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Organic Carbon Speciation in Urban Anthrosols—The Legacy of Historical Waste Management

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Abstract: The impacts of waste management on various soils of agricultural and urban lands may last centuries or even millennia; however, generally, most studies tend to focus only on decadal or shorter timescales. This study investigates the characteristic properties of anthrosols in and around the urban settlement of St Andrews (Scotland), in the context of soil management and organic carbon content and speciation. Formed by the repeated application of fresh organic and pyrogenic wastes since the medieval period, these soils provide a 1000-year urban research context based on historical accounts of town waste management. We employed complementary methods of high-field solid-state ^{13}C-CPMAS NMR, in situ magnetic susceptibility measurement, elemental micro-analysis and portable optically stimulated luminescence (OSL). A significant proportion of the soil organic carbon was present as refractory aromatic C structures, including aryl-C moieties. Portable OSL assessment revealed differences in the intensity and rate of sediment accumulation. The medieval urban areas had higher soil phosphorus concentrations, organic carbon content and magnetic susceptibility relative to the extra-urban site located outside of the medieval burgh. The study confirms that specific signatures, including carbon group functionalities, do reveal evidence of such induced long-lasting past anthropogenic soil modifications.

Keywords: ^{13}C-CPMAS NMR spectroscopy; urban anthrosols; soil organic carbon; pyrogenic material; carbon speciation; medieval; extra-urban

1. Introduction

As the rate of growth of urbanised human populations continues to increase, urban land expansion has accelerated yet further [1–4]. In a meta-analysis by Seto et al. [5] on urban land expansion for the period 1970–2000, urban land expansion rates across all continents were greater or equal to urban population growth rates. The consequences of this dramatic change in land use include an increase in the global abundance of anthropogenically altered soils; these soils are therefore of increasing concern in terms of sustainable management and retaining the provision of ecosystem services such as carbon storage, climate regulation, water flow and filtration, waste recycling, etc. [6–8]. The role of urban soils in carbon sequestration is increasingly being recognised by policy makers, and several major urban areas have been studied to try to understand this role [4,9]. Comparisons between and within such studies suggest that urban soils will play a major and increasing role in the storage of sequestered carbon. However, our understanding of the impact of changing environments on such soils and their properties remains limited. While there are increasing numbers of studies examining changes in soil properties during shifts from

low-intensity agricultural use to urban use, and the factors that influence these environments, such as elevated urban temperatures, many such studies lack an understanding of the changes likely to occur over long periods. Similarly, while successful models of pedogenesis for anthrosols can be developed [10], the fate of organic matter in these soils has focused on understanding present-day ongoing processes of microbial activity. A greater consideration to the fact that these soils represent the consequences of a specific set of historical land uses, and understanding that there is a time-depth linkage associated with such soils, in relation to their characteristics and management that varies by location, are therefore paramount. A recent study by Esiana et al. [11] on soil organic matter (SOM) dynamics on urban anthrosols highlighted the biochemical interactions at play, and the role of the extracellular enzyme phenoloxidase in the decomposition of SOM.

Soil formation resulting from the anthropogenic use of wastes and sediments for soil improvement is a widely recognised northern European practise. In Scotland, the historical application of various types of waste to soil played a key role in urban agricultural economy since it was recognised that higher productivity could be achieved when used for soil amelioration [12,13]. The development of urban centres during the medieval period reflected dramatic changes in economic and environmental activity [14,15]. These activities included specialist crafts, such as iron smithing, leather tanning, processing of animal materials in abattoirs and fish gutting [13,16], which produced mixtures of organic (i.e., plant and animal remains) and inorganic (e.g., charred material) wastes. The burgesses or townsmen were, however, also cultivators who grew many of their own dietary staples in the backlands of their towns. The capitalisation of soil as a resource to the townspeople was therefore achieved in such medieval centres by recycling composted urban (domestic and industrial) waste for use as manure, and was normally accomplished by charging for waste collection and charging again for composted waste [17–21]. Studies by Brothwell [22] suggest that an estimated 182,500 litres of urine, 36,500 kg of human faeces, 182,500 kg of solid waste (e.g., food waste) and 8100 kg of wood ash from cooking and heating were produced annually per 100 households in such pre-industrial societies. Composted urban waste, which generally consisted of human and animal excrements and urine, food waste, fuel residue (ash, soot and charcoal), butchery shambles (bones, flesh, shells) and other debris, was a particularly valued commodity by both subsistence and commercial farmers prior to the widespread use of industrial fertilisers in the 20th century [13].

Geoarchaeological investigations have shown that heavily modified soils occur within or in close proximity to the core areas of settlements, although significant deepening of soil outside this area is not uncommon and has been documented [12]. This spatial variation in soil distribution where highly altered soils, with typically higher nutrient status, are found within and/or closer to the settlement is prevalent in various anthropogenic soil formation from elsewhere around the world. Such formation includes the plaggen soil distribution in Europe [23,24], and the Amazonian dark earth (terra preta and terra mulata) in South America [25,26]. Past studies on the development of anthrosols have often reported on the similarities in the characteristic properties of such soils. These properties involve changes to soil pH (usually from acidic to more alkaline), depletion and/or enrichment of certain groups of elements, primarily phosphorus, the increase in soil magnetic properties through burning, decrease in grain size, and high frequency occurrence of carbonised material [27,28]. The high occurrence of charred organic carbon, sometimes apparent from soil colour, is a particular prominent characteristic property of heavily modified anthropogenic soils. The sources of charred materials are normally attributed to the deliberate addition of ash, soot and charcoal from cooking fires and hearths (fireplace) onto soil, although natural processes such as forest/bush fires may also give rise to these materials [29,30].

