such a design

195    follows a fixed pattern but the location of the origin is selected at random. When such a design is

196    used the mean of $z$ across the study region can still be estimated from Eqn. 3 because each site has

197    an equal probability of being included in the design and the estimator is $p$-unbiased. However, if

198    $z(\mathbf{x})$ is spatially correlated then Eqn. 5 will be a biased estimate of the variance of $z(\mathbf{x})$ because the

199    pattern of sampling locations is not random. In the case of a regular grid with good coverage of the

200    study region, Eqn. 6 will over-estimate the variance of $z(\mathbf{x})$ since the smallest lag between pairs of

201    observations is equal to the grid-spacing. Therefore, Eqn. 5 will over-estimate the expected squared

202    estimation error. Domburg *et al.* (1994) proposed a method by which the expected squared error of

203    $\hat{\bar{z}}$ can be estimated for a systematic design using simulated realizations of an estimated model of

204    the random function $Z(\mathbf{x})$.

205    **Methods**

206    *The French National Soil Monitoring Network (RMQS)*

207    The RMQS database (Arrouays *et al.*, 2002) primarily consists of over 2 000 observations of soil

208    properties on a 16-km regular grid across the 550 000 km$^2$ French metropolitan territory (Fig. 2a).

209    Twenty six additional observations were positioned within the grid. The locations of these

210 observations targeted specific combinations of soil type and land use. If it was not possible to

211 sample at the selected site (*e.g.* in urban areas, in rivers or on roads) an alternative cultivated or

212 undisturbed location was selected as nearby as possible within a 1-km radius. When this was not

213 possible the cell was omitted from the survey. This baseline survey of the RMQS was completed in

214 2009.

215 At each site, 25 individual core samples were taken of the topsoil (0–30 cm) layer, using an unaligned

216 sampling design within a 20 × 20-m area. The 0–30 cm layer was chosen to ensure consistency with

217 existing surveys and because in France 30 cm is the maximum depth at which topsoil is affected by

218 ploughing (Arrouays *et al.*, 2001). Core samples were bulked to obtain a composite sample for each

219 site.

220 *Preparation and analysis of soil samples*

221 The inorganic carbon concentration was determined for a 0.5–10 g subsample of each composite

222 sample. The size of the subsample was selected according to the expected calcium carbonate

223 concentration. The subsamples were dried at 30 °C, sieved to 2 mm and subsequently ground to 250

224 μm. The samples were acidified in a closed flask with a solution of 1/5 dilute hydrochloric acid (37%

225 v/v). The volume of carbon dioxide released was measured using a Bernard calcimeter (a graduate

226 tube filled with 200 mL of water) and was compared to the volume of carbon dioxide produced by

227 pure calcium carbonate under the same temperature and pressure conditions. The kinetics of

228 decomposition by acid varies according to chemical species; decomposition is rapid for calcite and

229 slow for dolomite. The INRA laboratory of Arras has a COFRAC accreditation for calcimetry analysis

230 and follows the French standard procedure. The detection limit of this procedure was 1 g/kg.

231 The mass of fine earth (i.e. particles which pass through a 2-mm sieve) for each observation site was

232 determined for three samples of known volume that were extracted from a soil pit adjacent to the

233 site. The methods varied according to the particle size distribution of the samples. The samples were

234 dried prior to analysis. The cylinder method (procedure reference NF X 31-501 in AFNOR, 1999) was

235 used for soils with little to no gravel. The cylinder was 90 mm high with a diameter of 84 mm, *i.e.*,

236 500 cm$^3$. When the cylinder method was not possible, *i.e.* for gravelly or stony soils, the water

237 method was applied. The water method is adapted from the sand method (procedure reference NF

238 X 31-503 in AFNOR, 1999). In this method, circular holes of between 1 000 and 3 000 cm$^3$ are dug

239 into the soil. The exact volume of soil extracted is determined by lining the hole with a plastic bag

240 and measuring the volume of water required to fill the hole.

241 *Soil parent material*

242 Information on soil parent material was derived from the 1:1 000 000 scale soil database of Europe

243 (King *et al.*, 1995). The classes from this database were amalgamated into five broader classes (Table

244 1 and Fig. 2b) for this study. These classes were created according to their natural geochemical

245 concentration of calcium and magnesium carbonate according to the attribute tables of the

246 database. The parent material classes were marls (covering 3.1% of the area of France), chalk (5.3%),

247 other calcareous rocks (21.2%), dolomitic rocks (1.1%) and non-calcareous rocks (69.3%).

248 *The French Soil Test Database*

249 The results of the soil analyses compiled in the French Soil Test database are a consequence of

250 requests from farmers and landowners for help to improve the management of their crops and

251 pastures (Lemercier *et al.*, 2008). The motivation for each analysis request was not recorded. The

252 analysed samples were taken from topsoil horizons of cultivated fields or fields under pasture. In

253 each sampled field 10–15 samples of the ploughed layer (or the 0–30 cm topsoil layer in the case of

254 pastures) were collected with a hand auger. These samples were bulked and the composite sample

255 was sent to a laboratory certified by the French Ministry of Agriculture. The results of standardized

256 analytical procedures were stored in the national database. The sample coordinates could not be

257 stored in the database because of confidentiality concerns. The most accurate geo-referencing that

258    could be recorded was the name of the local authority or canton which contained the sampled field.

