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Methods for estimating types of soil organic carbon and their application to surveys of UK urban areas

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Abstract

The occurrence of substantial quantities of black carbon (BC) in urban soil due to local dispersal following incomplete combustion of fossil fuel complicates the determination of labile soil organic carbon (SOC). Estimates of SOC content were made from LOI (loss on ignition) analyses undertaken on samples (0 to 15 cm depth) from comprehensive soil geochemical surveys of three UK urban areas. We randomly selected ten samples from each decile of the LOI distribution for each of the surveys of Coventry (n=808), Stoke-on-Trent (n=737) and Glasgow (n=1382) to investigate the proportions of labile SOC and BC. We determined their total organic carbon (TOC) and BC contents, and by difference the labile SOC content, and investigated the linear relationship of the latter with SOC estimates based on LOI analyses. There was no evidence for difference in the slope of the regression for the three urban areas. We then used a linear regression of labile SOC based on LOI analyses ($R^2 = 0.81$) to predict labile SOC for all survey samples from the three urban areas.

We attribute the significantly higher median BC concentrations in Glasgow (1.77%, compared to 0.46% and 0.59% in Coventry and Stoke-on-Trent) to greater dispersal of coal ash across the former. Analysis of the thirty samples showed that LOI at 450 ° C accounts for a consistent proportion of BC in each sample ($R^2=0.97$). Differences between TOC (combustion at 1050 ° C after removal of inorganic carbon) and an LOI estimate of SOC may be a cost-effective method for estimation of BC. Previous approaches to estimation of urban SOC contents based on half the mean SOC content of the equivalent associations under pasture, underestimate the empirical mean value.

Keywords: urban soil, black carbon, loss on ignition, linear regression, Stoke-on-Trent, Coventry, Glasgow

Introduction

Urban soils are by their nature complex, representing various combinations of *in situ* formation and the introduction of *ex situ* material with differing physical, chemical and biological properties. Such soil performs a range of functions; modulating flow to groundwater, filtering contaminants, a resource for recreation (parks), and domestic-scale food production in gardens and allotments. They also act as a store of organic carbon (OC), which is of considerable interest given its role in the global carbon cycle, and at national scales for the estimation of soil-related carbon-dioxide emissions as part of commitments to the UNFCC (United Framework Convention on Climate Change). In the UK and elsewhere, attention has typically focussed on rural, as opposed to urban soil, as the former accounts for the vast majority of soil organic carbon (SOC) content; (Bradley *et al.*, 2005). However, urban development currently represents a substantial 14% of land use in the UK (DEFRA, 2004), and this proportion will increase over the next decade following proposed expansion of housing, particularly in south-east England (Office of the Deputy Prime Minister, 2003).

Although several EU member states have established some form of monitoring system for detecting changes in SOC in soil, these do not currently include urban soils (Working Group on Monitoring: Task Group on Existing soil monitoring systems, 2004), a weakness also identified in a recent report concerning current soil monitoring schemes in the UK (SNIFFER, 2006). We believe greater scrutiny of available data which could be used as a basis for evaluating organic matter status and estimating SOC stocks in urban areas is warranted.

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The total organic carbon (TOC) content of urban soil typically comprises two dominant components; labile carbon of which the vast majority has turnover rates of a few years (Parton *et al.*, 1987) and more recalcitrant black carbon (BC), with turnover times of up to hundreds or thousands of years (Preston, 2006), representing a potential long term carbon sink. However, a recent study has suggested short residence times for significant proportions (27-39%) of BC in soil where carbon added as char was recovered from the soil mineral phase in a six month incubation experiment (Hilscher & Knicker, 2007). In this paper we use the term BC to refer to that fraction of SOC which remains following the application of the chemothermal oxidation (CTO) procedure described by Kuhlbusch (1995). A large proportion of this BC will have residence times greater than a few hundred years. We refer to the shorter residence time SOC fraction which is removed during application of the CTO procedure as 'labile' carbon.

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Black carbon is formed by the incomplete combustion of plant material and fossil fuels, and can account for up to 70% of the OC in urban soil samples (Lorenz *et al.*, 2006). To understand changes in the state of urban soils and establish effective policies for their management, policymakers need accurate measurements of SOC through time which are not biased by contributions from BC. Without such data, changes in soil organic matter status, which supports many soil functions, may not be recognised.

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For the purpose of estimating UK SOC stocks, Bradley *et al.* (2005) assumed that built over (urban) soils had zero SOC, and that suburban soils had half the OC content of the equivalent soil series under pasture. We found three studies comparing urban and rural SOC contents; for forest stands along an urban-rural gradient in New York (Pouyat *et al.*, 2002), five cities in the USA (Pouyat *et al.*, 2006), and another

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3 around Stuttgart in Germany (Stahr *et al.*, 2003). In recent years, the British
4 Geological Survey has undertaken a series of soil surveys across twenty urban
5 environments in the UK, with the primary objective of establishing spatial variation in
6 soil geochemistry (Rawlins *et al.*, 2005). For seven of these surveys, comprising
7 around 4000 individual sampling locations, estimates are available for topsoil (0-15
8 cm depth) SOC based on LOI (loss on ignition) analysis at 450 ° C.
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18 Soil organic carbon content is estimated from LOI analyses on the assumption
19 that carbon accounts for around 58% of the mass reduction following the complete
20 removal of organic matter (Broadbent, 1953). In recent years, the use of LOI as a
21 means of estimating SOC has become less common, largely due to the potential for its
22 overestimation due to the presence of structural water in clay and oxyhydroxides. For
23 example, in heavily textured soil, loss of structural water from clay can account for 4-
24 6% of total weight loss, which if not identified as such would represent an extra 2-3%
25 OC (De Leenheer *et al.*, 1957). One potential advantage of an LOI analysis is that a
26 significant component of BC will not be oxidised at temperatures of 450 ° C. When
27 applied to samples with large proportions of BC, an LOI analysis will provide a closer
28 approximation to labile SOC content than TOC analyses based on combustion at 1050
29 ° C in which any BC is included. By establishing whether a consistent proportion of
30 BC is oxidised by LOI analysis, it may be possible to provide a cost-effective
31 approximation of the BC content of a soil sample based on the difference between
32 LOI and TOC analyses applied sequentially to the same sample. This might be of
33 practical use in situations where loss in the accuracy of estimates of BC is outweighed
34 by the lower overall laboratory cost.
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58 The aim of this paper is to investigate and apply statistical relationships between
59 different methods for the estimation of SOC in urban soils, which can be complicated
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3 due to the presence of significant quantities of BC. To do this, we selected a subset of
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5 10 topsoil samples (0 to 15 cm depth) from each of three urban centres and estimated
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7 their labile SOC content as the difference between their TOC and BC contents. We
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9 investigated the statistical relationship between this labile SOC and the estimates of
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11 SOC based on the original LOI analyses. If a statistical relationship could be
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13 established, it may then be possible to estimate labile SOC in all the original survey
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15 samples. The benefits of such an approach include a firmer basis for the estimation of
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17 SOC stocks in UK urban areas, and the establishment of a baseline which could be
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19 used for monitoring change. In combination with data for rural areas, we also tested
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21 whether the assumption proposed by Bradley et al., (2005) for estimating urban SOC
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23 based on local rural soils under pasture is supported based on empirical data. Finally,
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25 we investigated whether combining sequential LOI and TOC analyses could provide a
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27 cost-effective method for the estimating the BC content of a soil sample.
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Methods*Urban centres, soil survey and sample selection*

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38 We chose to select a subset of soil samples for detailed analysis based on archived
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40 material from the urban surveys of Coventry, Stoke-on-Trent and Glasgow (Table 1
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42 and Figure 1). Here we summarise the soil survey methodology in each urban centre.
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44 Each of the urban areas was defined approximately by the area within a boundary of
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46 continuous urban development, and was sampled at a resolution of 4 samples per
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48 square kilometre. Sample sites were selected from open ground as close as possible
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50 to the centre of each of four 500-metre squares, within each kilometre square of the
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52 British National Grid (BNG). Typical locations for sampling were gardens, parks,
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54 recreational fields, road verges, schoolyards and various types of made ground. It
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involved collection of a number of samples from 0-15 cm depth of mineral soil on a specified support using an auger with a flight diameter of 35 mm, and combining them into a single sample weighing between 0.5 and 1 kg.