Determining the provenance of black carbon materials is increasingly being considered through methods that allow an understanding of the pyrolytic processes involved in the production of these materials [31–33]. In this study, however, our focus was not on the source, but on the fate of such materials in the soil over extended periods of time.

Spectroscopic examinations of anthrosols from elsewhere around the world using ^{13}C-CPMAS NMR have repeatedly reported higher aromatic C content relative to the adjacent natural/background soil in the area [28,34–36]. At present, many urban core areas from the medieval period do remain, but evidence of past activity in these land areas within the town is typically lost through burial under urban structures or obliterated by modern land uses. However, in St Andrews, Scotland, both the street layout and much of the land used by the townspeople remains relatively intact in the medieval core of the town. This setting provides a unique environment to assess the development and nature of anthrosols that have formed through long-term sustained addition of organic materials. The increased need for understanding paedogenic processes in a period of global climatic change is coupled here to the specific understanding of the growing inventory of anthropogenic soils in urban landscapes worldwide. Using urbanisation as a proxy for the growth of anthropogenic soils, Capra et al. [37] reports that globally more than 3% of the land surface is now impacted. With an increasing importance placed on soil management within such landscapes [4,38,39] and their carbon sink potential, we investigated the impacts of historical management practices on soil properties, revealing features of centuries of interaction of complex and diverse anthropogenic and natural impacts on extant urban anthrosols.

2. Materials and Methods

2.1. Study Site

St Andrews (56°20′29.15″ N, 2°47′53.84″ W) is a small coastal settlement on the east coast of Scotland (Figure 1). The burgh was established circa 1150, according to Bishop Robert's foundation charter [40]. St Andrews was a thriving medieval burgh which was a centre for a variety of functions, including ecclesiastical, educational and commercial functions. It has a temperate maritime climate with annual precipitation at 690 mm and an annual average temperature range of 5.1–12.5 °C [41]. The parent material is raised beach sands and gravels derived from old red sandstones sediments and lavas, and the immediate surrounding soils, other than those reported as anthrosols, are mainly brown soils and podzols [42]. The present-day land use around the town is arable and improved grassland [43]. Urban agriculture in St Andrews in the medieval periods involved the use of organic wastes for soil improvement. St Andrews is representative of many other medieval Scottish burghs where sustained additions of these wastes have resulted in the development of deep organic-rich anthrosols (technic hortic anthrosols) [12,19,44,45]. The practice continued until at least 1832 and went into decline in the late 18th century due to urban expansion and new sanitary reforms [14,18,46,47]. Within the medieval urban areas of St Andrews, where organic-rich wastes were once deposited, we now see garden areas and public parks dominated by grass cover.
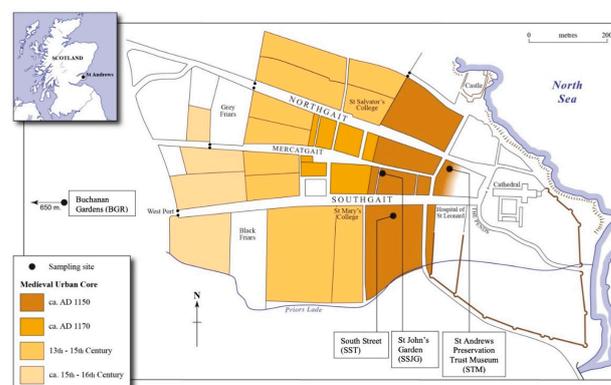

Figure 1. Main: map of medieval St Andrews showing the street layout and development of the burgh. The urban core sampling sites all fall within the central and earliest urban settlement. Development stages outlined are after Brooks and Whittington (1977); inset: location of St Andrews, Scotland, UK. *STM*, *SST* and *SSJG* are urban core sites; *BGR* is an extra-urban site.

2.2. Sampling

Soil samples were collected in February 2013 from four locations across the study area, where there are minimal contemporary disturbances from modern land use practises. Samples from St Andrews Preservation Trust Museum (*STM*), South Street (*SST*), and St John's Garden (*SSJG*), hereafter collectively referred to as urban core sites/areas, were collected at various points within the urban core area of the settlement (Figure 1) while samples from Buchannan Garden (*BGR*), referred to as an extra-urban site, were collected from a relatively undisturbed site away from the core areas. All samples were collected from within areas of similar parent material and background soil type. For all the sites, soil samples were collected from freshly dug and exposed soil profiles. Sampling was carried out on two occasions; first, auger sampling for physico-chemical analyses, followed by soil pit sampling for portable OSL analysis and magnetic susceptibility measurement. Sampling points were selected at random from within the respective sampling area. Auger samples labelled *STM, SST, SSJG* and *BGR* were collected with varying depth increments ($+/-$ 15 cm) until the auger could go no deeper into the soil profile. A series of copper tubes, 25 cm × 2 cm in diameter, were used to sample exposed soil profiles for portable optically stimulated luminescence (OSL) analysis. Both ends of the tubes were covered and sealed with adhesive tape after sampling to prevent further re-exposure to light. Kubiena tins (8 cm high × 6 cm wide × 5 cm deep) were used to sample soil profiles for charcoal content analysis. Samples were collected at various depths along the profile corresponding to the profile stratigraphy identified. Due to property redevelopment in the South Street site (*SST*), it was not possible to collect soil pit samples. Soil colour assessment was determined in situ [48]. A total of 42 samples were collected for ex situ analysis.

