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Industrial carbon input to arable soil since 1958



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ABSTRACT

Tracing the history of industrial fossil fuel combustion on the carbon stock in soil is challenging, since it is mixed with other soil organic carbon (SOC). Isolation of black carbon (BC) yields a mixture of diagenetic fossil C and pyrogenic BC from biomass and fossil fuel combustion. We investigated the degree to which fossil fuel combustion emissions have contributed to SOC and BC and how deposition dynamics have changed in the last century. As only biomass-derived BC contains ¹⁴C, we determined the content and ¹⁴C signature of the benzene polycarboxylic acid (BPCA) fraction as the product of total BC oxidation. From an isotopic mass balance model, the proportion of fossil BC deposition and its contribution to SOC was calculated. Soil samples were taken from 1958–2002 from a long term agricultural field experiment in Halle, Germany; the area represents one of the most productive lignite mining areas in the world. Between 1958 and 1971, total BC content increased significantly (1.9 ± 0.1 – 2.30 ± 0.06 g/kg soil), and the BC-specific radiocarbon content decreased from 29.6 ± 0.4 to 26.9 ± 0.2 pMC, corresponding to 1.35 ± 0.07 and 1.8 ± 0.08 g/kg BC from diagenetic C and fossil fuel combustion (denoted here as fossil BC). We infer an increase in fossil BC content of 30% within this timespan, with a net input rate of $9 \text{ g/m}^2 \text{ yr}$. In the 1970s, after railway electrification, reduction of lignite mining and related heavy industries, fossil BC deposition to soil was no longer significant. Overall, about 120 g/m^2 fossil BC was deposited between 1958–1971, with 390 g/m^2 before 1958. Fossil BC contributed ca. 75% of total BC and 15% SOC to arable soil, without any significant change in the following 30 yr (1971–2002).

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1. Introduction

Human activity like fossil fuel combustion, with the subsequent release of black carbon (BC) has a significant impact on the global C cycle. BC emissions are in debate for their relevance for climate change (Reddy et al., 2002). Historical industrial BC emissions have been estimated by Bond et al. (2007). They estimated an almost linear increase in global industrial BC emission from 1000 Gg (10^{12} g) in 1850 to 4400 Gg in 2000. They found that coal burning dominated BC emission until 1975; after that, biofuel contributed the greatest fraction of BC (numbers estimated from per head consumption). The hot spot region for BC emission was in Central Europe until the 1980s, contributing 900 Gg (ca. one third) of the total BC emission on Earth, and 45% of global coal-related emissions

(Bond et al., 2007). In accord with these numbers, sediments in northern Europe were found to receive 1100 Gg BC from the atmosphere each year (Sánchez-García et al., 2012). However, directly tracing the impact of fossil fuel combustion on the soil C pool is difficult, because the residues are usually mixed with biomass BC and other compounds in the soil organic matter (SOM) pool. Indeed, biomass BC emissions were assumed to be ca. $10 \times$ greater than fossil BC emissions (Reddy et al., 2002). Biomass BC has a contemporary radiocarbon concentration, whereas fossil fuel BC is free of ¹⁴C (e.g. Lichtfouse and Eglinton, 1995; Reddy et al., 2002). Hence, tracing the lack of ¹⁴C in the BC of archived soils could serve as a tracer for the impact of past industrial activity on the soil BC pool.

The typical European emission situation for the 1950s to the 1980s was a heavily industrialized region rich in power plants fueled by coal and energy intensive industries using coal as energy source. Germany is in the top 10 of countries using coal for power production (Enerdata, 2014). Industrial activity has been accompanied by incomplete fossil fuel and biomass combustion and

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¹ In memoriam, August 2011.