259    France is divided into 4 032 cantons which are intended to have approximately equal populations of

260    around 20 000. Hence, urban cantons tend to be small but rural ones can have areas of over 100

261    $km^2$.

262    *Model-based analyses*

263    We used model-based analyses to predict (i) maps of the inorganic carbon concentrations and stocks

264    across France, (ii) the mean inorganic carbon concentration and (iii) the total soil inorganic carbon

265    stocks within France. We also determined the uncertainty of these predictions.  The histograms of

266    inorganic carbon stock and concentration observations (Fig. 3) indicated that the distributions of

267    these properties were non-Gaussian. Therefore, we normalized these observations by the rank order

268    transform (Goovaerts, 1997) before estimating an LMM of the transformed properties. The

269    observations that were located away from the nodes of the 16-km grid were included in this analysis

270    since they provided useful information about the variation over small lag distances. We compared

271    two different fixed effects models. The first assumed a constant mean and the second assumed that

272    the mean was constant within each of the five geological classes. We estimated both of these

273    models by ML and calculated the AIC to determine which was the more appropriate. Then the more

274    appropriate model for each property was re-estimated by REML before we predicted the

275    transformed properties on a 2.5-km grid across France by kriging. These predictions were back-

276    transformed and finally the mean inorganic carbon concentration and total stocks at the national-

277    scale were estimated using the multivariate LU simulation approach described in the Theory section.

278    *Design-based analyses*

279    We re-estimated the mean inorganic carbon concentration and the total inorganic carbon stocks

280    using design-based methods. This analysis used only the observations that were located on the

281    nodes of the 16-km grid. We assumed that the origin of the RMQS grid was selected at random and

282    that Eqn. 3 yielded a *p* unbiased estimate of these quantities. We determined the estimation

283    variance using the constant mean LMMs fitted to the observed data and the approach suggested by

284    Domburg *et al.* (1994).

285    *Analyses of the Soil Test Database*

286    The samples contained in the Soil Test Database were selected according to the concerns of farmers

287    rather than a statistical design. We assumed that farmers only requested analyses of inorganic

288    carbon at locations where they thought the soil was alkaline and they expected reasonably large

289    concentrations. Therefore, the samples for which inorganic carbon has been measured was

290    unrepresentative of the distribution of soils across France. We adjusted for this preferential

291    sampling by considering the samples for which analyses of pH but not inorganic carbon had been

292    requested. We assumed that inorganic carbon analyses had not been requested because the

293    concentrations were thought to be small. Therefore, we treated such observations as zero inorganic

294    carbon concentrations provided that the pH was less than 6.5.

295    The mean value of the inorganic carbon concentrations was calculated for each canton and these

296    values were used to map inorganic carbon concentration across France. The mean inorganic carbon

297    for the whole of France was calculated from the mean of the canton means, weighted according to

298    the area of the canton. Since these data were not gathered according to a statistical design we do

299    not quote a standard error on the estimates. For comparison we also used the estimated LMM of

300    inorganic carbon concentrations to estimate mean values for each canton.

301    **Results**

302    *Mapping soil inorganic carbon*

303    There were substantial differences between the inorganic carbon concentrations observed in each

304    parent material class (Table 1). The AICs for the estimated LMMs of both concentrations and stocks

305    with fixed effects that varied according to parent material were less than the AICs for the constant

306    fixed effect models. Therefore, we included parent material classes as fixed effects in our model-

307    based analyses. All of the estimated LMMs had mean $\theta$ equal to 1.00 and median $\theta$ close to 0.45

308    (Table 2) indicating that the residual variation had been adequately modelled.

309    Figure 4 shows the variograms of the random effects of the variable fixed effect LMM for both the

310    transformed inorganic carbon stocks and concentrations. These plots show how the expected

311    squared difference between observations increases with the distance between the locations of the

312    samples. The variogram sills were close to 0.87 in both cases. This is less than 1.0, the variance of the

313    transformed property, and indicates that a proportion of the variation had been explained by the

314    fixed effects. For both variograms, around 75 % of the total variance occurred over distances of less

315    than 1 km but some spatial correlation was apparent up to distances over 200 km.  The

316    corresponding maps of inorganic carbon stocks and concentrations and the prediction of

317    uncertainties are shown in Figure 5. The full pattern of variation is more evident in the maps with

318    nonlinear scale in Figure 6. The prediction variances can be seen to increase with the magnitude of

319    the prediction. The map of inorganic carbon concentrations (Fig. 7a) based upon the Soil Test

320    Database showed a similar spatial pattern to those based upon the RMQS data. However, when the

321    estimated mean concentrations for each canton calculated from the Soil Test Database and RMQS

322    were compared a clear bias was evident (Fig 7b). The Soil Test Database estimate was greater than

323    the RMQS estimate in 65 % of cantons.

324    *National estimates of inorganic carbon*

325    The estimates of average inorganic carbon concentrations and total stocks are shown in Table 3. The

326    design-based estimates were 6.46 g/kg and 1070 Tg respectively. Both of the model-based estimates

327    were larger but were approximately one standard deviation from the design-based ones. The

328    estimate of mean concentration based on the Soil Test Database was substantially larger at 8.45

329    g/kg.

