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Centennial black carbon turnover observed in a Russian steppe soil

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Abstract

Black carbon (BC), from incomplete combustion of fuels and biomass, has been considered highly recalcitrant and a substantial sink for carbon dioxide. Recent studies have shown that BC can be degraded. We use soils sampled 100 years apart in a ⁵ Russian steppe preserve to generate the first whole-profile estimate of BC stocks and turnover in the field. BC stocks (initially 2.5 kg m⁻²) decreased 25% with cessation of biomass burning. BC turnover in the soil was 293 y (best estimate; range 212–541 y), much faster than inert/passive carbon in soil models. Such results provide a new constraint on theories of soil carbon stabilization. Most importantly, BC cannot be assumed chemically recalcitrant in all soils; other explanations for very old soil carbon are needed.

1 Introduction

Black carbon (BC) is a product of incomplete combustion of fossil fuels and biomass burning (Goldberg, 1985) and is found in almost every environment, either formed there or transported through various means, including aeolian and riverine transport 15 (Kuhlbusch, 1998). BC deposited in soil constitutes a significant, yet relatively poorly understood component of soil organic carbon (Schmidt, 2004). Until recently, BC was thought to be generally recalcitrant, with an average turnover rate in soil of millennia. This assumption was based on charcoal findings in soil that were radiocarbon dated to be thousands of years old (Skjemstad et al., 1996; Forbes et al., 2006), as 20 well as evidence of millennial turnover of BC in marine sediments (Masiello and Druffel, 1998). This inert character made BC an ideal candidate for an atmospheric carbon sink (Kuhlbusch, 1998). However, significant BC degradation was also observed in marine sediment where a relict turbidite lost around 64% BC over 10-20 millenia (Middelburg et al., 1999). Additionally, recent short-term laboratory and field studies have shown 25 evidence for degradation of BC in soil (Bird et al., 1999; Hamer et al., 2004; Brodowski,

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2005; Hockaday et al., 2006). Incubation studies, conducted for two months to two years, showed BC turnover times of decades (Hamer et al., 2004; Brodowski et al., 2005). However, these studies have limitations that make extrapolation of data difficult: (i) only topsoil was incubated (up to 20 cm), (ii) the studies were short-term, (iii) repre-

- sented laboratory conditions, and (iv) used low-temperature, artificially produced char. Direct field measurements and long-term in situ confirmation of how stable this sink is, i.e. what the actual BC turnover is, is still lacking. We took advantage of a 100-year interval soil sampling of a Russian Chernozem to study long-term change of BC in the field.
- ¹⁰ Chernozems are the 8th most common soil order and are estimated to cover 900 million ha or approximately 7% of the ice-free land area on earth (Bell and McDaniel, 2000). Nearly all of the 117 million ha of Chernozems in the Russian steppe and 12 million ha of Chernozems in the Ukrainian steppe are used for agriculture (Stolbovoi and McCallum, 2002). Russian Chernozems have substantial organic carbon stocks of 28–34 kg m⁻² for the top 1 m under native (undisturbed) grassland (Mikhailova, 2006).
- ¹⁵ 28–34 kg m⁻² for the top 1 m under native (undisturbed) grassland (Mikhailova, 2006). Native Chernozems can be found only in a few preserves, including the Kamennaya Steppe created between 1882 and 1885 (51°0′ N, 40°7′ E, Torn et al., 2002).

At about the same time as preserve establishment, almost all of the region's steppe was converted to agriculture and, most importantly for our study, fires which were fre-

quent on the steppe, were suppressed by human activity, resulting in almost total cessation of once frequent biomass burning inputs of BC to soil. These circumstances gave us the unique opportunity to study the response of BC stocks over time, and to estimate a turnover rate of the BC in the soil, with the following advantages: (i) a long time period (ca. 100 years), (ii) in situ field site, with (iii) natural char produced in situ,
 (iv) a deep soil profile (>1 m) and (v) without land use change.

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Estimates of black carbon stocks and turnover in soil are urgently needed to fill knowledge gaps on its importance in the global carbon cycle.