thereby by the formation of 'anthropogenic' BC, that is, highly aromatic soot and charcoal particles (Goldberg, 1985). However, a significant contribution of aromatic structures, assigned to BC in the course of analysis, was also found in diagenetic coal (Laskov et al., 2002; Roth et al., 2012) via, for example, blown or washed out material from open cast lignite mining areas. Together, both biomass burning and fossil fuel emission led to a high BC contribution of up to 45% of the organic C (OC) in some East German soils (Schmidt et al., 1996, 1999, 2002). A comparable input history is likely for the soil at the long term agricultural experiment station near Halle, Germany. This station has archived soil for the last 50 yr (Merbach et al., 2000), allowing study of the fossil BC deposition history by way of, for example, radiocarbon tracing of BC or BC-specific markers like benzene polycarboxylic acids (BPCAs; Glaser et al., 1998).

Oxidation of BC to BPCAs provides a quantitative estimate of the BC load in soil, being sensitive for different BC forms, i.e. diagenetic coal, charcoal and soot (Roth et al., 2012). The composition of individual BPCAs with a different degree of carboxylation was found to depend on the combustion process, i.e. with high temperature combustion, typical of industry, yielding a dominant proportion of mellitic acid (B6CA; Brodowski et al., 2007; Schneider et al., 2010; Wolf et al., 2013). However, since the BPCA pattern may also result from high temperature combustion of biomass BC (Wolf et al., 2013), differentiation from fossil BC is difficult. Meanwhile, Rodionov et al. (2010) showed that it is possible to isolate BPCAs without impurities for compound-specific $\delta^{13}\text{C}$ analysis; this procedure also holds true for compound class-specific ^{14}C analysis (Currie et al., 2002; Ziolkowski and Druffel, 2009). Indeed, Currie et al. (2002) revealed the fossil/biomass partitioning in urban dust by using a comparative approach with different BC methods, recovering different parts of the BC spectrum, along with ^{14}C analysis. As the isolation of single BPCAs for radiocarbon analysis is complex, Rodionov et al. (2010) utilized the complete fraction of BPCAs after hot HNO_3 digestion for ^{13}C analysis. The acid treatment was shown to oxidize all non-aromatic compounds (Brodowski et al., 2005); also, the liquid nuclear magnetic resonance (NMR) spectrum of the sum of all HNO_3 oxidation products pointed solely to aromatic, carboxylic C (Rodionov et al., 2010). Indeed, almost all species included in this fraction were identified as BPCAs and nitrated BPCAs, stemming from aromatic precursors (Ziolkowski et al., 2011) as part of charcoal, soot and lignite. Here, we suggest that a ^{14}C BPCA approach, due to its ability to detect biomass and fossil BC at the same time, should be able to allow elucidation of the fossil/biomass BC abundance ratio in soil.

Radiocarbon analysis of biomass derived BC extracted from German chernozemic soils by way of photooxidation suggested an age of 1160–5040 yr (Schmidt et al., 2002). Total soil BC was assigned a long mean residence time (MRT) of 300–4000 yr (Hammes et al., 2008; Lehdorff et al., 2014; Kuzyakov et al., 2014). Another study differentiated a fast cycling BC pool from a slow cycling BC pool by way of MRT of ca. 3 and 800 yr, respectively (Singh et al., 2012). The slowly decomposing BC form comprised ca. 75–83% of total soil BC (Hammes et al., 2008; Singh et al., 2012). However, assessment of an overall residence time is not possible when emissions of anthropogenic, fossil fuel-derived C from coal mining, traffic and industrial activity bias the total amount and the apparent radiocarbon age of SOC and BC. For previous studies of the Halle field trial, the SOC of surface soil appeared older than that of the subsoil, due to contamination by fossil C input estimated to amount to 50–80% (Schmidt et al., 1996; Rethemeyer et al., 2004) of the total soil C. Yet, these data could not be used to reconstruct past industrial activity, because only bulk SOM and SOM fractions had been radiocarbon dated and fossil BC estimates were lacking.