In the case of Coventry and Glasgow, the sampling support was a square of side length of twenty metres, with a sample at each corner and the centre, combined to form one composite sample. In the case of Stoke-on-Trent, the support was a square of side length two metres, with nine samples combined from the corners, the centre and the centres of each side. The locations of sampling sites in Stoke-on-Trent were recorded using 1:10 000 scale Ordnance Survey maps, whilst handheld GPS systems were used in Glasgow and Coventry. A description of any visible contamination (e.g. industrial waste, pottery, bricks, plastics etc.), soil clast lithologies (e.g. sandstone, limestone, etc.), and basic land use information was also recorded for each site.

On return to the laboratory the samples were air-dried at 40 ° C, and plant roots were removed during sieving through a 2 mm; the fraction passing through the sieve was retained for analysis. Loss on ignition was estimated for each sample by heating to 450 ° C for eight hours, and TOC estimated by multiplying the mass difference by 0.58 (Broadbent, 1953). The coefficient of variation for this method for 174 replicate analyses of a sample standard was 3.6%. The summary statistics presented in Table 2 show that the statistical distributions of SOC estimated from LOI analyses for the three urban centres are quite different; median values range from 3.3% (Coventry), to 6.8% (Stoke-on-Trent); Glasgow had an intermediate median value of 5.2%. These differences are likely to reflect a combination of the inherited properties of the soil and varying land management in the three urban centres.

We considered whether it would be possible to use the available land use information to stratify the sites by some measure of cultivation, but we did not

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3 consider it to be sufficiently detailed to do so. To encompass the variation in OC
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5 using a subset of the urban samples, we randomly selected one archived soil sample
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7 from each decile of the SOC distribution (based on the LOI analyses) for each of
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9 these three urban centres – thirty samples in total. For each of the samples we
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11 estimated the concentration of TOC, TIC (total inorganic carbon) and BC using the
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13 methods described below. We also estimated the TOC content of the residue from
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15 each sample following application of the LOI procedure. A summary of the analytical
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17 techniques is provided in Table 3. Finally, for any samples where there was a large
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19 discrepancy between SOC estimated by the LOI and TOC analyses, we analysed its
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21 clay mineral composition by XRD (X-ray diffraction).
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Selection of procedure for determination of Black carbon.

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31 A variety of analytical methods have been developed to quantify BC in soils and
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33 sediments, including thermal, chemical and optical determination as well as other
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35 indirect methods (Schmidt & Noack, 2000). The primary objective of these
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37 procedures is to distinguish thermally modified carbon (BC) from unaltered
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39 biopolymers and their geological counterparts, as well as inorganic carbonate C.
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41 Comparative analysis of eight Australian soils by six established methods revealed
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43 non-systematic variations by factors of between 14 and 571 (more than two orders of
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45 magnitude) for an individual sample (Schmidt *et al.*, 2001). The large differences in
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47 BC concentrations from an individual sample were attributed to the variable abilities
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49 of each method to remove non-BC due in part to the different forms of natural organic
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51 matter. Thus each method had a differing analytical window depending on which pre-
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53 treatment, oxidation and determination technique was applied (Schmidt *et al.*, 2001).
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Currently there are no standardised procedures for BC determination. The CTO method yields more conservative estimates of BC when compared to: i) chemical oxidation by treatment with high energy UV-¹³C NMR or, ii) chemical oxidation using HNO₃ and quantification of derivatized benzocarboxylic acids (BCA) using gas chromatography (GC) and combined GC-mass spectrometry (GC/MS; see Schmidt et al. (2001). Two advantages of the CTO method are that the chemical pre-treatment stage minimizes charring of non-BC components and its former application to urban soils, sediments and residues from vegetation fires, so the results can be compared with other studies (Kuhlbusch, 1995; Gustafsson *et al.*, 1997; Reddy *et al.*, 2002; Lorenz et al., 2006). The main uncertainties of the CTO procedure for BC quantification include possible oxidation of BC and loss of small particles of BC during the centrifugation/decantation stage (Kuhlbusch, 1995). Nevertheless, these uncertainties are no greater, and in many instances less, than those of other BC methods (Schmidt & Noack, 2000; Nguyen *et al.*, 2004). We therefore selected a modified CTO method to quantify BC in our urban soil samples.

Analytical methods

The method used in this study to determine BC was based on that described by Kuhlbusch (1995). In summary, soils were extracted with aqueous solvents to remove as much inorganic carbon (IC) and OC as possible. The samples were then thermally treated in order to remove the remaining inorganic and organic C. The BC content of each sample was directly quantified after these two steps by TOC analysis of carbon at 1050 ° C (after removal of inorganic carbon).

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Sample preparation. Soils were sieved to pass a mesh of aperture 2 mm and the <2 mm fractions ground to a fine powder (<63 μm) using an agate ball mill (Retsch PM400).

Total Carbon and TOC. Soils were dried at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 3 h then treated with HCl (5.7 M), dried at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 1 h and TOC estimated using a Elementar Vario Max C/N analyzer at 1050°C . Total carbon (TC) was estimated using the same method but without acidification. Total inorganic carbon (TIC) was calculated by difference (i.e. $\text{TC} - \text{TOC} = \text{TIC}$). Procedural blanks were below instrumental response threshold. The limit of quantification for TOC for a typical 300 mg sample was 0.18%.

Wet extraction. For each soil a 2 g sub-sample was placed in a glass centrifuge tube and treated with 25 mL of solvents in the order: $2 \times \text{NaOH}$ (1 M), 1×70 mass % HNO_3 , 6×1 M NaOH, 1×1 mass % HCl, and 2×18 M Ω distilled, deionised water. After addition of each solvent the sample was sonicated in a heated ultrasonic bath (Camlab, 300W) for 15 min at 40°C , then centrifuged at 3000 rpm for 15 min (Fisher Scientific, acuuSpin 3) and the supernatant decanted and discarded. Following the final extraction with water, the sub-sample was dried ($100^{\circ}\text{C} \pm 5^{\circ}\text{C}$, 1.5 h) and the residue weighed.

Thermal Treatment and Black Carbon Determination. To remove the residual OC, 0.5-1.0 g of the wet extracted material was weighed in a glass centrifuge tube and placed in a furnace (340°C , 5 hours). The residue was re-weighed and quantified for TC. The carbon that is resistant to the wet extraction and the thermal treatment is defined as BC.