2 Materials and methods

2.1 Field site

The 100-year old soil monolith was collected between 1895 and 1903 (called 1900-soil from here on) within the Dokuchaev Institute located in the preserve, and is almost
 ⁵ 140 cm deep. According to the original sampling notes and current observations, the monolith was sampled without disturbing the horizon structure, and kept horizontal without any resin treatment in a wood box to keep it dust-free. The location of the sampled site and the collection procedures were detailed previously (Lapenis et al., 2000; Torn et al., 2002). In August 1997, a soil profile was sampled from exactly the same location under the same land use. Soil organic carbon and carbon isotopes (¹³C and ¹⁴C) were compared in archived and modern profiles (Torn et al., 2002). Another profile was sampled in 1997 (called 1997-2), for which only organic carbon data (but not BC data) is available (Torn et al., 2002).

2.2 Site climate

- The mean annual temperature from 1989-1998 was 6.6°C, which is 1.3°C warmer than the mean annual temperature from 1893–1950 (5.3°C). The total annual rainfall from 1989–1998 was 507.7 mm, which is an increase of 70 mm (mostly winter precipitation) from the period 1893–1950 (438.5 mm) (Sentsova, 2002). Additional information on the climate conditions in the area can be found at: http://data.giss.nasa.gov/gistemp/
 station_data/ using the stations Kamennaja Ste (51°0′ N, 40°7′ E) and Voronez (51°7′ N, 39°2′ E).
 - 2.3 Soil sampling

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In addition to the 1900 and 1997 samplings described in Torn et al. (2002), an additional Chernozem soil profile was sampled in August 2004 under the same steppe land cover. It was roughly 1 km from the earlier pits (1900 and 1997, see Table 1), but located near



another pit sampled in 1997 (1997-2, Table 1). This soil was sampled to a depth of 100 cm after scraping away the open wall of an existing soil pit. Samples were collected from the wall of the pit, starting from the bottom and sampling in a channel over the whole of each horizon. A plowed soil profile was also sampled next to the pristine steppe profile, with 10 cm depth increments, up to 70 cm. In calculating BC stock, we used bulk densities measured by Torn et al. (2002) in soil profiles sampled in 1997 (Table 1), which was assumed to be the same as in 1900. There was a good correlation between the 1900 profile and the two 1997 soils for both C-content and thickness of all horizons, supporting the assumption that the soil bulk density was similar (Torn et al., 2002). Although sampling increments for these soil profiles were not the same as for the 1900 and 1997 soils and the profile increments as such not comparable, total black carbon stocks were similar.

2.4 Representativeness of the soil monoliths

We believe that the soil profiles sampled in 1900, 1997, and 2004 are fairly representative of soil conditions under pristine steppe at the time of sampling. The watershed of the Kamennaya Steppe Preserve sits on aeolian deposits (yellow carbonate loess). Therefore, there is little spatial variation in the soil parent material, and the topography is very flat. The typical variation in height is on order of 5 m per km (except a few gullies). Replicate soil profiles sampled 1 km apart in 1997 had similar carbon content
and horizon characteristics with depth (Table 1). Landscape homogeneity and little variation among replicate soil pits in 1997 makes it reasonable to consider that the soil profiles analyzed here are fairly representative of a larger chernozem area in the steppe.

2.5 Black carbon analysis

²⁵ We analyzed BC in each soil horizon using benzene polycarboxylic acids (BPCAs) as markers for the presence of fire-derived organic matter (Brodowski et al., 2005). Briefly,



triplicate samples were digested with HNO₃ at 170°C for eight hours, purified, and the sum of BPCAs in each sample analyzed after derivatization on a gas chromatograph equipped with a flame ionization detector. The error bars for each point on the graphs are the standard errors of two to three single analyses of dry weight soil. In published literature, BPCA data was sometimes multiplied with a conversion factor of 2.27 to compensate for incomplete BC recovery (Brodowksi et al., 2005). However, this factor is currently disputed and we did not use it for our results. Furthermore, the BPCA method was recently evaluated in a comparative study on different BC methods used for soils and sediments (Hammes et al., 2007). This study concluded that different methods measure different parts of the BC continuum, with varying biases to non-BC 10 being measured as BC. Some of the most important results for the present study was that the BPCA method (i) can be used for a conservative quantification of BC in a soil matrix, (ii) additionally yields information on BC guality (reflected by its molecular marker pattern), and (iii) can be reproduced with a standard error (<10%) typical for

many measurements in environmental matrices. 15

Statistics 2.6

A one-tailed t-test with matched pairs was done to test the hypothesis that the 1997-soil does not have less BC than the archive soil (JMP 5.1.2, SAS).