**Discussion**

There is a growing consensus that soil inorganic carbon might play a major role in the global carbon cycle (Sanderman, 2012) and that it must be accounted for within carbon budgeting exercises (Guo *et al.*, 2006). However, many SMNs omit soil inorganic carbon (Arrouays *et al.*, 2008). We have demonstrated that when soil inorganic carbon is measured within an SMN it is possible to produce unbiased design-based estimates of the total stock and to estimate a statistical model of the spatial variation of these stocks. Upon validation, the model was found to be consistent with the design-based mean stocks and the variability of stocks was accurately represented. Therefore, it was possible to use the model to quantify the uncertainty of the design-based total stocks and to map the variation in these stocks. These uncertainties are proportionally smaller than those reported for the estimate of soil organic carbon stocks in the USA that was calculated from the State Soil Geographic Database (Guo *et al.*, 2006). Other surveys of soil inorganic carbon based on linear regressions (Rawlins *et al.*, 2011) or legacy data (Lettens et al., 2004) do not quantify uncertainties.

We quote the design-based estimate of inorganic carbon stocks because it is known to be unbiased. The estimated total inorganic carbon stock in the top 30 cm of French soils of 1070 Tg or 6.54 kg/m$^3$ is approximately one third of the stock of organic carbon estimated on the same depth in other studies of French soils. For example, the estimated organic carbon stocks according to Arrouays *et al.* (2001), Martin *et al.* (2011) and Meersmans *et al.* (2012) were 3 100 Tg, 3 260 Tg and 3 700 Tg respectively. The stocks per unit volume are more than ten times larger than those observed in neighbouring Belgium (Lettens *et al.*, 2004). This reflects an absence of large calcareous deposits in Belgium. The influence of parent material on the maps of inorganic carbon stock and concentrations in France was clearly evident. The largest values were recorded in the calcareous and shallow chalky soils of the Champagne region, on the Jurassic rocks of the Charentes region (south-west France) and on various calcareous rocks of the Mediterranean region of southern France. The concentrations of around 60 g/kg predicted in the Champagne region are comparable with the values measured in

15

355    the south of England by Rawlins *et al.* (2011). The inorganic carbon concentration observed on

356    dolomitic rocks was surprisingly small (Table 1).  This might be because weathering of these topsoils

357    had led to the removal of a large proportion of the geogenic magnesium carbonate or the carbonate

358    concentration of the soils might have been underestimated since magnesium carbonate is harder to

359    extract with acid than calcium carbonate.

360    The map of inorganic carbon concentrations based upon observations from the Soil Test Database

361    was similar in appearance to the RMQS map. However, the national-scale mean was substantially

362    larger than the RMQS value and the estimated means for the majority of cantons exceeded the

363    corresponding value predicted from the RMQS data. This is presumably because the soil tests were

364    not sampled according to a statistical design and in particular because farmers would not have

365    measured inorganic carbon where they expected concentrations to be small. We attempted to

366    adjust the dataset to account for this effect but our adjustment was not sufficient. If the Soil Test

367    Database were to be used to estimate inorganic carbon concentrations a better calibration of the

368    model to adjust for these preferences would be required. These findings illustrate that although

369    such legacy data can provide useful information about the variation of soil properties it is important

370    to understand exactly how the observed samples were selected.

371    **Conclusions**

372    The data collected in the RMQS was used to estimate that there are inorganic carbon stocks of 1070

373    ±61 Tg in the top 30 cm of French soil. This is approximately one third of the organic carbon stocks to

374    the same depth. The mean concentration was estimated to be 6.46±0.38 g/kg. This inorganic carbon

375    is likely to decrease through acidification that will result from atmospheric and voluntary application

376    of nitrogen and sulphur to the soil. Future phases of the RMQS will monitor changes in these

377    baseline stocks of inorganic carbon.

378    **Acknowledgements**

388    **References**

389    AFNOR, 1999. *Qualité des sols, 2*. AFNOR, Paris.

390    Akaike, H. 1973. Information theory and an extension of the maximum likelihood principle. In:

391    *Second International Symposium on Information Theory* (eds B.N. Petrov and F. Csáki), pp. 267–281.

392    Akadémiai Kiadó, Budapest.

393    Arrouays, D., Deslais, W. & Badeau, V. 2001. The carbon content of topsoil and its geographical

394    distribution in France. *Soil Use and Management*, **17**, 7–11.

395    Arrouays, D., Jolivet, C., Boulonne, L., Bodineau, G., Saby, N. & Grolleau, E. 2002. A new initiative in

396    France: a multi-institutional soil quality monitoring network. *Comptes Rendus de l'Academie*

397    *d'Agriculture de France*, **88**, 93–105.

398    Arrouays, D., Richer de Forges, A.C., Morvan, X., Saby, N.P.A., Jones, A.R., Le Bas, C. (eds). 2008.

399    Environmental Assessment of Soil for Monitoring: Volume IIb Survey of National Networks.

400    EUR23490 EN/2B, Office for the Official Publications of the European Communities, Luxembourg,

401    254pp.