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XRD analysis. This was undertaken using a PANalytical X'Pert Pro series diffractometer equipped with a cobalt-target tube, X'Celerator detector and operated at 45kV and 40mA. The micronised sample was scanned from 4.5-85°2 θ at 2.76°2 θ /minute. Diffraction data were initially analysed using 2004 PANalytical X'Pert Highscore Plus software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database. Following identification of the mineral species present in the sample, mineral quantification was achieved using the Rietveld refinement technique (Snyder & Bish, 1989) using PANalytical Highscore Plus software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically $\pm 2.5\%$ for concentrations >60 wt%, $\pm 5\%$ for concentrations between 60 and 30 wt%, $\pm 10\%$ for concentrations between 30 and 10 wt%, $\pm 20\%$ for concentrations between 10 and 3 wt% and $\pm 40\%$ for concentrations <3 wt% (Hillier *et al.*, 2001).

Results and statistical analysis

Types of soil carbon

The analytical data from the analysis of the thirty samples for the different types of soil carbon are shown in Table 4, in addition to the land use information recorded at these sites. With relatively few sites we have not attempted to make any inferences regarding the significance of land use, although there does not appear to be a strong bias towards a particular land use class in any of the urban centres. Total inorganic carbon generally accounts for a small fraction of TC, with a mean of 3.9% and minimum and maximum of 0.12 and 12% of TC, respectively.

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Median BC concentrations were 0.46%, 0.59% and 1.77% for Coventry, Stoke-on-Trent and Glasgow, respectively. We also calculated the proportion of BC relative to TOC in each sample; the median of these proportions for samples in Stoke-on-Trent (12.4%) is similar to that for Coventry (16.4 %), whilst that for Glasgow is significantly larger (32.8 %). A sample from Glasgow also had the highest proportion (61 %) of BC to TOC, which is approaching the 73 % value reported by Lorenz et al. (2006) using a CTO method. The soil parent materials for Stoke-on-Trent and Glasgow comprise similar Carboniferous lithologies which suggests that anthropogenic sources may account for the larger amounts, and proportions of BC to TOC, in Glasgow. It is known that coal ash was widely dispersed across urban Glasgow as a soil conditioner (Pers Comm., Paul Mellon – Glasgow City Council).

Organic carbon in soil residues after LOI analysis

The relationship between the quantity of OC in soil residue after application of the LOI procedure and the BC content of the original soil is shown in Figure 2. For this subset of samples, their BC content is a linearly related to the quantity of TOC remaining in the soil after LOI analysis at 450 ° C. As neither of these variates had a strongly skewed distribution, we calculated a linear regression equation by the method of least squares using the original data. The equation is of the form,

$$y = \alpha + \beta x + \varepsilon \quad (1)$$

in which residual TOC after analysis was the explanatory variable (x), with which we wish to predict the BC content of the original sample (y), with ε representing any unexplained variation. The coefficients for the regression equations are shown in

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Table 5a and the regression line is shown in Figure 2. The residuals from the regression were approximately normally distributed. The regression equation captures 97% of the variance representing a very strong linear relationship for these samples based on these two methods. The position of the regression line shows that the LOI analysis removes a small, but consistent proportion of BC from each urban soil sample. The small residual standard error of 0.23% suggests this relationship may be useful for prediction. Such a relationship could be of practical use; the procedure for BC analysis is considerably more costly and complex than estimating its concentration based on a combination of LOI followed by TOC analysis.

Prediction of labile SOC using LOI values

We explored the relationship between labile SOC, that is TOC minus BC, versus SOC estimated by the LOI procedure for which we have analyses for all the urban soil samples. Neither of these variates was strongly skewed so we pursued our analysis using the original, untransformed data which are plotted in Figure 3. There is a clear linear relationship, with the exception of one sample, denoted A. For this sample, the LOI analysis appeared to significantly overestimate the SOC content. Hence, we estimated the proportions of the different soil minerals in this sample by XRD (X-ray diffraction).

Using the Rietveld refinement technique, we estimated that the mineral kaolinite accounted for around 23.6% of the soil mineral component (see Figure 4). It has been reported that the structural water in kaolinite can account for between 13 and 20% of weight loss at 850 ° C (Grim, 1953). In our sample above, therefore, loss of structural water could account for between 3.1 and 4.7% of the reported organic matter content (estimated by mass difference), and multiplying by 0.58 to account for the OC

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3 fraction, between 1.8 and 2.8% of the estimated SOC. This sample was collected in
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5 Stoke-on-Trent which has a long history of ceramics production, waste from which
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7 could account for large quantities of kaolinite in the soil. We believe this may account
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9 for the overestimation of SOC using LOI and so we felt justified in excluding this
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11 sample from the next stage of our statistical analysis.
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15 We wished to assess whether a single linear regression relationship could be
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17 used to estimate labile SOC based on estimates from LOI analyses for the different
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19 urban centres. To do this we tested for evidence of non-parallel slopes for each of the
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21 three cities between labile SOC (TOC minus BC) and SOC estimated by LOI. We
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23 undertook a two-factor ANOVA with LOI as a covariate in which city was an
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25 interaction term (Table 6a). We also tested for evidence of a quadratic term in the
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27 linear regression model (Table 6b). In both cases the statistical significance for each
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29 was weak; P values of 0.32 and 0.14, respectively. We proceeded by calculating a
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31 linear regression (equation 1) using the method of least squares based on the original
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33 data with the kaolinite-enriched sample excluded. In this case, SOC based on LOI
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35 analysis was the explanatory variable (x), with which we wish to predict the labile
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37 SOC (TOC-BC) content of the original sample (y), with ε representing any
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39 unexplained variation. The coefficients for the regression equations are shown in
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41 Table 5b and the regression line in Figure 3. The residuals from the regression were
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43 approximately normally distributed and the model accounted for 81% of the variance,
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45 suggesting it could also be useful basis for prediction. It is important to note that we
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47 would not expect a 1:1 relationship between the estimates of SOC based on LOI and
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49 the labile SOC (TOC minus BC) because a proportion of BC in each of the samples is
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51 not included in the former. We used the regression equation to predict labile SOC
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53 using the LOI data multiplied by 0.58 for all the soil samples from each of the three
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3 cities, and plotted them as empirical cumulative distributions (Figure 5). We also
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5 plotted symbols to show the position of the median SOC estimates based on the
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7 original LOI analyses. For each urban area the median predicted labile SOC is
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9 significantly less than the median estimates of SOC, for which there are two main
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11 reasons. First, the LOI analysis includes a fraction of the BC which is removed from
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13 the estimate of labile SOC by applying the regression equation. Second, it is likely
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15 that the LOI analyses will slightly overestimate SOC due to the liberation of small
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17 quantities of structural water from clay minerals, and this will be corrected in the
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19 regression equation based on the TOC analyses. The estimates of labile SOC could
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21 be used as a basis for mapping, or with assumptions for bulk density, the estimation of
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23 OC stocks in these urban areas.
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Comparison of labile urban SOC and rural SOC.