- Turnover time model 2.7
- The turnover time of BC was estimated with a one-pool, donor-controlled model, with 20 the following equation:

 $\tau = -t / ln(f - b / (f - 1))$

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where τ =turnover time (years); t=time between samplings (years); t=ratio of modern BC input flux to historic input flux; *b*=fraction of original BC stock remaining. For this model we made three assumptions: (1) BC is homogenous with respect to turnover, (2)



(1)

loss of BC from the soil is a first order decay process, i.e. the loss of BC per unit time is proportional to the BC stock, and (3) after the 1900 sampling, BC inputs decreased in accord with the decrease in regional fire frequency (Torn et al., 2002).

2.8 Model sensitivity analysis

- We chose very conservative estimates to test our model. The archive soil was sampled 5 somewhere between 1898 and 1903, which gives a six year variation on the 100-year period to 1997, i.e. t could be from 94 to 102 years. Thus, we chose t=102 and t=94years to test model sensitivity. Since there have been climatic changes in the region, it could be that the bulk density of the soil had changed over the 100 year period. We varied the bulk density from -10% change (less dense) to +10% change (denser) 10 from the measured bulk density of 1997 (Torn et al., 2002). These bulk density values (0.9 to 1.1) were multiplied with b (fraction of original BC stock remaining), b=1.92 kg $m^{-2}/2.55$ kg m^{-2} to give an estimate of the fraction of BC remaining with different bulk density values. The fire frequency in the region has decreased, and thus so has the BC input to the soil. Since we cannot quantify the reduction in BC input, we chose 15 two input levels (f): f=0, where there has been no BC input for 100 years and f=0.1, assuming a 90% reduction in BC input. If we assume long-range input of BC via aerial
- transport (Koch and Hansen, 2005), and accordingly increased the input factor in the model, this will further increase the turnover time of BC in this soil. It should, however, 20 be noticed that BC as defined for atmospheric measurements is not equal to BC as
- defined for soils and sediments (Andreae and Gelencsér, 2006; Hammes et al., 2007).

3 Results and Discussion

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3.1 Black carbon concentrations

The 1997 BC concentrations (reported as g BC kg^{-1} soil dry weight, without correction factor throughout the paper) are significantly lower than the 1900 BC con-



centrations throughout the soil (P=0.015), decreasing with depth to almost zero at around 120–130 cm (Fig. 1a, Supplement: http://www.biogeosciences-discuss.net/5/661/2008/bgd-5-661-2008-supplement.pdf). Few other studies to date have quantified BC concentrations over the whole soil profile (Kleber et al., 2003; Wang et al., 2005; Rodionov et al., 2006). Most BC concentration studies report only the topsoil values

- (to 30 cm depth). However, the observed maximum concentration of BC is below the topsoil. BC makes up a substantial 7% of OC in the whole profile in these soils, with a maximum contribution to OC of about 10% at 30–50 cm (Fig. 1b). The 2004 BC concentrations also decrease with depth, but this soil has its maximum concentration
- nearer to the surface (5–20 cm, inset to Fig. 1a). Studies limited to surface horizons miss the location of most concentrated BC, and where BC contributes most to soil or-ganic C. Analyzing BC with the same method, another study on Russian Chernozems further north (Kursk) also found the maximum BC concentration between 30 and 50 cm (49–75 g BC kg⁻¹C with the correction factor, 22–33 g BC kg⁻¹C without) (Rodionov et al., 2006). That study did not report BC stocks or bulk density, and almost no other
- studies have either, making it almost impossible to determine storage and BC turnover rates in other soils (Preston and Schmidt, 2006).

3.2 Black carbon stock loss

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The profile-total black carbon stocks of the 1997 and 2004 soils are 25% lower than that of the 1900 soil (1.9 kg C m⁻² and 2.0 kg C m⁻² vs. 2.5 kg C m⁻², respectively). These values were adapted for the soil samples taken in 2004 according to the sampling increments, by using bulk density values measured under similar land cover of other samples taken in the area before. Our results suggest that BC was lost from the soil over 100 years. Other studies, summarized by Forbes et al. (2006), indirectly suggest substantial losses of BC in other soils in hundreds of years (when inputs were reduced).