2.3. Soil Chemical and Physical Analysis

Soil samples were air-dried, sieved to <2 mm and homogenised before analysis. Carbonates, due to the presence of ecofact fragments (bones, marine and eggshells), particularly in samples from the urban core areas, were removed using a hydrochloric acid (HCl) pre-treatment prior to total organic carbon (TOC) analysis. Total organic carbon (TOC) and nitrogen (TN) were measured by dry combustion using an elemental micro-analyser (EA1108 CHNS-O, Carlo Erba Instruments, Milano, Italy). A subsample of each soil was oven-dried at 105 °C and afterwards ground to powder [49,50]. Aliquots of 20 mg ($\pm$0.20) were combusted in an oxygen-rich environment (flash combustion), and elemental composition and content determined by gas chromatography. Blank values were run with empty tin capsules. For calibration, the analysis of a Low-Organic-Content Soil (B2152) standard with C–1.26% and N–0.10% was performed (reference material supplied by the instrument manufacturer). Soil pH was measured in 0.01 M $CaCl_2$ (1:2.5 soil:solution ratio) suspension [51]. Total P was measured by microprobe analysis using an X-ray fluorescence analyser (XRF) (Niton XL3t-Goldd+, Thermo Scientific, Billerica, MA, USA). All measurements were carried out in mining Cu/Zn mode. Particle size distribution was measured using a Coulter LS230 series Laser Diffraction Particle Size Analyser (Coulter Corporations, Miami, FL, USA) following defloculation with sodium hexametaphosphate and 30 min of mechanical agitation. The measurement range of the apparatus is 0.04 to 2000 μm. Particle size distribution was categorised using Wentworth [52] classification.

2.4. Magnetic Susceptibility and Charcoal Content Analysis

The magnetic susceptibility of exposed profiles was measured in the field using an MS2F surface probe sensor coupled to a Bartington MS2 susceptibility meter (Bartington Instruments, Oxford, UK). Measurements were made at 10 cm intervals to the maximum depth of the profile. Corrections were made for temperature drift during measurement sequences [53]. Values are expressed as the dimensionless ratio Volume Susceptibility (ß) calculated in SI units (10^{-5}). For charcoal content, soil thin sections were manufactured using standard procedures (www.thin.stir.ac.uk: accessed on 11 May 2022) adapted from Murphy [54]. Intact samples were dried using a vapour-phase acetone-exchange

method and then impregnated under vacuum using Polylite® polyester resin. After cutting, mounting and grinding, samples were polished to 30 μm thickness. The thin sections were examined using a petrological polarising microscope (BX-50, Olympus Corp., Tokyo, Japan) in plain polarised illumination (PPL). Observations were made on each thin-section slide. For each sample, a set of 20 images, each capturing an area of 5.7 mm by 4.2 mm, were recorded at fixed intervals across the slide. The quantification of the charcoal seen in each image was undertaken using standard image analysis thresholding methods [55] in AnalySIS-Pro software (Olympus Corp., Tokyo, Japan).

2.5. Site Chronological Profiling by Portable OSL Reader

Samples from each profile were analysed using a portable OSL reader (SUERC, East Kilbride, UK). For each measurement, about 10 g of the bulk sample was placed into the device in a 50 mm-diameter Petri dish under red-light conditions. During sample preparation prior to analysis, the sediment at both ends of the sampling tubes was discarded to prevent contamination of OSL signal from any materials that may have been exposed to light during sampling. All measurements were carried out in continuous-wave mode. Signal separation during measurement was selectively performed by the excitement of feldspar with infrared (IR) light and quartz with post-IR blue OSL. These signals were plotted to produce luminescence profiles that depict the variation in the luminescence signal with depth. To account for the effects of mineralogy on background/natural radiation dose rate, IRSL/OSL ratio was used as a proxy for mineralogical characteristics [56].

2.6. Solid-State ^{13}C-CPMAS NMR Spectroscopy

A mixed acid (HCl/HF) pre-treatment was carried out on soil samples prior to performing solid-state Carbon-13 Cross-Polarization Magic Angle Spinning (^{13}C-CPMAS NMR) analysis. Approximately 5 g of each sample was initially treated with concentrated hydrochloric acid (HCl). A further hydrofluoric acid (HF) treatment, modified from Schmidt et al. [57], was then applied. These procedures were aimed at improving spectra quality that is otherwise impaired by presence of paramagnetic materials such as iron minerals. Solid-state ^{13}C-CPMAS NMR analysis of pre-treated soil subsamples was performed on a 7.05 T Varian INOVA™ Unity spectrometer (Varian Inc., Palo Alto, CA, USA) operating at a ^{13}C resonance frequency of 75.4 MHz. We used 6 mm-diameter cylindrical zirconia Pencil® rotors with Vespel® drive tips. Samples were spun at 8000 ± 3 Hz in an HX Apex probe at the magic angle. A contact time of 1.5 ms and a 1.5 s recycle delay time were used. Optimal contact times and recycle delays were previously determined in separate experiments on several samples [58]. The ^{1}H radio frequency (RF) field strength was set to 48 kHz and the ^{13}C RF field strength to 40 kHz during cross-polarisation. A ramped ^{1}H-RF field of 16 kHz was used during contact time to circumvent inhomogeneities of the Hartmann–Hahn condition [59]. Proton decoupling was carried out using a SPINAL sequence with an ^{1}H field strength of 55 kHz, a phase of 4.5° and a pulse length of 12 μs. A sweep width of 25 kHz and an acquisition time of 20 ms were applied during spectra collection.