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33 We compared the mean labile SOC (TOC minus BC) values for each of the three
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35 urban centres with half the mean SOC for the equivalent local Soil Associations in
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37 England and Scotland under pasture (Figure 1) according to the method adopted by
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39 Bradley et al. (2005). For the soils around Coventry and Stoke-on-Trent the sampling
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41 depths for the rural samples were consistent with those in the urban environment (0 to
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43 15 cm depth). For samples around Stoke-on-Trent, we removed from the calculation
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45 those from the Wilcocks series as this outlier (SOC 24.8%) would have seriously
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47 biased an estimate of the mean (Figure 1). The rural samples around Glasgow,
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49 supplied by the Macaulay Institute, are horizon specific. As information was not
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51 available on stratification, the closest possible comparison was to use data for samples
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53 from a soil depth range of 5 to 15 cm.
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The mean labile SOC content (TOC minus BC) of urban samples from Coventry was 3.1%, compared with a value of 2.0% for half the mean content under local pasture. In Glasgow, mean labile SOC is 3.7%, compared to 2.9% which is half of the mean under pasture from the local Rowanhill association. Finally, mean labile SOC in Stoke was 4.6%, whilst half the mean content in local pasture is 1.9%. In each case, taking the value of half the mean from local pasture underestimates the mean labile SOC of the ten urban samples. For Coventry and Glasgow the differences are 1.1 and 0.8 % respectively, whilst the 2.7% difference for Stoke is considerably larger.

Discussion

Our findings showed that the assumption used by Bradley et al. (2005) for estimation of carbon stocks in suburban areas of the UK would underestimate, to varying degrees, labile SOC content and hence carbon stocks. We would need to test the regression relationship we established for predicting labile SOC using data from other centres before it could be applied more widely. If this relationship proved to be robust, then it could be a cost-effective method for estimating labile SOC using a limited number of soil samples from large urban centres. Although SOC was the focus of this study, it is also important to consider the potentially significant contributions from IC to soil carbon stocks.

More knowledge of the variation in quantity and type of SOC across the entire depth range of differing urban soil materials would significantly improve our estimates of urban carbon stocks. For example, archived soil material is available from the original urban surveys for depths of between 35 and 50 cm, although no information is available on total soil depths at these sites. Another potential limitation

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3 on our understanding of urban soil carbon distributions is a detailed knowledge of
4 changes in land use history. The interpretation of its influence and that of local
5 pollution sources was not an aim of this study. Such an approach based on relatively
6 few samples may be problematic due the large number of carbon sources that may be
7 introduced as unrecorded applications of soil material or fill, reflecting the dynamic
8 and complex history of urban soils in the UK. Despite such concerns, a recent case
9 study in Nanjing (China) has shown significant differences in BC contents in areas of
10 differing land use, such as roadsides, parks and residential areas (He & Zhang, 2007).
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22 The major environmental problems caused by atmospheric emissions of BC
23 particles such as smog formation and local air pollution are not necessarily mirrored
24 in the subsurface. One beneficial effect of BC in soils is their ability to bind
25 persistent organic pollutants (POPs) such as polynuclear aromatic hydrocarbons
26 (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenylethers
27 (PBDEs) (Gustafsson et al., 1997; Bucheli & Gustafsson, 2003). Combined,
28 conceptual models, field-data and column experiments suggest that adsorption of
29 POPs to BC surfaces can reduce uptake in organisms by up to two orders of
30 magnitude (Koelmans *et al.*, 2006). Soils with elevated BC contents, such as the
31 urban soils analysed here, may effectively bind POPs and decrease the bioavailable
32 concentrations of these toxic compounds.
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48 Total organic carbon analysis of soil residue following application of the LOI
49 procedure showed that a small, but consistent proportion of the BC is removed at 450
50 °C. This suggests that the LOI procedure is differentiating between two forms of BC,
51 one which is oxidised below 450 °C, and a more recalcitrant form which combusts at
52 higher temperatures. More research is required to determine whether TOC analysis of
53 the soil residue following LOI could be a practical, cost-effective method for
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estimating BC contents of soil. By reducing the temperature in the LOI procedure to
between 350 and 380 ° C, it may be possible to avoid part of the BC oxidation from
this part of the analysis. This approach would need to be tested on different
combinations and types of black and labile carbon before it could be applied more
widely. Such inexpensive methods for estimating BC contents in soil may be required
if carbon sequestration resulting from the application of char is widely adopted as a
mechanism to ameliorate rising atmospheric CO₂ concentrations (Lehmann, 2006).
Urban soils may also provide man-made observatories for research investigating the
potential side-effects of black carbon sequestration (Fowles, 2007).

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We suggested that the significantly higher mean BC contents of soils in
Glasgow, by comparison to those in Coventry and Stoke-on-Trent, were attributable
to greater historical BC dispersal across the former. By analysing the BC content of
local rural soils developed over the same parent material types, we should be able to
determine whether geogenic sources of BC could account for the observed
differences. It may also be of interest to establish whether the beneficial effects of
char on soil fertility (Steiner *et al.*, 2007) could be established for these BC enriched
urban soils of Glasgow in relation to their rural equivalents.

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To our knowledge, the survey data published in this paper are the first to
establish a baseline which could be used for subsequent monitoring of change in OC
contents of UK urban soil and assessing changes in the functions they can perform.
The dynamic nature of urban environments will present particular challenges to soil
monitoring for the assessment of changes in soil function. Detailed information will
be required on any local addition or removal of soil material or fill which could lead
to abrupt changes in SOC contents and other indicators of soil quality.

Conclusion

The main findings of our study are:

1. By subtracting estimates of BC from TOC for a subset of thirty urban soil samples – ten from each of three urban areas – we estimated their labile SOC contents. We demonstrated a strong linear relationship between this estimate of labile SOC and the original LOI estimates of SOC. In addition, there was insufficient evidence for the application of differing slopes in the regression relationships for the three urban areas, so we applied the same equation to all the LOI data from the original surveys to provide improved estimates of labile SOC. This relationship needs to be tested further before it could be applied more widely.
2. We showed that an assumption for estimating the SOC content of urban soils, based on half the mean value under pasture for local soil associations is likely to underestimate their content, and would therefore lead to an underestimate of SOC stocks.
3. There were significant differences in the BC contents for the three urban centres studied, with the largest values occurring in Glasgow where coal ash was known to have been used widely as a soil conditioner.
4. A TOC determination of the residue of a soil sample subjected to LOI may be a cost-effective approach for providing an estimate of its BC content. However, further research is necessary to determine an optimum temperature for the LOI part of the procedure.

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We thank all the staff of the British Geological Survey and volunteers involved in the collection and analysis of soil samples in the G-SUE (Geochemical Surveys of Urban

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Environments) project. We are grateful to Mr Ian Bradley (formerly of the National Soil Resources Institute) for the provision of the summary data on soils around Coventry and Stoke-on-Trent, and to the Macaulay Land Use Research Institute for summary information on the Rowanhill formation. We also wish to thank Murray Lark of Rothamsted Research for helpful discussions concerning the sampling design and aspects of the statistical analysis, and two anonymous reviewers for their comments on an earlier draft of the manuscript. This paper is published with the permission of the Director of the British Geological Survey (Natural Environment Research Council). Unless otherwise stated BGS © NERC 2007. All rights reserved.

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Figure captions

Figure 1 Location of the three urban centres in the United Kingdom and the extent of their associated pasture soils in surrounding rural areas based on 1:250,000 scale soil maps. The Soil Associations in England were derived from NATMAP ©Cranfield University (Hallett *et al.*, 1996), and the Scottish Associations are from the Scottish Soil Map (Soil Survey Staff, 1981) © The Macaulay Institute 2002.

Figure 2 Plot of total carbon (%) remaining in soil residue after LOI analysis versus BC (%) in the original samples (n=28) and linear regression line (---).