While the BC stocks for the 1900 and 1997 soils are similar in the top 20 cm, in the 40– 80 cm region the 1997 soil has a consistently lower BC stock than the historic, 1900-soil (Figs. 1c and 2). Data on soil BC stocks worldwide are scarce (Preston and Schmidt,



2006) and no data were found on other Russian Chernozems. BC stock (using the same quantification method) in a German Chernozem was lower than at our site, with 1.0 kg m⁻² to 1 m depth, but had larger BC stock in the subsoil than in the topsoil as we observed (Kleber et al., 2003). For comparison with our surface soil BC stocks (values in Fig. 1c), in the surface soil of a North American prairie, BC stocks were 0.1-1.5 kg m⁻² for the top 10 cm (Glaser and Amelung, 2003). In a study using a different BC quantification method (UV oxidation), BC stocks were 0.3–0.4 kg m⁻² for the top 20 cm under mixed-grass savanna in Texas (Ansley et al., 2006). The stock in the top 5 cm of a savanna soil in Zimbabwe was 0.04 kg m⁻² (using a dichromate oxidation method) (Bird et al., 1999). The fact that BC stocks are usually only determined for the top 10–20 cm means that most studies dramatically underestimate the black carbon (and carbon) stocks of deep, carbon-rich soils (Torn et al., 2002; Preston and Schmidt, 2006). The total carbon stocks and sink or source potential in these soils is much larger than that conveyed by only considering the topsoil.

15 3.3 Quality of black carbon

An advantage of the BPCA method is that it can give an indication of the change in quality of BC in a soil. A change in black carbon structure during the course of degradation can be explained using the BPCA pattern. The BPCA markers used in our quantification method were formed during the HNO₃ oxidation of BC. The maximum

- ²⁰ number of carboxylic groups reflects the number of formerly found quaternary C atoms (Brodowski, 2005). Thus, BC with a higher degree of condensation should result in higher proportions of the penta- and hexacarboxylic benzoic acids relative to BPCAs with less quaternary C atoms (Brodowski et al., 2005, 2007). Figure 3 shows an increase in the proportion of highly condensed B6CA over the 100-year period. When
- ²⁵ looking at the BPCA pattern for all BPCAs of black carbon over time (Fig. 4), it is evident that the less-condensed (and thus more easily degradable) BPCAs were preferentially degraded over the 100 years compared to the highly condensed (and more recalcitrant) BPCAs – a pattern consistent with a degradation of black carbon during the past



100 years.

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3.4 Black carbon turnover time

Having BC stock at two points in time allowed us to estimate the turnover time of the BC using the stock values in a simple model. We calculated the maximum turnover time of

- ⁵ BC in this soil to be between 444 and 541 years, and the minimum to be 212–262 years, with the ranges due to assumptions about sampling interval, fire cessation, and bulk density (Fig. 5). The conservative, maximum turnover time of 541 years is calculated assuming post-1900 inputs of BC were reduced completely, bulk density had increased by 10% over the 100-y period, and the soil was sampled in the earliest year mentioned (1905).
- (1895; *t*=102 y). Our best estimate, calculated with previously published sampling date (1903) and bulk density (no change from present), and the assumption of a 90% reduction in pre-1900 BC inputs from biomass burning, is 293 y. The Zimbabwe study mentioned earlier was done over a shorter time period (in 1999 it was 50 years since burning stopped) (Bird et al., 1999). The BC had a turnover time between 50 and 100 years, which is faster than ours, but was estimated only for 0–5 cm and in a warm, tropical climate.

Black carbon with ages >1000 years has been found preserved in soil, suggesting a long turnover time (millennia) in some cases (Forbes et al., 2006), but like all soil organic matter, BC exists in a continuum of turnover times. If all BC had such long turnover times there would be much more BC present in soil, given what is known about

- BC inputs rates to soil (because at equilibrium, stock=input rate×turnover time). The majority of ecosystem BC is thought to be either consumed in subsequent fires (Preston and Schmidt, 2006) or lost through other mechanisms when fire is suppressed (Forbes et al., 2006). The rate of soil BC turnover is a function of its formation condi-
- tions (e.g., fire temperature, duration, and oxygen supply) (Baldock and Smernik, 2002; Brodowski et al., 2006; Cheng et al., 2006) and the environment (e.g., climate, soil aggregation, mineralogy, biological activity) (Masiello, 2004). Variations in formation conditions and the environment support the idea of BC as a continuum of more or less



condensed elemental carbon with different chemical and physical reactivity (Forbes et al., 2006; Preston and Schmidt, 2006). Oxidized BC has been found in dissolved organic matter in a forest soil with visible pieces of 100-year-old charcoal in the topsoil, where filamentous bacteria were seen growing (Hockaday et al., 2006). Black carbon particles, deposited about 6000 years ago and collected from a tropical subsoil, displayed a highly aromatic core, and a highly functionalized (carboxylic and pheno-