The free induction decays (FIDs) were recorded with VnmrJ 2.2D (Varian Inc., Palo Alto, CA, USA) and processed by MestRe-C 4.9.9.9 (Mestrelab Research, Santiago de Compostela, Spain). The number of transients collected lay between 40,000 and 250,000, depending on the organic carbon content of the samples. All FIDs were Fourier transformed with an exponential filter function with a line broadening (LB) of 20 to 50 Hz depending on the sample. Baseline correction was carried out using the manual baseline correction function of Mestre-C. The chemical shifts are reported relative to tetramethylsilane (=0 ppm) using adamantane as an external reference. The spectra were integrated across five chemical shift regions, assigned to carboxyl/carbonyl C (215–160 ppm), aromatic C (160–110 ppm), anomeric C (110–90 ppm), O/N alkyl C (90–45 ppm) and aliphatic C (45–(−10) ppm). The relative intensities of the regions were determined using the integration routine of the MestRe-C software, and, subsequently, correction for the spinning side bands (SSBs) was carried out as

described in Conte et al. [58]. The alkyl C to *O/N*-alkyl C ratio (Equation (1)) and aromaticity index (Equation (2)) were used to assess the degree of decomposition [60–62].

$$\text{Alkyl C} : O/N\text{-alkyl C} = \frac{\text{Alkyl C } (0 - 45 \text{ ppm})}{O/N - \text{alkyl C } (45 - 110 \text{ ppm})} \tag{1}$$

$$\text{Aromaticity } (\%) = \frac{\text{Aromatic C } (110 - 160 \text{ ppm})}{\text{Aromatic C } (110 - 160 \text{ ppm}) + \text{ Aliphatic C } (0 - 110)} \times 100 \tag{2}$$

3. Results and Discussion

3.1. Soil Physical and Chemical Analysis

The physical and chemical analysis of soil samples are displayed in Figure 2A,B. Total organic carbon (TOC) and nitrogen content (TN) are noticeably higher across soil depth in the urban core areas relative to the extra-urban area, decreasing with depth, although variations in measure exist between the various urban core samples. The same is true for phosphorus (P) concentration across the study area. Soil pH values differed with depth between urban core and extra-urban areas; additionally, urban core samples have near neutral pH (6.3–7.2) while extra-urban samples are moderately to slightly acidic (5.5–5.8). Weak correlation between soil pH and P concentration indicates that P retention has not been significantly influenced by post depositional effects. Soil particle size distribution is dominated by silt and fine sand in the upper horizons, and by silt and clay at depths in both urban core areas and extra-urban areas (Table S2 in SI). Soil clay fraction in urban core areas and the extra-urban area are not too dissimilar, although extra-urban profiles generally have higher clay content, particularly at depths where up to two-fold increases can be observed. Volume magnetic susceptibility (ƙ) measurements (SI (10^{-5})) showed a substantial increase in the magnetic properties of soil in the urban core areas relative to the extra-urban area (Figure 2B).

The observation of more extensively modified soils within urban core areas at the study site is in line with observations reported in previous works carried out in other medieval Scottish urban towns, including Nairn, Perth, Pittenweem, Lauder and Wigtown. Soil modification in these locations was reportedly more intense within urban backlands (i.e., gardens) than in the extra-urban areas [20,63–65]. Marked variations observed in the soil parameters measured within the urban core areas and between the extra-urban area reflect the differences in the management strategy employed on individual plots of land by the landowner or leasehold at various stages of land use and corresponding soil development. These lands were either used by their owners or leased to other townsmen and/or in-dwellers, i.e., burgh residents who lacked the economic privileges of full burgess status [12,13,16]. Factors such as the onset of use of urban waste, the quantity of manure accessible to the keeper/landowner, size of the plot and period of active deposition, all of which are influenced by the social status of the individual and thus how much of these fertilisers can be procured, in addition to their own waste production, will influence soil development. These result in spatial variations in soil properties (organic matter, nitrogen content, element concentration and distribution, magnetic susceptibility, soil pH) even within relatively small distances.

Changes in the background concentration of suites of anthropogenic-marker elements are an inevitable outcome of occupational activities from daily living [66,67]. Among these groups of elements, phosphorus is most routinely used in archaeological prospection as indicator for human activity due to its relatively high retention rate and stability in the soil [67–71]. Elevated *P* concentrations found in the urban core areas (*STM*, *SST* and *SSJG*) relative to the extra-urban area (*BGR*) reflect the degree of anthropogenic influence in these locales, that is, the scale of activity and length of time over which these areas have been utilised (Figure 2A). Similarly, measured volume magnetic susceptibility showed a more significant increase within the urban core areas than in the extra-urban area (Figure 2B). The firing or burning of materials has long been associated with human habitation in archaeological sites because it results in the increase in soil magnetic properties known