Figure 3 Plot of SOC estimated by LOI analysis versus labile TOC (elemental analysis) after subtraction of BC (n=28). The regression line (---) omitted the sample labelled A for reasons explained in the text.

Figure 4 Powder X-ray diffraction trace for sample denoted A in Figure 3, compared to component mineral standard 'stick' patterns (below).

Figure 5 Cumulative distributions of predicted labile SOC (%) in three urban centres (lines) based on LOI analyses for all soil samples in the urban centres and the regression equation in Table 5b. The symbols show median estimates of SOC (%) based on the original LOI analyses. Labile refers to TOC minus BC.

Table captions

Table 1 Details of the three urban centres and the urban soil surveys

Table 2 Summary statistics for estimates of SOC (%) from soil surveys in three urban centres based on LOI (loss on ignition) analysis

Table 3 Summary of analytical techniques and types of soil carbon estimated for survey and selected samples (n=30)

Table 4 Soil carbon fractions in selected topsoil samples from the three urban areas and the land use at each site.

Table 5 Coefficients for regression equation relating: a) TOC (%) in soil residue after LOI analysis to BC (%) in the original soil sample and b) SOC estimated by LOI analysis versus labile (TOC-BC) SOC (elemental analysis)

Table 6 Analysis of variance of labile SOC (TOC minus BC) for: a) SOC estimated by LOI as a covariate and the three cities as an interaction term, and b) SOC estimated by LOI as a covariate and as a quadratic term.

Table 1 Details of the three urban centres and the urban soil surveys

Urban centre	Parent material (bedrock geology; overlying Quaternary deposits)	Dominant Soil Association - description: ^a WRB classification	Industrial and developmental history	Soil survey sampling configuration	Year in which survey undertaken	Current urban pop ⁿ
Coventry	Permo-Triassic (sandstone and mudstone); riverine deposits	^b SALOP- Slowly permeable, seasonally waterlogged reddish fine loamy over clayey fine loamy and clayey soils: Eutri-luvic STAGNOSOL	C13th – centre of textile trade. C14th – 4 th largest city in England. C19th – world's largest bicycle trade. C20th – major centre for weaponry manufacture for WW2 – large areas destroyed by aerial bombing, then rebuilt	Star pattern of 5 subsamples from a square of side length 20 metres	2000	301,000
Glasgow	Carboniferous Coal Measures, (sandstones and limestone); glacial tills and riverine deposits	^c ROWANHILL- Non calcareous gleys, imperfectly and poorly drained: STAGNOSOLS	C16th to 18 th – centre for merchant shipping and trade (tobacco and sugar) C19th – shipbuilding, textile manufacture, one of world's richest cities (construction of public transport system, parks, museums) Late C20th – industrial decline, loss of ship-building and manufacturing).	Star pattern of 5 subsamples from a square of side length 20 metres	2001	578,000
Stoke-on-Trent	Carboniferous Coal Measures and Permian sandstone; glacial till	^b BARDSEY- Slowly permeable seasonally waterlogged loamy over clayey and fine silty soils over soft rock: Dystri-stagnic	C12th – market town C13th to C16th – Coal and ironstone mining C17th- 19th – world leader in ceramic production, some steel production. C20th – industrial decline, legacy of	Grid pattern of 9 subsamples from a square of side length 2 metres	1993	240,500

GLEYSOL industrial waste

^a FAO/ISRIC/ISSS (1998)

^b Soil Survey of England and Wales (1983)

^c Macaulay Institute for Soil Research (1985)

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Table 2 Summary statistics for estimates of SOC (%) from soil surveys in three urban centres based on LOI (loss on ignition) analysis

	Coventry	Glasgow	Stoke-on-Trent
Minimum	0.9	1.4	0.4
Mean	3.5	5.5	7.3
Median	3.3	5.2	6.8
Maximum	18.6	21.0	42.5
Standard Deviation	1.6	1.9	3.2
Standard Error of the Mean:	0.05	0.05	0.12
Number of samples	808	1382	737

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Table 3 Summary of analytical techniques and types of soil carbon estimated for survey and selected samples (n=30)

Techniques (samples)	Types of soil carbon estimated			
	TC (total carbon)	TOC (total organic carbon)	TIC (Total Inorganic Carbon)	BC (black carbon)
Loss on ignition (survey samples)	n/a	Estimate using assumption of 58% of weight loss is carbon – includes a component of BC and water from clay minerals	n/a	n/a
TOC (n=30 selected samples)	Estimated Elementar Vario Max C/N analyzer (1050 °C) after removal of inorganic carbon	Estimate of organic carbon in the sample after removal of inorganic C – includes all BC	n/a	n/a
TC (n=30 selected samples)	Estimated Elementar Vario Max C/N analyzer (1050 °C)	n/a	Estimated by TC-TOC	n/a
BC (n=30 selected samples)		Labile C removed by chemical and thermal oxidation	Removed by acidification	Estimated as C remaining after chemical and thermal oxidation
TOC (residue of n=30 selected samples after LOI procedure)	n/a	n/a	n/a	BC that was not oxidised at 450 °C.

Table 4 Soil carbon fractions in selected topsoil samples from the three urban areas and the land use at each site.

City / Sample	Total Carbon (%)	^a Total Organic Carbon (TOC %)	Total Inorganic Carbon (TIC %)	^b Black Carbon (%)	^c Soil Organic Carbon estimated by LOI (%)	TOC in residue of sample following LOI analysis (%)	Land use recorded at each site during the soil survey
Glasgow1	2.78	2.68	0.10	0.50	3.13	0.20	grassed area (made ground)
Glasgow2	4.10	4.06	0.04	1.26	4.00	0.58	grass verge
Glasgow3	5.12	4.85	0.27	1.32	4.48	0.61	grassed area (made ground)
Glasgow4	3.78	3.71	0.07	0.60	4.64	0.20	grassed area
Glasgow5	5.99	5.82	0.17	2.43	5.19	1.35	grassed area (made ground)
Glasgow6	6.16	6.06	0.10	2.09	5.37	0.76	grassed area (made ground)
Glasgow7	5.76	5.65	0.11	1.46	5.99	0.68	grassed area (made ground)
Glasgow8	9.86	8.64	1.22	5.25	6.44	3.54	grass verge
Glasgow9	8.96	8.85	0.11	3.55	7.10	2.05	grass verge
Glasgow10	10.12	10.17	<0.18	4.68	8.44	2.63	lawn of residential property
Stoke1	2.70	2.64	0.06	0.48	4.00	0.20	lawn of residential property
Stoke2	3.07	3.00	0.07	0.35	4.26	0.20	recreational land
Stoke3	1.20	1.09	0.11	0.13	5.41	0.06	grassed area
Stoke4	3.90	3.86	0.04	0.35	6.16	0.12	grass verge
Stoke5	6.67	6.35	0.32	1.93	6.33	1.13	grassed area in parkland
Stoke6	4.91	4.89	0.02	0.63	6.91	0.28	lawn of residential property
Stoke7	5.62	5.48	0.14	1.11	8.00	0.45	grass verge
Stoke8	8.22	8.21	0.01	0.55	8.53	0.31	lawn of residential property
Stoke9	9.33	9.13	0.20	3.16	9.62	1.71	grass verge
Stoke10	14.44	12.74	1.70	3.03	12.03	1.88	grassed area (made ground)
Coventry1	0.75	0.68	0.07	n/a	1.10	<0.18	small overgrown field
Coventry2	2.38	2.14	0.24	<0.10	2.17	0.24	grassed area (made ground)
Coventry3	4.83	4.70	0.13	1.75	2.42	0.97	grassed area
Coventry4	2.33	2.29	0.04	0.48	2.76	0.24	roadside grass verge
Coventry5	2.83	2.77	0.06	0.31	3.12	0.14	grassed area (made ground)
Coventry6	2.93	2.85	0.08	0.41	3.32	0.22	recreational land
Coventry7	3.18	3.00	0.18	0.55	3.75	0.25	recreational land
Coventry8	1.96	1.78	0.18	0.16	4.00	<0.18	overgrown formerly tilled land
Coventry9	6.50	6.42	0.08	1.26	5.05	0.52	lawn of residential property
Coventry10	6.30	6.16	0.14	0.44	6.23	0.31	grass verge