- lic groups) outer surface where microbial and chemical degradation have taken place (Lehmann et al., 2005). Incubation studies show that BC stimulates the growth of microorganisms, providing more growth surfaces, which in turn break down the BC. With
- the addition of glucose, BC mineralization is further enhanced. Co-metabolism could thus be an important mechanism of BC decay (Hamer et al., 2004). Bird et al. (1999) found that BC can undergo natural degradation or loss, but could only speculate as to the mechanisms: oxidation to CO₂, illuviation to deeper parts of the soil profile, or solubilization and loss as dissolved organic matter. All these mechanisms have been
 observed in various independent studies (see above), but further studies are needed to elucidate the circumstances under which is BC lost in a particular way, which in turn
 - is important for compiling a BC budget in a specific environment.

3.5 Role of black carbon in the global carbon cycle

In addition to the reduction of BC inputs due to cessation of biomass burning, atmo spheric trends over the past 100 years may have affected the loss of BC from the soil. There has been trend of increasing precipitation and temperature since the 1950's in our study area (Sentsova, 2002), which could have altered the decomposition rate of the soil organic matter by increasing soil moisture and chemical and microbial activity. The influence of environmental conditions on BC degradation is not well known,
 but warming can enhance decomposition even of relatively recalcitrant organic matter (Knorr et al., 2005). Thus it is possible that these climatic trends have accelerated BC degradation rates in this region relative to their rates before 1950. In that case, our estimated turnover time is possibly slower than expected for the current climatic con-



ditions, since the period around the turn of the previous century had a less favorable climate for decomposition in this region.

The region's subsoils have also lost Ca²⁺ and CO₃⁻ over the past 100 years, which has been linked to the trend in increasing precipitation (Lapenas et al., in press). It is considered likely that calcium is involved in stabilization reactions with BC (Czimczik and Masiello, 2007), and there is circumstantial evidence that the loss of calcium from soil is associated with the loss of BC (Clough and Skjemstad, 2000).

Black carbon in this soil turns over on a 212–541 y time-scale, which is much faster than previously thought for soil BC (IPCC, 2001). Moreover, this BC turns over more rapidly than the bulk organic matter at this site (Torn et al., 2002), meaning that the BC

- ¹⁰ rapidly than the bulk organic matter at this site (forn et al., 2002), meaning that the BC we analyzed here is more labile than some other soil constituents. As a caveat, the residence time reported here is a whole-profile average value whereas, considering the strong depth dependence of soil organic matter turnover, there is likely a gradient in turnover time with depth. Studies are needed to investigate the depth dependence of BC turnover in soil, to increase the accuracy of carbon cycle budgets and response
- ¹⁵ of BC turnover in soil, to increase the accuracy of carbon cycle budgets and response times.

There has been a search for the source or underlying mechanisms of stable soil organic carbon, intrinsic chemical recalcitrance being one type. Our results on BC turnover appear to remove one of the last potential candidates for chemically recalcitrant carbon inputs, termed passive or inert in soil organic matter models. There is,

- ²⁰ trant carbon inputs, termed passive or inert in soil organic matter models. There is, however, evidence that BC together with other organic soil compounds can be very stable when stabilized in microaggregates (<250 μ m) and/or bound in organo-mineral complexes (for example with iron or aluminum oxides) and clay minerals in the soil where it is protected from fast degradation (Torn et al., 1997; Golchin et al., 1997; Eu-
- sterheus et al., 2005; Brodowski et al., 2006). An improved process-level understanding of the physical and mineral controls on BC and OC turnover is needed to better quantify the role that soil can play in sequestrating carbon or generating feedback that amplifies climate change.

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4 Conclusions

In this study we have shown that BC in soil can be degraded over hundreds of years and is thus not as recalcitrant as previously thought. Further detailed studies are necessary to explain the various mechanisms involved in the degradation and stabilization of BC 5 in soil.

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Table 1. Selected characteristics of soil profiles. The site sampled in 1900 and 1997 is compared to other soil profiles ca. 1 km away sampled in 1997 and 2004. All of the soils developed on the same loess parent material.