We have used BPCAs as specific markers for BC (Brodowski et al., 2005) to directly (i) trace the total and fossil BC repository

and its proportion of SOC in the surface soil of the Halle field trial back to 1958 and (ii) quantify the historic input rate of fossil fuel combustion derived BC between 1958 and 2002. For this, archived soil samples were analyzed for the ^{14}C content of the BPCA fraction.

2. Material and methods

2.1. Samples

Since 1878, the field experiment 'Ewiger Roggenbau' (Eternal Rye) was carried out on the long term 'Julius Kühn' field trial in Halle (Saale; Fig. 1; Merbach et al., 2000). The soils were classified as Haplic Phaeozems (FAO, 2006) derived from sandy loess. Surface soil samples (0–20 cm), continuously cropped with rye (*Secale cereale* L.) and treated with N, P, K fertilizer, were sampled in 1958, 1960, 1963, 1967, 1971, 1975, 1978, 1990, 1994, 1998 and 2000 (0–25 cm sampling depth) and 2002 (0–30 cm). In the early 1970s, the plowing depth was extended from 20 to 25 cm and to 30 cm at the end of the 1990s (Fig. 2a; exact years unknown).

2.2. BC assessment

BC was determined by using BPCAs as specific markers for both the quantity and quality of BC in soil. They are formed during HNO_3 oxidation of BC and, if corrected for systematic loss during oxidation, represent a conservative minimum estimate of total BC (Glaser et al., 1998; Brodowski et al., 2005). The number of carboxyl groups on an aromatic ring reflects the extent of aromatic condensation of BC and thereby the combustion process (Wolf et al., 2013). The approach followed the procedure described by Brodowski et al. (2005). Briefly, metal elimination was achieved by subjecting the soil to digestion with 4 M $\text{CF}_3\text{CO}_2\text{H}$. BC was oxidized to BPCAs with 65% HNO_3 at 170 °C. One aliquot was dried at 50 °C and used for radiocarbon analysis and the other derivatized to trimethylsilyl derivatives of the BPCAs with N,O-bis(trimethylsilyl)-trifluoroacetamide and analyzed using a Hewlett Packard 6890 gas chromatograph (Hewlett Packard GmbH, Waldbronn, Germany) equipped with a flame ionization detector and a SPB-5 column. BPCA yield was multiplied by the minimum correction factor of 2.27 for BC content estimation (Glaser et al., 1998; Brodowski et al., 2005).

2.3. Radiocarbon analysis

Radiocarbon concentration of the extract was measured using accelerator mass spectrometry (AMS) at the Leibniz Laboratory (Kiel, Germany). Briefly, the samples were split into small aliquots (to reduce nitrate load) and combusted to CO_2 with CuO in sealed quartz ampoules and the gas reduced to graphite over an Fe catalyst with H_2 (Nadeau et al., 1997). ^{14}C concentration was calculated according to Stuiver and Polach (1977) and values are given in percent modern carbon (pmC). The pmC values were corrected for mass fractionation by ^{13}C analysis. Sample size was ca. 0.75 g soil (corresponding to ca. 0.53 mg C in the BC fraction). The proportion (%) of fossil carbon ($F_{\text{fossil-BC}}$) contributing to BC was calculated as $F_{\text{fossil-BC}} = [1 - (^{14}\text{C}_{\text{measured}}/^{14}\text{C}_{\text{recent}})] \times 100$ (e.g. Rethemeyer et al., 2007). $^{14}\text{C}_{\text{recent}}$ represents the input of biomass burning derived BC (Table 2).

Different $^{14}\text{C}_{\text{recent}}$ scenarios were tested to evaluate the robustness of the data vs. uncertainty that might occur due to ^{14}C input assumptions (Currie et al., 2002; Reddy et al., 2002; Chen et al., 2013; Zhang et al., 2014). We based the test on three scenario assumptions: (i) biomass burning concerns mainly annual crops; reported $^{14}\text{CO}_2$ values (Stuiver and Becker, 1993; Levin and Kromer, 2004; Levin et al., 2008) for each year of sampling were

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