^a elemental carbon analysis^b Kuhlbusch (1995)^c calculated as mass difference multiplied by 0.58 (Broadbent, 1953)

Table 5 Coefficients for regression equation relating: a) TOC (%) in soil residue after LOI analysis to BC (%) in the original soil sample and b) SOC estimated by LOI analysis to labile SOC (TOC-BC)

Dependent variable (y)	Independent variable (x)	Constant (α) ± Std. error	Slope (β) ± Std. error	R^2	Number of observations	Standard error of observation
a) BC (%) in original sample	TOC (%) in residue after LOI	0.229 ± 0.06	1.56 ± 0.05	0.97	27	0.23
b) Labile SOC (%) TOC minus BC	SOC (%) estimated by LOI	-0.101 ± 0.430	0.723 ± 0.071	0.81	27	0.84

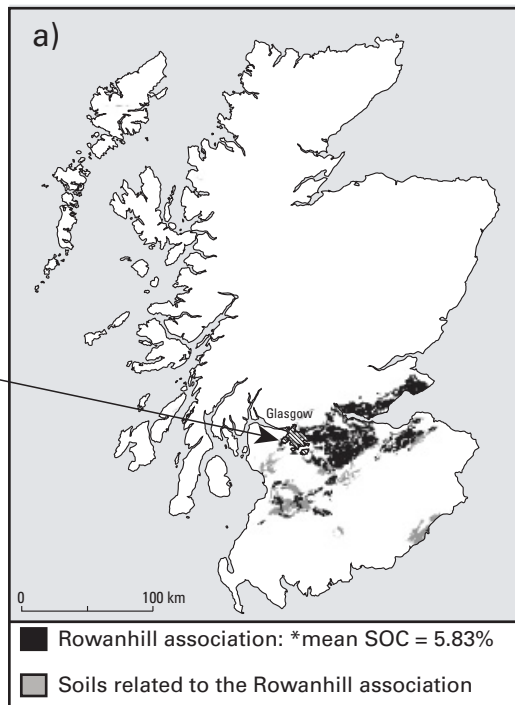
Table 6 Analysis of variance of labile SOC (TOC minus BC) for: a) SOC estimated by LOI as a covariate and the three cities as an interaction term, and b) SOC estimated by LOI as a covariate and as a quadratic term.

a)

Source	Degrees of freedom	Sum of squares	Mean square	F	P
SOC (LOI)	1	71.79	71.79	115.96	<0.001
City	2	2.874	1.437	2.322	0.123
SOC (LOI)*City	2	1.513	0.757	1.222	0.315
Residuals	21	13.000	0.619		
Total	26	89.176			

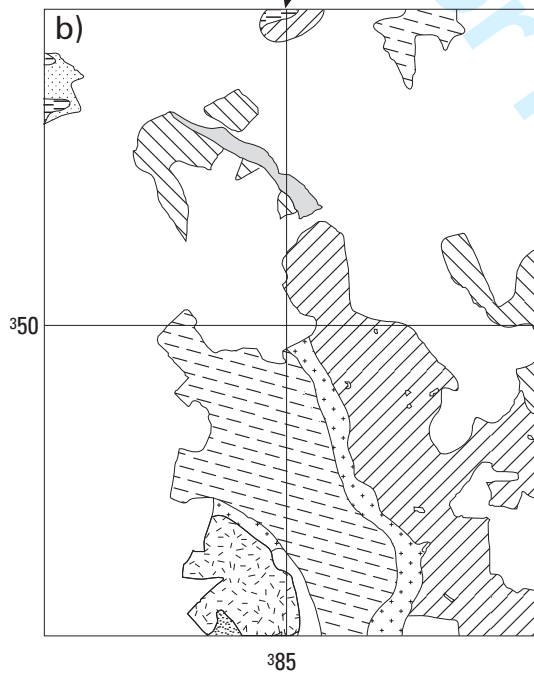
b)

Source	Degrees of freedom	Sum of squares	Mean square	F	P
SOC (LOI)	1	71.788	71.788	108.590	<0.001
SOC(LOI) ²	1	1.521	1.521	2.302	0.142
Residuals	24	15.866	0.661		
Totals	26	89.176			



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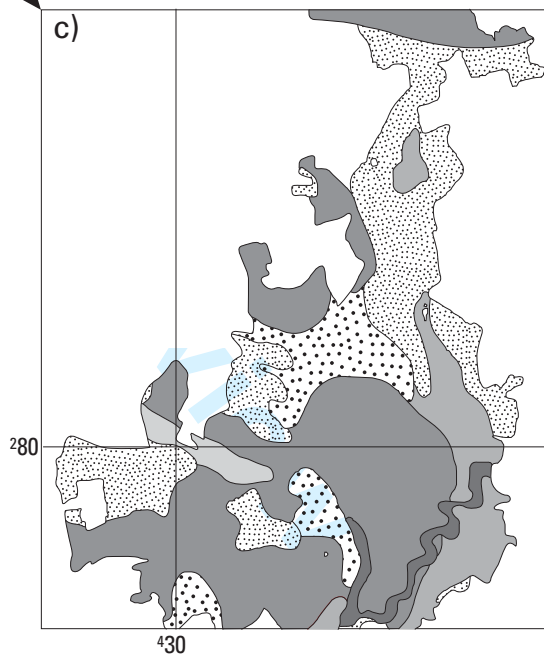
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Association	Dominant series	SOC (%)
541d	Eardiston	2.6
551d	Newport	2.6
572m	Salwick	3.5
711b	Brockhurst	3.5
713a	Bardsey	4.6
713g	Brickfield	4.8
721c	Wilcocks	24.8
811a	Enborne	5.3
821b	Blackwood	4.0
962	Manmade soils	Data not available