402     Arrouays, D., Marchant, B.P., Saby, N.P.A., Meersmans, J., Orton, T.G., Martin, M.P., Bellamy, P.H.,

403     Lark, R.M. & Kibblewhite, M. 2012. Generic Issues on Broad-Scale Soil Monitoring Schemes: A

404     Review. *Pedosphere*, **22**, 456–469.

405     Batjes, N.H. 1996. Total carbon and nitrogen in the soils of the world. *European Journal of Soil*

406     *Science*, **47**, 151–163.

407     Black, H., Bellamy, P., Creamer, R., Elston, D., Emmett, B., Frogbrook, Z., Hudson, G., Jordan, J., Lark,

408     M., Lilly, A., Marchant, B., Plum, S., Potts, J., Reynolds, B., Thompson, R. & Booth, P. 2008. Design

409     and operation of a UK soil monitoring network. Science Report SC060073, Environment Agency,

410     Bristol, UK.

411     Brus, D.J. & De Gruijter, J.J. 1997. Random sampling or geostatistical modelling? Choosing between

412     design-based and model-based sampling strategies for soil (with Discussion). *Geoderma*, **80**, 1–44.

413     Deutsch, C.V. & Journel, A.G. 1998. *GSLIB: geostatistical software library and user's guide.* Second

414     edition, pp. 369. Oxford University Press, Oxford, UK.

415     Domburg, P., de Gruijter, J.J. & Brus, D.J. 1994. A structured approach to designing soil survey

416     schemes with prediction of sampling error from variograms. *Geoderma*, 62, 151–164.

417     Efron, B. & Tibshirani, R. 1993. *An Introduction to the Bootstrap*. Chapman & Hall/CRC, Boca Raton,

418     FL.

419     Goovaerts, P. 1997. *Geostatistics for Natural Resources Evaluation*. Applied Geostatistics Series,

420     Oxford University Press, New York.

421     Guo, Y., Amundson, R., Gong, P. & Yu, Q. 2006. Quantity and spatial variability of soil carbon in the

422     conterminous United States. *Soil Science Society of America Journal*, **70**, 590—600.

423     Hannam, J.A., Hollis, J.M., Jones, R.J.A., Bellamy, P.H., Hayes, S.E., Holden, A., Van Liedekerke, M.H. &

424     Montanarella, L.V.M.U.R., 2009. SPADE-2: The soil profile analytical database for Europe Version 2.0

425    Beta. Joint Research Centre, 27pp. Available at:

426    http://eusoils.jrc.ec.europa.eu/Esdb_Archive/eusoils_docs/esb_rr/SPADE-2_Beta_Report.pdf,

427    accessed 21 March 2011.

428    King, D., Burrill, A., Daroussin, J., Le Bas, C., Tavernier, R. & Van Ranst, E. 1995. The EU soil

429    geographic database. In: European Land Information Systems for Agro-environmental Monitoring,

430    EUR 16232 EN (eds D.King, R.J.A.Jones & A.J.Thomasson), pp. 43–60. Office for Official Publications

431    of the European Communities, Luxembourg.

432    Lal, R. 2004. Soil carbon sequestration to mitigate climate change. *Geoderma*, **123**, 1–22.

433    Lark, R.M., Cullis, B.R. & Welham, S.J. 2006. On spatial prediction of soil properties in the presence of

434    a spatial trend: The empirical best linear unbiased predictor (E-BLUP) with REML.  *European Journal*

435    *of Soil Science*, **57**, 787–799.

436    Lemercier, B., Gaudin, L., Walter, C., Aurousseau, P., Arrouays, D., Schvartz, C., Saby, N. P. A., Follain,

437    S. & Abrassart, J. 2008. Soil phosphorus monitoring at the regional level by means of a soil test

438    database. *Soil Use and Management*, **24**, 131–138.

439    Lettens, S., Van Orshoven, J., van Wesemael, B. & Muys, B. 2004. Soil organic and inorganic

440    landscape units derived using data from 1950 to 1970. *Soil Use and Management*, **20**, 40—47.

441    Manning, D.A.C. 2008. Biological enhancement of soil carbonate precipitation: passive removal of

442    atmospheric $CO_2$. *Mineralogical Magazine*, **72**, 639–649.

443    Marchant, B.P. & Lark, R.M. 2007. The Matérn variogram model: Implications for uncertainty

444    propagation and sampling in geostatistical surveys. *Geoderma*, **140**, 337–345.

445    Martin, M.P., Wattenbach, M., Smith, P., Meersmans, J., Jolivet, C.C., Boulonne, L. & Arrouays, D.

446    2011. Soil organic carbon stocks distribution in France. *Biogeosciences*, **8**, 1053–1065.

447     Meersmans, J., Martin, M.P., Lacarce, E., De Baets, S., Jolivet, C., Boulonne, L., Lehmann, S., Saby,

448     N.P.A., Bispo, A. & Arrouays, D. 2012. A high resolution map of French soil organic carbon. *Agronomy*

449     *for Sustainable Development,* **32,** 841–851.

450     Na, M.I., Shaoqiang, W., Jiyuan, L.I.U., Guirui, Y.U., Wenjuan, Z. & Esteban, J. 2008. Soil inorganic

451     carbon storage pattern in China. *Global Change Biology*, **14**, 2380–2387.

452     Orton, T.G., Saby, N.P.A., Arrouays, D., Walter, C., Lemercier, B., Schvartz, C. & Lark, R.M. 2012.

453     Spatial prediction of soil organic carbon from data on large and variable spatial supports. II. Mapping

454     temporal change. *Environmetrics*, 23, 148–161.