as "thermoremanent magnetism" [72–74]. During burning, weakly magnetic iron oxides (magnetite–Fe_3O_4, and maghemite–Fe_2O_3) in the clay and silt particles heated above their curie temperature (~600–700 °C) can gain an enhanced magnetic signature. Similarly, fired bricks and pottery can also display greater thermoremanent magnetic properties in the presence of organic materials. Although magnetic properties are typically more strongly enhanced by onsite burning, the sufficient deposition of occupation debris from organic (e.g., charcoal, soot) and inorganic (e.g., ash, fragments of fired pottery and bricks) origins can potentially alter the magnetic properties of soil [75]. Furthermore, elevated soil magnetic susceptibility can result from the activities of magnetotactic bacteria that thrive in organic material [27,76,77]. Magnetotactic bacteria are known to internally synthesise magnetic nanoparticles (magnetite crystals) within themselves that act like very small magnets. Marked differences in the soil magnetic properties in the urban core sites and extra-urban site are largely due to the greater discard and burial of occupation debris of pyrogenic origin and organic material within high-activity areas (urban core) than in the low-activity area (extra-urban). Visual examination of the respective soil profiles showed high contents of fragmented and decayed pottery, bricks, and marine and eggshells. In addition, the reduction of haematite to magnetite by soil bacteria that grow in decomposing organic materials produced from human habitation, such as in middens, may also increase magnetic signatures, a process known as the "fermentation effect" [76].
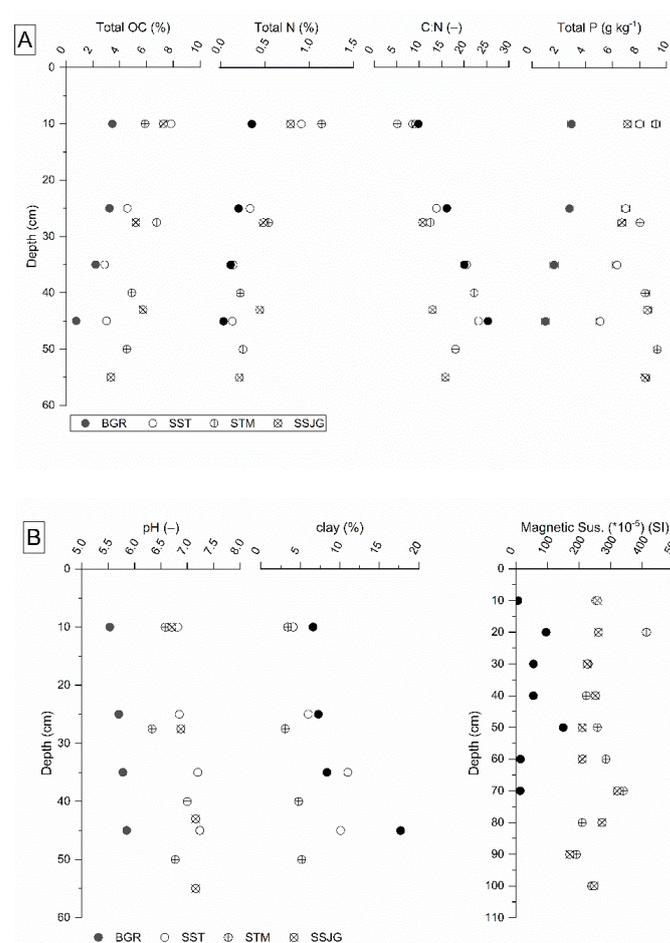

Figure 2. (**A**) Carbon, nitrogen and phosphorus contents of soil samples; (**B**) pH value, clay content, and magnetic susceptibility of soil samples; C, N, P, pH and clay values were determined from a pooled aliquot of the whole depth increment and are therefore displayed at the centre of the respective depth increment; magnetic susceptibility was determined on-site at an exposed profile at specific depths. *STM*, *SST* and *SSJG* are urban core sites; *BGR* is an extra-urban site.

Disparity in the soil pH values, where urban core areas exhibit near neutral-to-alkaline pH while extra-urban sites have a slightly acidic pH, results from incorporation of carbonate-rich materials such as shells and bones into compost mixtures—a well-known component of urban waste mixtures. Soil particle fractions consist predominantly of silt and fine sand, although the proportion of clay fractions increases at depth, in an inverse relationship with the fine sand fractions. The observed lower proportion of finer materials at surface or near-surface profiles is indicative of the input of coarser materials and contrasts with field and/or plaggen-type soil management systems where such soils are reported to consist of finer materials in upper horizons [12,65]. The *C/N* ratios are similarly distributed between sites but varied with depth. Values are higher in the subsoil (10.8–25.3) than in topsoil (5.2–9.9) and are indicative of the prolonged deposition of high-N materials onto soil during active management [78,79]. Soil colour is widely associated with the relative content of organic material in the soil. Darker colours are often associated with high-organic-matter content while lighter colours are more indicative of low-organic-matter content. Schmid et al. [27,80] and Downie et al. [36] reported a correlation between darker soil colour and organic carbon content in historic anthrosols. The authors attributed this association mostly to the higher contributions of aromatic C in the respective soils relative to the surrounding background soils. The soil colour *values* [48] for the urban core sites and the extra-urban site increased with depth, becoming progressively lighter (Table S1 in SI). The distribution of charcoal was such that no discernible link could be established between colour and the quantifiable charcoal on the thin-section slides (Table S1 in SI). Therefore, charcoal content and aromatic C distributions (Table S2 in SI) provide no evidence to support soil colour and carbonised–matter relationships at the study sites. The observation demonstrates that soil hue is not entirely defined by the amounts of charred organic material/aromatic C content and that other organic and inorganic pigments contribute to soil colour [34].

3.2. Site Chronology

Optically stimulated luminescence profiling is an intra-context relative dating protocol that allows investigation of the depositional history of sediments [56]. The luminescence signal of the profiles differed between urban core areas and extra-urban site (Figure 3A and Table S1 in SI). The *STM* site, nearest to the core area of the medieval burgh, has the highest luminescence signal of all the sites within the urban core area, and likely represents the oldest anthropogenic soil deposit sampled, since disturbances to soil and subsequent burial of occupation debris would have initially begun in areas that were first inhabited. The accumulation of sediment and debris on sites within the urban core area (*STM* and *SSJG*) appears to occur at different rates; notably, the materials in the *SSJG* site show a rapid rate of accumulation. Overall, the *SSJG* site produced the lowest luminescence signal, which indicates that the soil deposits at the site are younger than those at either the *STM* or *BGR* site, respectively.