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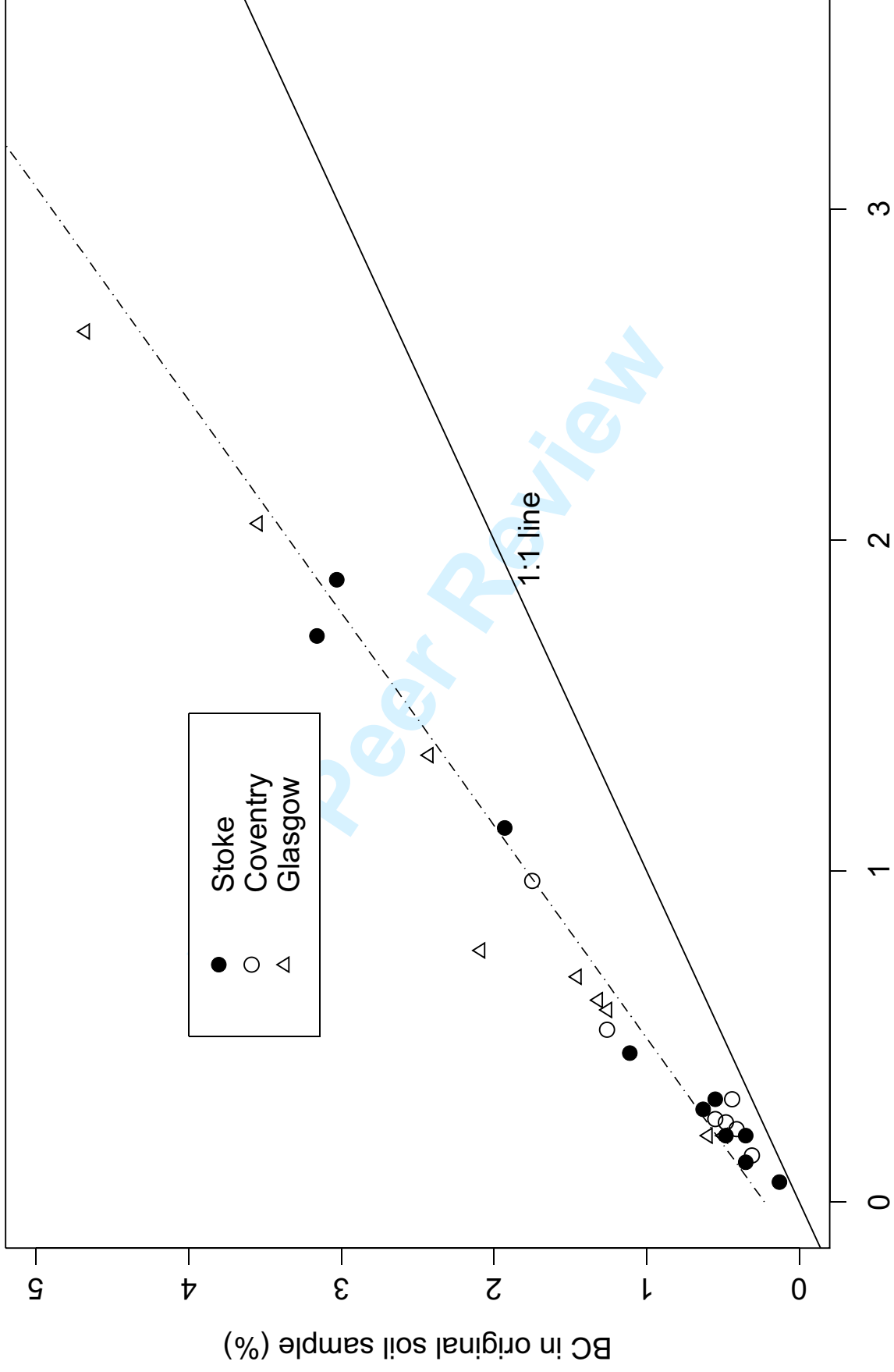


Association	Dominant series	SOC (%)
541b	Bromsgrove	2.2
541r	Wick	3.5
572e	Whimple	3.6
711b	Brockhurst	3.5
711m	Salop	3.6
813b	Fladbury	7.1

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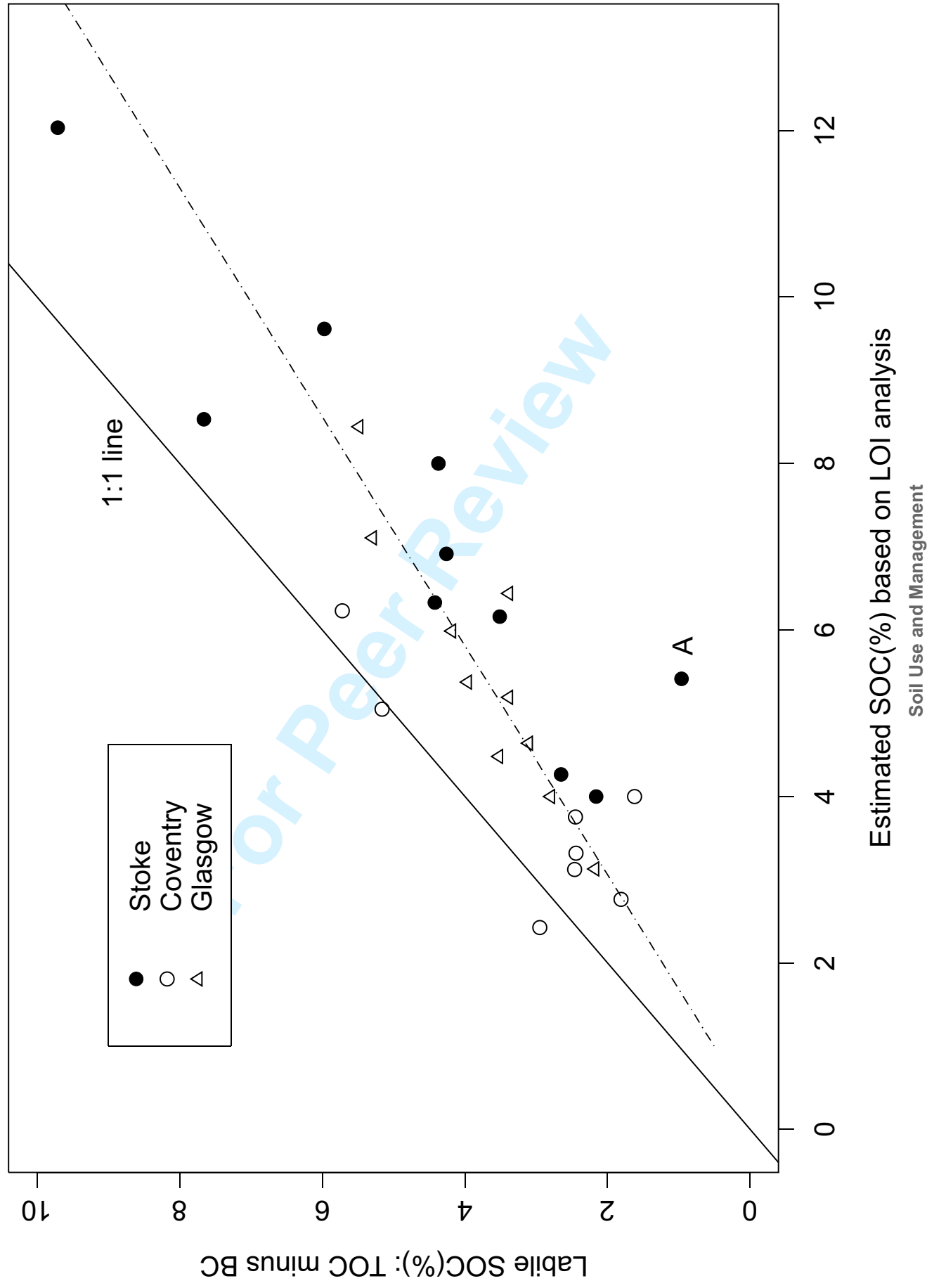
Figure 1