455     Rawlins, B.G., Henrys, P., Breward, N., Robinson, D.A., Keith, A.M. & Garcia-Bajo, M. 2011. The

456     importance of inorganic carbon in soil carbon databases and stock estimates: a case study from

457     England. *Soil Use and Management*, **27**, 312–320.

458     Sahrawat, K.L. 2003. Importance of inorganic carbon in sequestering carbon in soils of the dry

459     regions. *Current Science*, **84**, 864–865.

460     Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis,

461     A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J.,

462     Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant,

463     J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A. & Tarvainen, T., Geochemical

464     Atlas of Europe, P. B. I., Methodology and & Maps. Geological Survey of Finland, E., Finland. 2005.

465     Geochemical Atlas of Europe, part 1: background information, methodology and maps. Geological

466     Survey of Finland, Espoo, Finland.

467     Sanderman, J. 2012. Can management induced changes in the carbonate system drive soil carbon

468     sequestration? A review with particular focus on Australia. *Agriculture, Ecosystems and Environment*,

469     **155**, 70—77.

470    Sanderman, J., Baldock, J., Hawke, J., Macdonald, L., Massis-Puccini, A., & Szarvas, S. 2011. National

471    Soil Carbon Research Programme: Field and Laboratories Methodologies, CSIRO Land and Water,

472    Urrbrae, Australia.

473    Suarez, D.L. 2006. Inorganic carbon: land use impacts. In: Encyclopedia of Soil Science (ed R. Lal), pp.

474    895–897. Taylor and Francis, UK.

475    Washbourne, C.-L., Renforth, P. & Manning, D.A.C. 2012.  Investigating carbonate formation in urban

476    soils as a method for capture and storage of atmospheric carbon. *Science of the Total Environment*,

477    **431**, 166–175.

478    Webster, R. & Oliver, M. 2007. *Geostatistics for Environmental Scientists*. 2nd Edition, John Wiley &

479    Sons Ltd, Chichester UK.

480    Wu, H., Guo, Z., Gao, Q. & Peng, C. 2009. Distribution of soil inorganic carbon storage and its

481    changes due to agricultural land use activity in China. *Agriculture, Ecosystems and Environment*, **129**,

482    413—421.

483

**Figure Captions:**

485  Figure 1 France and surrounding countries.

486  Figure 2 (a) Sampling locations for the RMQS and (b) parent material classes.

487  Figure 3 Histograms of (a) measured inorganic carbon (IC) concentration (g/kg) and (b) stock (kg/m$^3$)

488  at RMQS sites.

489  Figure 4 Variograms of (a) random effects for normalized RMQS 0-30 cm observations of inorganic

490  carbon concentration and (b) stock. Fixed effect means vary according to parent material class.

491  Figure 5 (a) Map of predicted soil inorganic carbon concentration from 0-30 cm RMQS data (g/kg);

492  (b) map of predicted standard error of inorganic carbon concentration (g/kg); (c)  map of predicted

493  soil inorganic carbon stock from 0-30 cm RMQS data (kg/m$^3$); (d) map of standard error of inorganic

494  carbon stock (kg/m$^3$).

495  Figure 6 (a) Map of predicted 0-30 cm soil inorganic carbon concentration from RMQS data (g/kg)

496  presented on a nonlinear scale; (b) map of predicted 0-30 cm soil inorganic carbon stock (kg/m$^3$)

497  from RMQS data presented on a nonlinear scale.

498  Figure 7 (a) Map of predicted 0-30cm soil inorganic carbon concentration from Soil Test Database

499  (g/kg) presented on a nonlinear scale; (b) expected concentration of inorganic carbon estimated

500  from Soil Test Database (g/kg) plotted against corresponding estimate from RMQS data. The red line

501  is $y = x$.