In addition, given the younger appearance of the deposits, it is conceivable that the land use practices at the site continued to a later date while such practices had ceased at the other two sites. The gradual increase in the luminescence signals with depth at the *SSJG* site shows that the stratigraphic sequence has not been disturbed since it was last emplaced. In contrast, OSL signals fluctuate with depth at the *STM* site, indicating a post depositional disturbance from the mixing of sediments of varying depositional ages. Variations in the IRSL/OSL ratio can be used as a proxy for indicating changes in mineral characteristics within sediment stratigraphy [56,81]. Urban core areas have fairly constant IRSL/OSL ratios, as does the extra-urban site up to 60 cm, suggesting the profiles are of relatively similar mineral composition (Figure 3B). However, a pronounced change in the luminescence signal observed at 60 cm at the extra-urban site (Figure 3A) reflects a change in mineralogy which is indicative of the boundary between cultivated topsoil (A horizon) and the sub-soil (B/C horizon) material. This coincides with the observed several fold increases in soil clay fractions relative to the topsoil (Figure 2B).
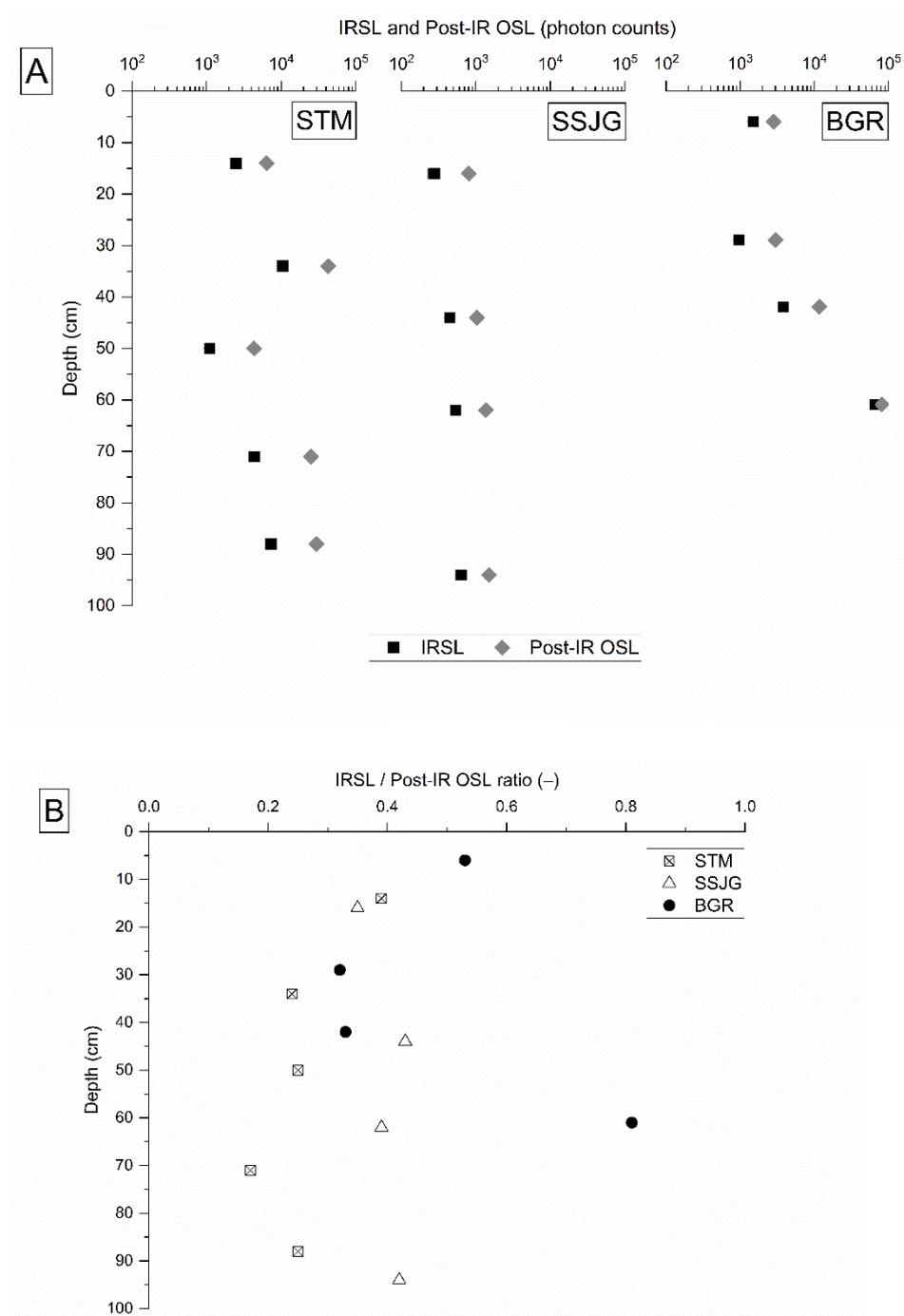
Figure 3. (**A**) Portable optically stimulated luminescence (IRSL and post-IR OSL) of soil profiles showing site depositional history (burial sequence); (**B**) infra-red (IRSL) to blue light (post-IR OSL) ratio of soil profiles showing mineralogical characteristics; values were determined on samples taken at specific depths with sampling tubes 5 cm in diameter and are displayed at the centre of the respective sampling point. *STM*, *SST* and *SSJG* are urban core sites; *BGR* is an extra-urban site.

3.3. Soil Organic Matter Speciation: ^{13}C-CPMAS NMR Spectroscopy

Solid-state ^{13}C-CPMAS NMR spectroscopy revealed the presence of heterogeneous organic C functionalities in soils from all the study sites. Despite the spatial variation between the sites, the NMR spectra show very strong similarities in the composition and distribution of C functional groups. Two representative spectra series from *SST* and *SSJG* (urban core sites) depicting these trends are provided in Figure 4, and the relative contributions of C functional groups to the soil organic carbon of all sample sites are