Figure 2



TOC(%) determined by elemental analysis in residue of soil after LOI procedure

Figure 3



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Figure 4

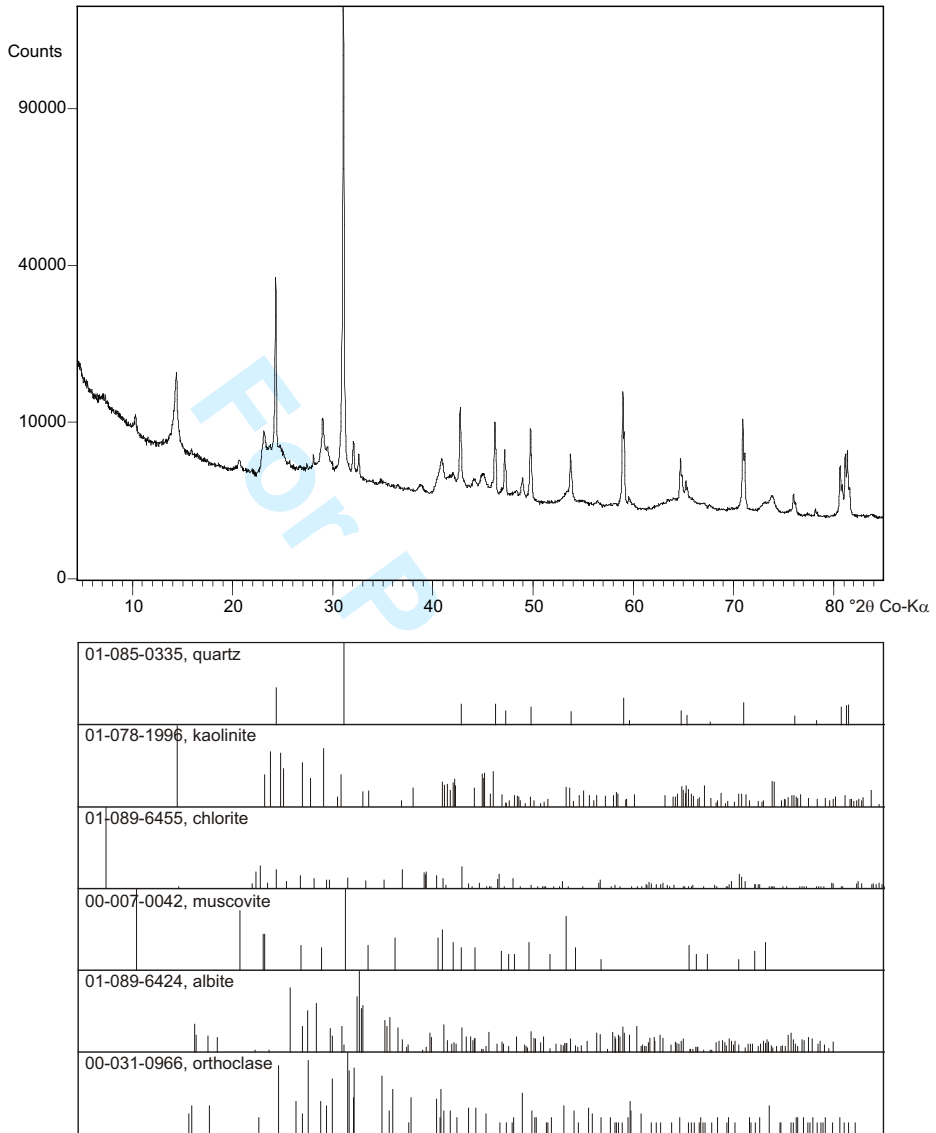
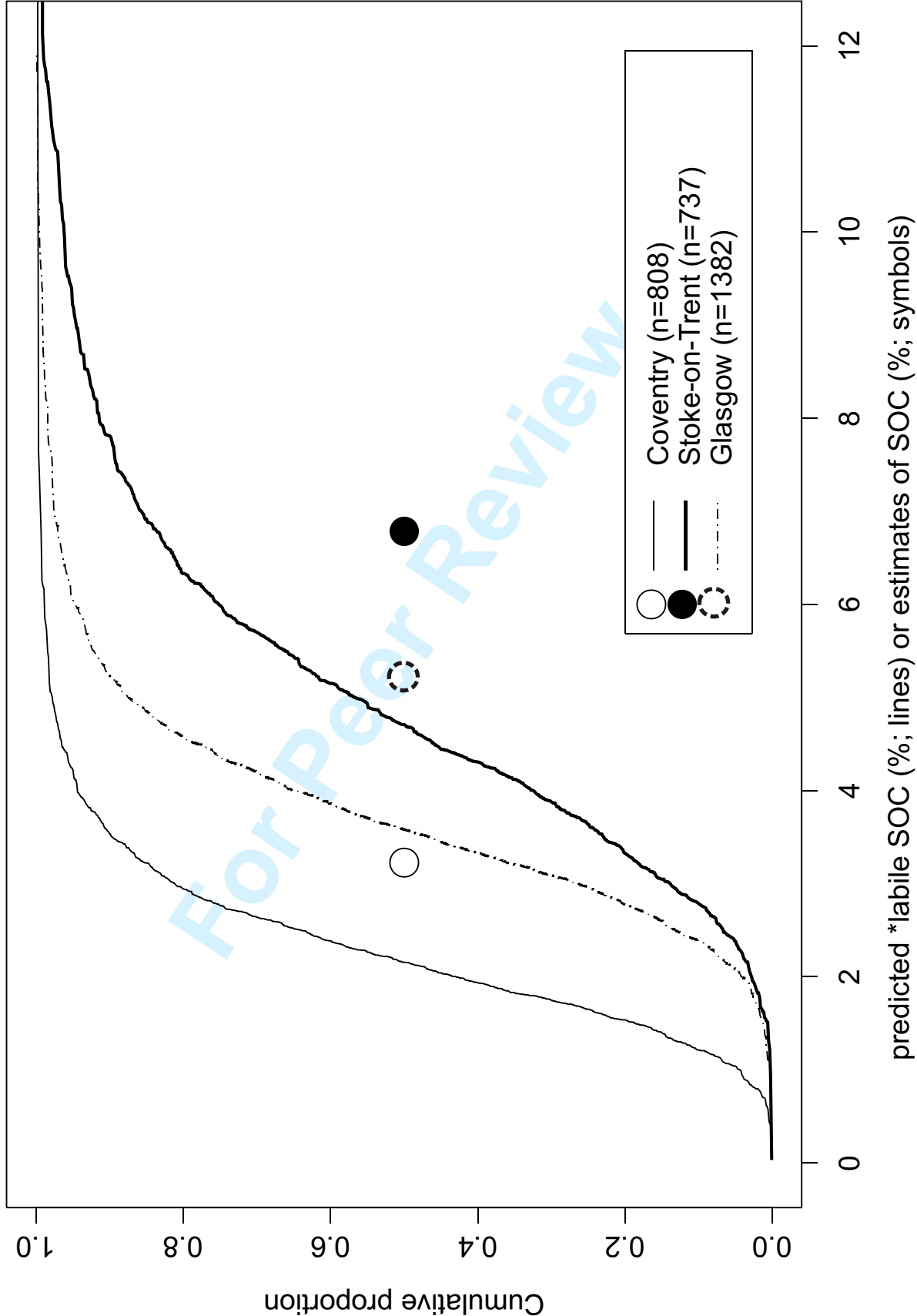


Figure 5



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