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The resistance of centennial soil charcoal to the "Walkley-Black" oxidation

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ABSTRACT

The "Walkley-Black" oxidation with dichromate is a routine protocol for the estimation of soil organic carbon (SOC) content. Dichromate oxidation is also used to quantify black carbon (BC) in soil and sediments based on the larger resistance of BC to dichromate oxidation than uncharred SOC. The aim of this study was (i) to evaluate whether dichromate-based SOC quantification methods discriminate between uncharred SOC and charcoal residues in the topsoil of pre-industrial charcoal kiln sites and (ii) to test the influence of aging on the recovery of charcoal by dichromate oxidation. We selected 40 topsoil samples from 20 pre-industrial charcoal kiln sites of Wallonia, Belgium, and adjacent reference soils unaffected by charcoal production. Samples included soils from forest and cropland, with a diversity of soil types and textural classes. SOC content was estimated by the original Walkley-Black procedure (results were multiplied by the traditional correction factor of 1.32), and by an adapted method that includes external heating of the digestion mixture to overcome incomplete oxidation of uncharred SOC and get rid of the correction factor of 1.32. Results were compared to the amount of total organic carbon (TOC) content, measured by dry combustion, and to the content of charcoal-C in soil, estimated by differential scanning calorimetry. The soil of a currently active charcoal kiln site was also analyzed and used as a reference subject to limited aging. 23.6% of charcoal-C was recovered by the Walkley-Black procedure in the soil of the currently active kiln site against 65% for the soil of pre-industrial kiln sites, which indicates that the resistance of charcoal to dichromate oxidation decreases with aging. The recovery of charcoal increased to 90% after boiling of the digestion mixture, providing evidence that heat catalyzes the oxidation of charcoal. The substantial oxidation of charcoal by dichromate and the variability of recovery according to the degree of alteration of charcoal and conditions of reaction support the idea that the quantification of BC based on its chemical resistance is challenging and can be subject to important biases if calibration is not adapted to the quality of BC of the sample of interest. Because the recovery of BC by the Walkley-Black method is incomplete, the presence of large amounts of BC in soils frequently affected by fire might be a significant cause of underestimation of SOC by the Walkley-Black method in regional and global databases.

1. Introduction

Wet oxidation of soil organic carbon (SOC) with a known excess of dichromate in a sulfuric acid medium and determination of SOC content by back titration of residual dichromate with ferrous sulfate is a routine protocol in soil science, commonly referred to as the "Walkley-Black" oxidation (Walkley and Black, 1934). Originally, this analysis was developed to meet the need for a rapid, inexpensive and simple method to estimate soil organic carbon (SOC) content (Walkley and Black, 1934). The convenience of the method is, however, at the expense of accuracy, because the oxidation of SOC is inherently incomplete, with a percentage of recovery that may vary to some extent depending on the conditions of reaction and the composition of soil organic matter (Walkley, 1947). To overcome incomplete oxidation, the results are generally multiplied by an empirical factor of 1.32. This corresponds to a recovery rate of 76.0 ± 5.6 (mean ± s.d.) % of the total SOC, calculated from a set of 20 soils from England (Walkley and Black, 1934). Adapted protocols that include external heating of the digestion mixture were developed to decrease the variability of the recovery by making the oxidation complete, or close to (e.g. Anne, 1945). Nevertheless, none of these protocols has been as successful as the Walkley-Black procedure, perhaps because the heating step diminishes the convenience of the method. The presence of inorganic soil components (e.g. Cl^-, Fe^{II}) that react either with dichromate or with carbon during digestion are sources of error in the estimation of SOC content (Walkley, 1947) because the determination is based on the back titration of dichromate rather than on direct measurement of CO_2 emitted during reaction. In carbonate-rich soils, however, the approach by back titration has the advantage to provide an estimation of organic C without taking into account inorganic C from carbonates. Oxidation

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Table 1
Description of topsoil samples from charcoal sites (K) and adjacent reference (R) soils for the 10 sites from forest (F), the 10 sites from cropland (C) and for the currently active kiln site (AK). Data includes World Reference Base (WRB) soil class and texture, depth of sampling, total organic carbon (TOC) content, soil organic carbon (SOC) contents estimated by the Walkley–Black procedure ($SOC_{W\&B}$) and by Anne's method (SOC_{Anne}) and the contents of charcoal-C and uncharred SOC ($SOC_{uncharred}$).