given in Table S2 in the Supplementary Information. Figure 5 depicts the amount of each chemical shift region per depth, calculated from their respective relative contributions in the NMR spectra and the amount of total organic carbon found at the depth increment. The resonance line around 30 ppm, in the region of alkyl C (0–45 ppm), is assigned to methylene groups within long saturated C-chains (fatty acids, waxes, resins), while the shoulder around 24 ppm is due to methylene groups adjacent to terminal methyl groups, which in turn resonate at 19 ppm [27,82,83]. The small peak around 56 ppm, in the region of *O/N*-substituted alkyl C (45–90 ppm), is ascribed to methoxyl groups and/or N-substituted alkyl C [84], while the signal peak at 72 ppm is assigned to O-alkyl C structures present in carbohydrates. The resonance signal intensity between 90 and 110 ppm is generated by di-O-alkyl C structures of anomeric C in polysaccharides [28,80,85]. The prominent signal in the region of aryl C (110–160 ppm), peaking at 130 ppm, originates from C- or H-substituted aromatic carbon, as well as from unsaturated alkyl structures. The resonance signal near 170 ppm in the chemical shift region of carbonyl/carboxyl C (160–215 ppm) can be ascribed to carboxyl and amide functional groups.
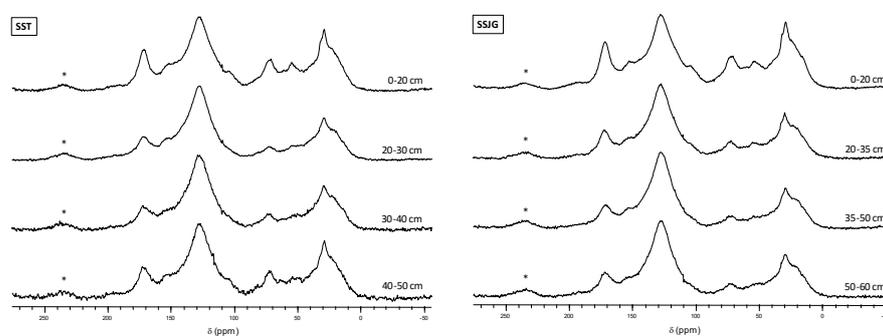

Figure 4. ^{13}C-CPMAS NMR spectra of soil samples from *SST* and *SSJG urban core* sites. The spectra are graphically normalised to the dominant aromatic region centred at 129 ppm. (* = spinning side bands).
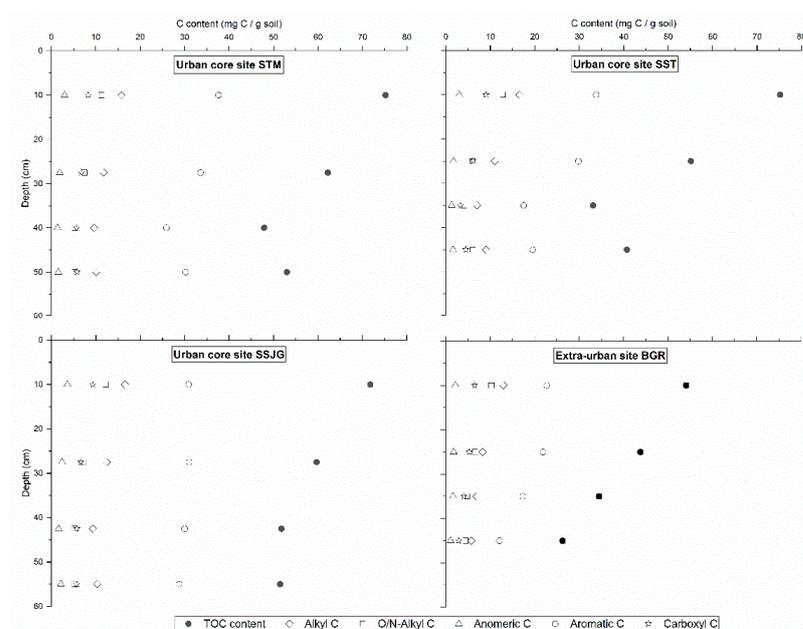

Figure 5. Amount of organic carbon species in mg C/g soil as determined from their respective relative contribution to solid-state NMR spectra and amount of total organic carbon. Spectra and TOC values were determined on a pooled aliquot of the whole depth increment, and values are therefore displayed at the centre of the respective depth increment. *STM*, *SST* and *SSJG* are urban core sites; *BGR* is an extra-urban site.

The aromaticity (Equation (2)) in SOC (Table S2 in SI) is generally higher in soils from the urban core areas (48.9–65.2%) relative to the extra-urban area (47.2–56.8%). This observation is analogous to the small number of reported patterns of aromatic C distribution in historic anthrosols from elsewhere around the world where similar land management practices have been documented. Examples include Neolithic settlement sites in Europe [80], Aboriginal sites in Australia [36] and in Amazonian dark earth (terra preta) in the Brazilian Amazon basin [28]. The dominance of the aromatic C region at the study sites is the consequence of the sustained anthropogenic inputs of organic wastes and debris to soil. Sources of condensed aromatic structures in the soil are reported to be biomass-derived char and fuel residues (e.g., soot) from coal and/or peat and turf burning [27,34]. In pre-industrial societies, such pyrogenic materials generated from the burning of wood, coal, peat and turf in hearth (fireplace), kilns and cooking fires were constituent matter for manure production, together with other waste and midden contents composted and used for soil capitalisation [12,13,16].

The sites *STM* and *SST* both display a dip in the amount of aromatic C content in the layers between 35 and 45 cm (30 to 40 cm for *SST*, respectively) mainly due to the overall drop in total organic carbon contents of these sites (Figure 5). Luminescence data show that site *STM* has been subject to post-depositional disturbances, and although luminescence data are not available for the *SST* site, the similar curve progression at the site suggests that the *SST* site was also subject to post-depositional disturbance at some point. However, surprisingly the disturbance of the layers did not result in higher aromatic contents in deeper layers, as would be expected if charred material is buried in deeper layers (Figure 5), but a markedly lower organic C, and, consequently, lower aromatic C content was observed. This could be due to the physical disturbance of the layers, possibly resulting in an improved aeration of deeper layers, in turn triggering an increased decomposition of organic carbon structures [86]. The *SSJG* site, identified as the youngest deposition site with a rapid accumulation rate via luminescence data, displays a very homogeneous aromatic C content of around 30 mg of aromatic C/g soil across all layers. The decrease in organic C with depth is mainly due to a decrease in the aliphatic structures at this site.