**Table captions**

503 Table 1 Summary statistics (number of observations $n$, mean, median and standard deviation sd) for

504 RMQS observations of inorganic carbon concentration and stock divided according to parent
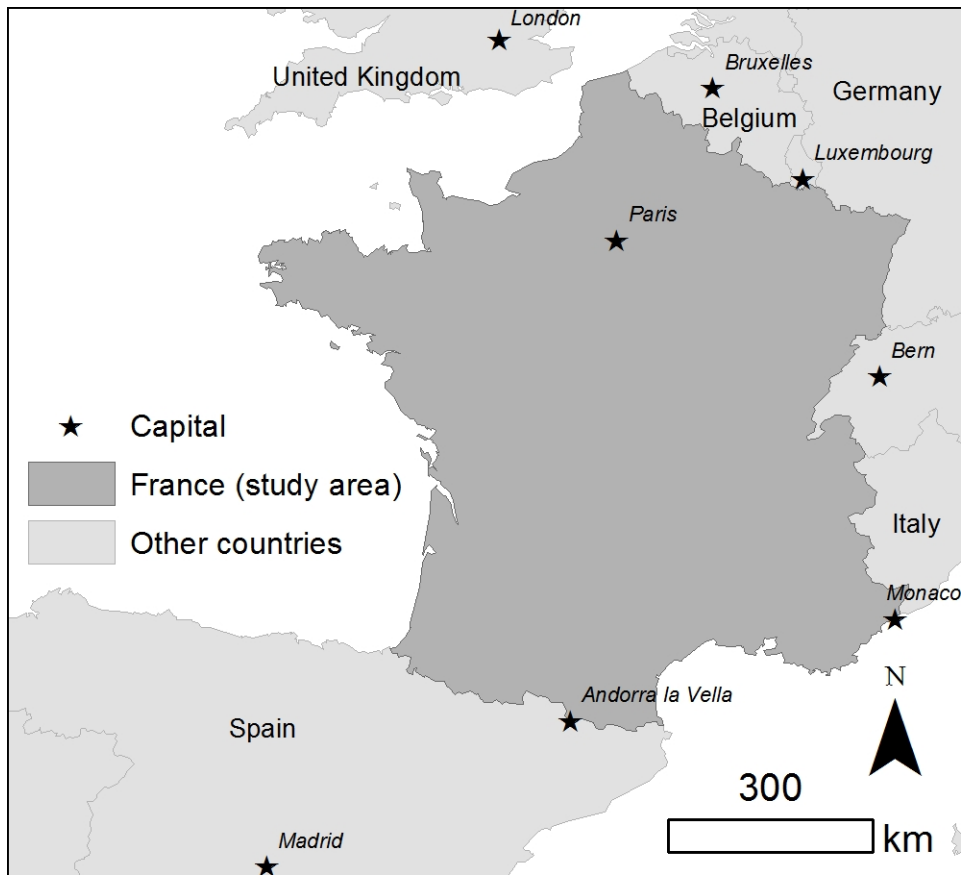
505 material (PM) class.

506 Table 2 Cross-validation statistics and AIC for estimated LMMs of inorganic carbon (IC) concentration

507 and stock.

508 Table 3: Model- and design-based estimates of mean inorganic carbon concentration across France

509 and total inorganic carbon stock.