Sampling year	Depth	Bulk density	Organic carbon	δ^{13} C of OC
(description) 1900 ^a (archive steppe soil)	cm 0-5 5-12 12-20 20-36 36-50 50-65 65-78 78-100 100-120 120-134	g cm ⁻³ 0.52 0.68 0.73 0.86 0.85 1.12 1.17 1.23 1.24 1.32	g kg ⁻¹ dry weight 105.3 81.5 59.7 45.9 38.2 31.7 17.2 7.7 4.7 5.1	% -25.8 -25.9 -25.4 -25.3 -25.4 -25.4 -24.8 -24.8 -24.2 -23.6 -23.8
1997 ^a (sampled at site of archive steppe soil)	0-5 5-13 13-21 21-37 37-45 45-53 53-68 68-90 90-107 107-130	0.52 0.82 0.84 0.86 0.99 1.12 1.32 1.32 1.32 1.32	100.3 61.0 55.3 46.6 36.7 25.9 13.4 8.7 4.0 7.4	-28.0 -26.2 -26.0 -25.8 -25.6 -25.6 -25.0 -24.9 -24.7 -24.0

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Table 1. Continued.

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Sampling year	Depth	Bulk density	Organic carbon	δ^{13} C of OC
1997-2 ^a	0–5	0.61	78.0	-27.7
(sampled ca. 1 km from archive steppe soil)	5–12	0.68	68.0	-25.8
	12–20	0.73	66.2	-25.6
	20–36	0.72	49.6	-25.4
	36–50	0.85	34.9	-25.2
	50–58	1.01	28.6	-24.5
	58–75	1.17	21.6	-25.0
	75–82	1.20	17.3	-25.0
	82–102	1.23	6.5	-24.8
	102–122	1.24	4.8	-24.0
	122–142	1.24	4.5	-23.3
2004	0–5	0.52	74.2	-25.9
(sampled ca. 1 km from archive steppe soil)	5–20	0.83	55.7	-25.4
	20–50	0.99	28.8	-25.0
	50-80	1.25	26.0	-24.9
	80–100	1.25	27.5	-21.4
2004-plowed	0–10	0.77	47.3	-25.0
(sampled ca. 1 km from archive steppe soil)	10-20	0.93	45.5	-25.0
	20–30	0.93	44.0	-24.9
	30–40	0.91	41.4	-24.8
	40–50	0.94	33.4	-24.9
	50–60	0.97	30.8	-25.3
	60–70	0.95	33.0	-25.2

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^a Data based on Torn et al., 2002.



Fig. 1. (A) Black carbon concentrations (g kg⁻¹ dry weight soil) of the 1900 soil (thin black line, open squares), 1997 soil (thick black line, filled circles) compared to a nearby Chernozem sampled in 2004 (inset, depth increments and axes labels are same as in main graph). The data are without the 2.27 correction factor often used with the BPCA method to compensate for the fact that not all BC is converted to BPCA (Brodowski et al., 2005). Error bars are standard errors (n=2–3). (B) Black carbon as proportion of organic carbon for the 1900 soil, 1997 soil and comparative 2004 soil (inset, depth increments and axes labels are same as in main graph). (C) Black carbon stock of the 1900 and 1997 soils (2004 soil only shown as profile total).

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Fig. 2. Total profile BC stocks of steppe soil sampled in 1900, 1997 and 2004. The BC stock decreased 25% between 1900 and 1997. The comparative 2004 soils are also about 25% lower.



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Fig. 3. Distribution of B6CA (mellitic acid) over the profile for 1900 (thin black line, open squares), and 1997 (thick black line, filled circles) samples.



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b (BC stock remaining as fraction of historic BC stock)

Fig. 5. Estimated turnover times in years for black carbon in the Russian steppe soil, with model sensitivity analysis that includes $\pm 10\%$ change in bulk density (BD) over 100 years: (a) (solid line) 100% reduction in BC inputs (*f*=0), monolith 102 years old (*t*=102 years); (b) 90% reduction in BC inputs (*f*=0.1), monolith 102 years old (*t*=102 years); (c) 100% reduction in BC inputs (*f*=0.1), monolith 94 years old (*t*=94 years); and (d) (dotted line) 90% reduction in BC inputs (*f*=0.1), monolith 94 years old (*t*=94 years). The minimum and maximum turnover times for each scenario is indicated on the left- and right-hand side of the lines, respectively.