Alkyl C contribution accounts for between 18 and 24% of the signal intensity, while *O/N*–alkyl C comprises between 10 and 19%. The lesser contribution of the *O/N*–alkyl C region of the spectra shows that fresh plant material does not presently constitute a major part of the soil organic carbon in these urban anthrosols. The *O/N*–alkyl C generally has a shorter resident period in the soil due to a lower requirement for oxygen on the part of the microbial community to degrade carbohydrate or protein structures. A lower quantity of *O/N*–alkyl C (45–90 ppm) in urban core sites relative to the extra-urban site may be attributed to variations in the biological activity between both sites due to the differing nutrient status and the various other agents of decomposition. Carboxyl C (10–13%) and anomeric C (3–5%) contributions remain relatively unchanged with depth on all the sites, although values are marginally higher in topsoil profiles. The contribution of carboxyl C content in the samples indicates that the charred organic materials have undergone some degree of oxidation from microbial activity [87]. Mcbeath and Smernik [88] demonstrated that the number of aromatic compounds formed during pyrolysis coincides with thermal treatment temperature. In the present case, the dominance of aromatic constituents, followed by high alkyl C contributions, show that the charred organic residues deposited on soils were generated under moderate-to-high pyrolysis temperatures [89,90].

Many studies have demonstrated that lignin distribution in soil generally declines with depth, particularly from the litter layer to the A horizon (mineral horizon) and subsoil horizons [91]. Lignin units are generally represented by the combination of resonance signals in the spectra regions of 56, 72 and 150 ppm [27,28,84,92]. Distinct resonance signals indicative of lignin compounds can be identified in the top layers of the sites (Figure 4). The contribution of these resonance signals, however, is marginal and diminishes with depth, indicating that lignin is not a major component of the soil organic carbon in urban anthrosols [36,83]. According to Baldock and Preston [60] and Baldock et al. [61], the

ratio of alkyl C to *O/N*-alkyl C (Equation (1)) can be used as an indicator for assessing the extent of decomposition of organic materials. A higher ratio of alkyl C to O/N-alkyl C is associated with a higher level of decomposition. The ratio of alkyl C to *O/N*-alkyl C is higher in the urban core sites, and increases with depth. These ratios show that organic matter decomposition has progressed further in urban core sites than in the extra-urban site. The increase in this ratio with depth indicates that subsoil profiles have undergone a greater extent of decomposition than topsoil [62,83].

On all sites, clay content increases with depth, in varying degrees. This mostly concurs with an increase in the alkyl C to *O/N*-alkyl C ratio. Clay minerals are known to slow decomposition in the soil due to a shift in pore size distribution towards smaller pores, which severely impedes gas diffusion, specifically that of oxygen [86]. Furthermore, adsorption of organic components to clay minerals can reduce substrate availability and/or accessibility to soil microorganisms, additionally slowing decomposition [93–100]. Unlike natural soils, the development of urban anthrosols is subject to the interaction of complex and diverse anthropogenic impacts over extended, but varying, periods of time. It is this condition that results in peculiar assemblages of particles (aggregates, biological community, substrates, etc.) [101], that, when acting together with various other environmental factors, govern the processes and rate of organic matter transformation.

Minor alterations to the natural conditions of soil are often difficult to detect in areas susceptible to high post-depositional effects (dynamic environment), and signals can be concealed and/or erased by post-depositional processes. However, signals from soil modifications arising from longstanding practices such as burning, and the inputs of waste products on soil, can persist in the soil. Evidence of soil modification arising primarily from the addition of urban wastes is still visible to date in St Andrews. Understanding both soil fertility and a wider set of ecosystem service provisions provided by such anthropogenic soils, such as carbon sequestration [4,6,7], is essential, and increasingly recognised by aspects of government policy and guidance in several countries. At a more global level, assessments of the inherent qualities of anthropogenic soils in respect to their potential as carbon sink, and the trade-offs arising from the implications of external disturbances such as urban development, will be needed for considerations of new developments and management practises that will reduce disturbances to the wide range of functions that these soils provide. Generally, evidence for micro-level intra- and inter-site variations is visible in the dataset, further highlighting the complexity in the distribution and heterogeneity of urban anthrosol, and therefore challenges in the development of management policy.

4. Conclusions

This study demonstrates the extent of soil alterations in urban settlements from past anthropogenic intervention, showing also that we have a means of understanding the intensity and implication of these interventions. Furthermore, the fate of landscapes and soils alike in urban or rural environments presently subject to parallel management systems can be inferred. Soil molecular analysis by ^{13}C-CPMAS NMR, with complementary physicochemical techniques, has shown that the soils in St Andrews were significantly altered from anthropogenic interventions. Soil samples within the urban core areas where activities are more pronounced are characterised by high phosphorus concentrations, high organic carbon content and high magnetic susceptibility relative to the extra-urban site where such modifications occur comparatively to a lesser degree. Portable OSL analysis highlighted the differences in the rate of sediment accumulation, intensity and duration of use, as well as post-dispositional disturbances on respective sites. Solid-state ^{13}C-CPMASNMR spectroscopic analysis revealed the predominance of aromatic C structures. The abundance of polyaromatic structures indicates that the pyrolysis material originated from moderate- to high-temperature burning. Our study supports that past human-induced alterations to soils within urban settlements have long-lasting effects on soil properties and, more importantly, on organic carbon content and speciation. Their long-term carbon sink potential and role in terrestrial carbon cycling merits further consideration and assessment.

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