510

511 **Figures:**

512 Figure 1



513

514

515

516

517

518

519

520

521

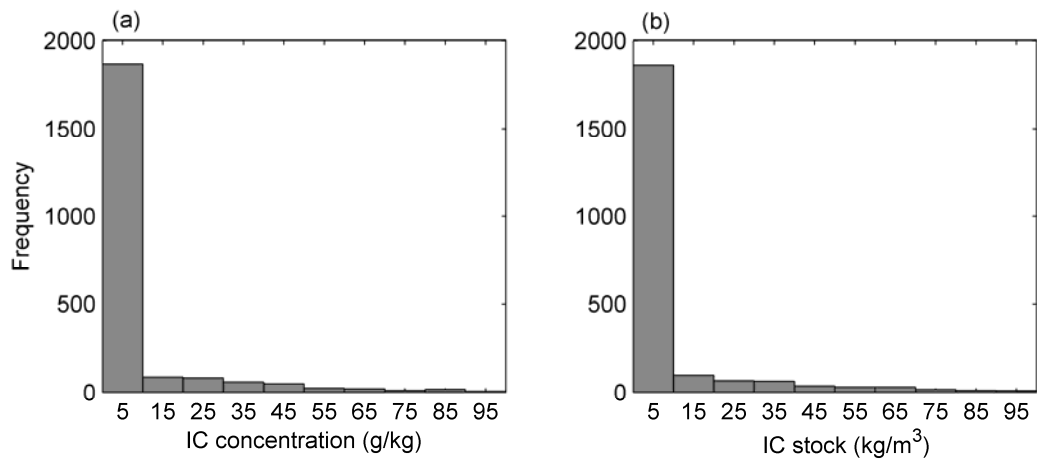522    Figure 2

523
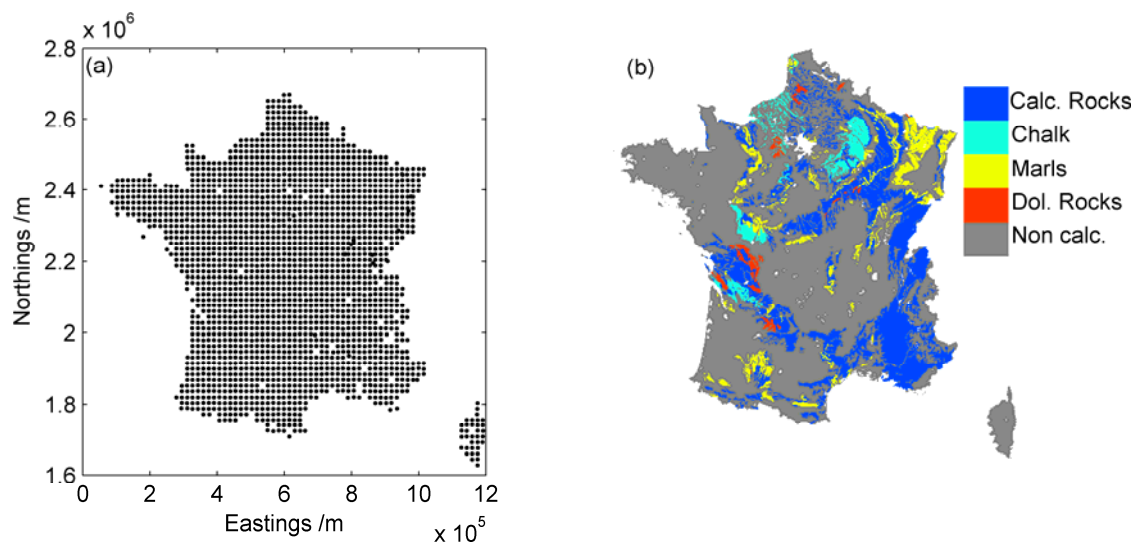


524
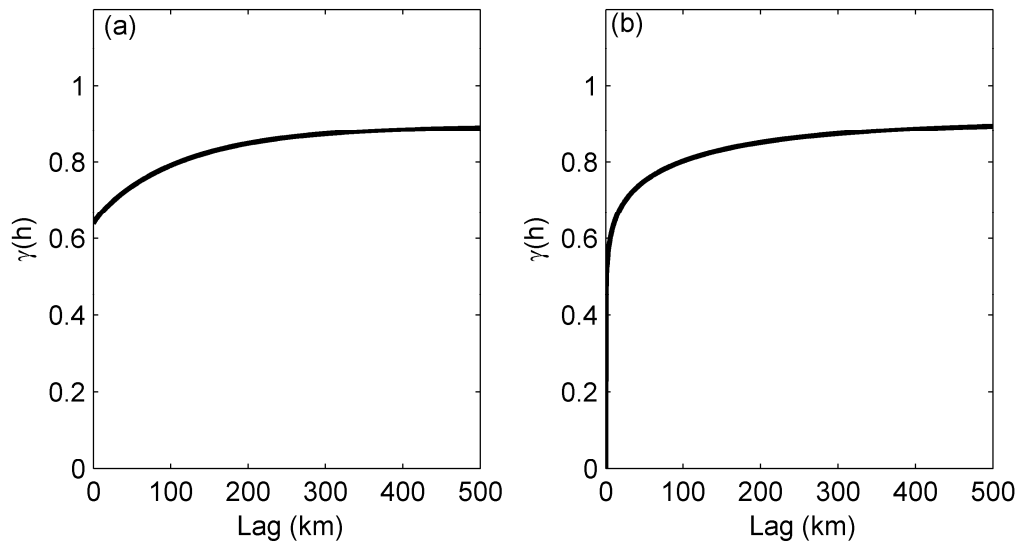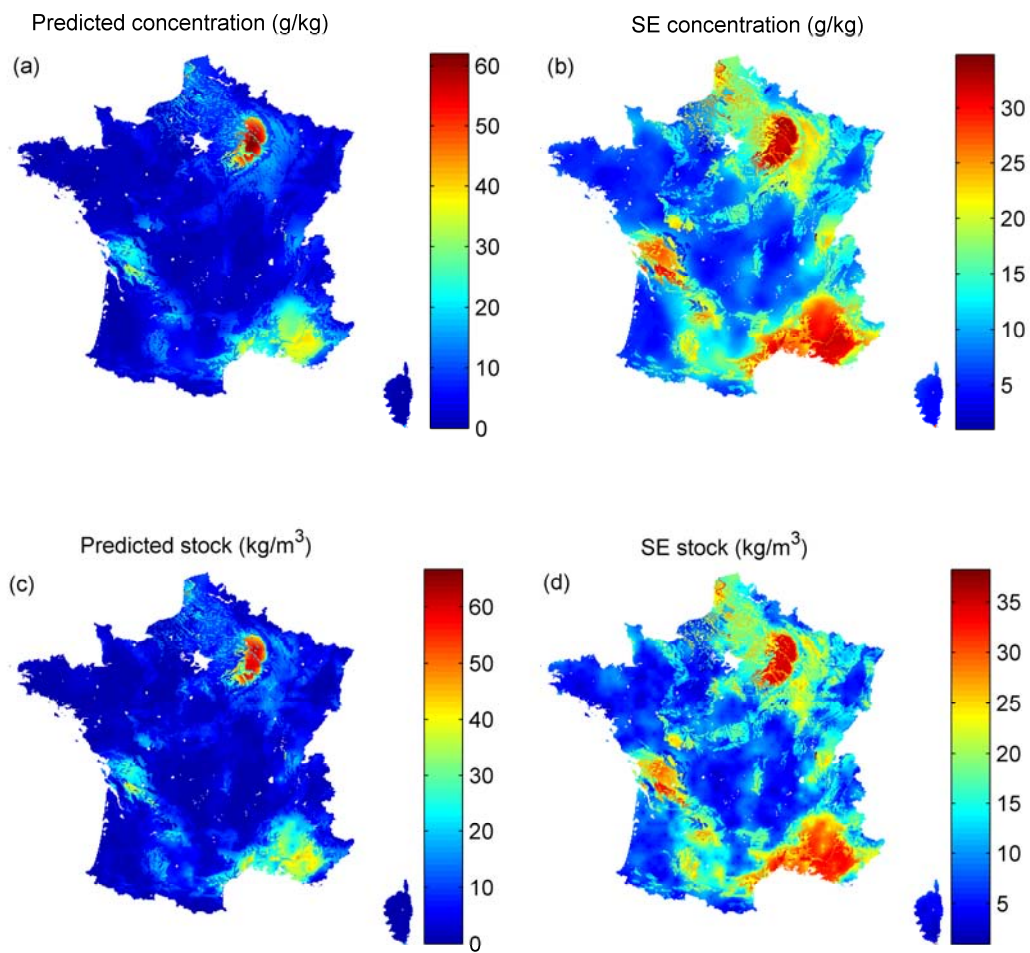
525

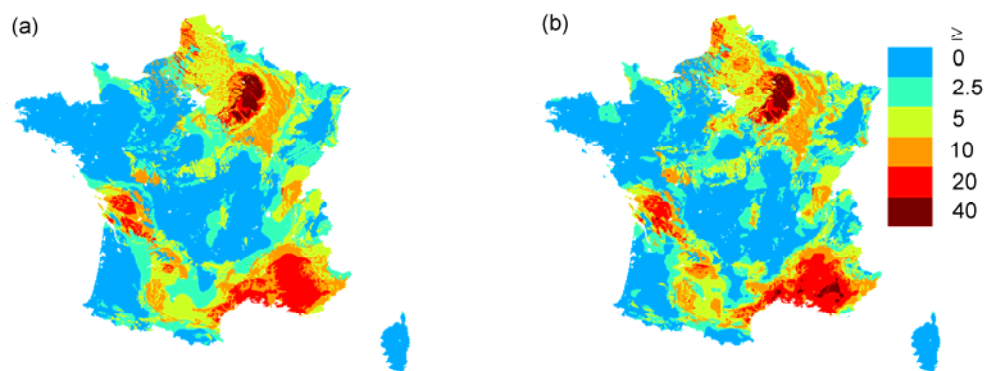526      Figure 3



527

528

529

530

531    Figure 4



532

533

534

535     Figure 5



Predicted concentration (g/kg)          SE concentration (g/kg)

Predicted stock (kg/m$^3$)          SE stock (kg/m$^3$)

536

537

538

539    Figure 6



540

541
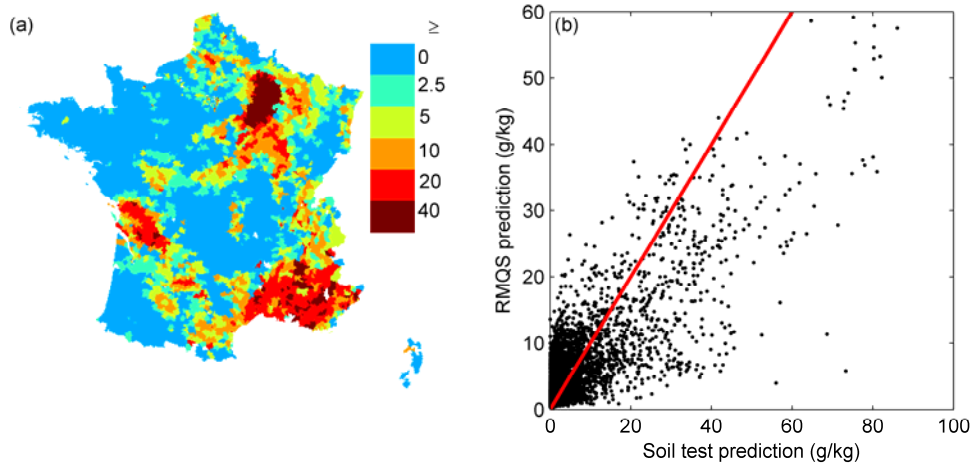
542

543

544

545

546    Figure 7



547

548

549

550

551

552

553

554

555

556

557

558

559

560 **Tables**

561 Table 1

| PM class | Concentration (g/kg) | | | | Stock (kg/m$^3$) | | | |
|---|---|---|---|---|---|---|---|---|
| | *n* | mean | median | sd | *n* | mean | median | sd |
| All | 2168 | 6.46 | 0.06 | 16.00 | 2168 | 6.54 | 0.06 | 16.30 |
| Calcareous rocks | 471 | 12.53 | 1.17 | 19.31 | 471 | 12.07 | 1.20 | 19.07 |
| Chalk | 64 | 39.19 | 28.13 | 38.65 | 64 | 38.05 | 25.45 | 37.82 |
| Marls | 109 | 8.61 | 0.21 | 15.91 | 109 | 9.64 | 0.27 | 17.61 |
| Dolomitic rocks | 24 | 0.49 | 0.05 | 1.41 | 24 | 0.51 | 0.06 | 1.38 |
| Non-calcareous | 1499 | 3.04 | 0.05 | 10.05 | 1499 | 3.34 | 0.05 | 11.16 |

562

563

564     Table 2

| Property | Fixed effects | Mean θ | Median θ | AIC |
|---|---|---|---|---|
| IC concentration | Constant | 1.00 | 0.41 | 1550.4 |
| IC concentration | P. material | 1.00 | 0.43 | 1532.3 |
| IC stock | Constant | 1.00 | 0.40 | 1642.3 |
| IC stock | P. material | 1.00 | 0.40 | 1528.5 |

565

566

567    Table 3

568

| Estimator | Concentration (g/kg) | Stock (Tg) |
|---|---|---|
| Design-based RMQS | 6.46±0.38 | 1070 ± 61 |
| Model-based RMQS | 6.79±0.28 | 1136± 45 |
| Soil Test Database | 8.45 | na |

569

570

571

572