Site	WRB soil class	Texture	K/R	Depth cm	TOC g kg^{-1}	$SOC_{W\&B}$ g kg^{-1}	SOC_{Anne} g kg^{-1}	Charcoal-C g kg^{-1}	$SOC_{Uncharred}$ g kg^{-1}
F1	Dystric Cambisol	Sandy loam	R	0–30	29.3	24.6	24.6	–	–
			K	0–30	45.7	30.7	43.4	38.3	7.4
F2	Albic Luvisol	Silt loam	R	0–10	60.1	65.5	61.4	–	–
			K	0–46	95.9	62.5	82.1	83.2	12.7
F3	Dystric Cambisol	Silt loam	R	0–12	54.8	51.6	52.2	–	–
			K	0–17	119.6	87.9	112.5	95.9	23.6
F4	Eutric Cambisol	Loam	R	0–15	36.1	35.8	32.9	–	–
			K	0–20	116.4	84.6	102.6	85.6	30.8
F5	Albic Podzol	Sand	R	0–11	17.8	19.5	18.3	–	–
			K	0–30	38.1	32.3	36.1	33.8	4.3
F6	Dystric Cambisol	Loam	R	0–15	92.9	96.8	93.2	–	–
			K	0–10	182.2	144.6	178.7	125.2	57.0
F7	Dystric Cambisol	Silty clay loam	R	0–10	75.0	79.3	72.4	–	–
			K	0–21	187.6	129.3	169.1	173.0	14.6
F8	Calcaric Cambisol	Silty clay loam	R	0–15	40.3	36.5	38.7	–	–
			K	0–21	88.9	67.6	80.3	48.4	40.5
F9	Eutric Cambisol	Silt loam	R	0–17	21.1	17.5	22.4	–	–
			K	0–19	80.0	53.6	80.8	50.3	29.7
F10	Dystric Cambisol	Silt loam	R	0–11	76.6	80.4	73.7	–	–
			K	0–35	106.5	71.1	93.9	92.0	14.6
C1	Haplic Luvisol	Silt loam	R	0–25	16.7	15.0	15.9	–	–
			K	0–25	38.4	31.4	35.1	16.2	22.2
C2	Haplic Luvisol	Loam	R	0–25	9.0	6.2	8.3	–	–
			K	0–25	14.3	10.1	12.7	1.8	12.5
C3	Haplic Luvisol	Silt loam	R	0–25	23.2	21.9	23.2	–	–
			K	0–25	64.4	51.9	57.3	33.1	31.3
C4	Haplic Luvisol	Silt loam	R	0–25	13.2	10.7	14.2	–	–
			K	0–25	28.5	21.8	26.4	12.3	16.2
C5	Haplic Luvisol	Silt loam	R	0–25	13.5	10.3	12.6	–	–
			K	0–25	23.2	19.1	21.4	6.5	16.7
C6	Eutric Cambisol	Silt loam	R	0–25	24.6	26.6	23.5	–	–
			K	0–25	58.3	50.0	52.2	22.5	35.9
C7	Haplic Luvisol	Silt loam	R	0–25	26.4	28.2	26.3	–	–
			K	0–25	43.8	38.0	38.5	14.0	29.8
C8	Colluvic Regosol	Silt loam	R	0–25	22.2	22.9	21.9	–	–
			K	0–25	42.7	35.5	39.0	16.3	26.4
C9	Haplic Luvisol	Silt loam	R	0–25	14.5	13.9	12.7	–	–
			K	0–25	24.5	21.8	23.1	10.3	14.2
C10	Haplic Luvisol	Silt loam	R	0–25	11.6	11.3	10.5	–	–
			K	0–25	18.2	14.9	18.1	5.8	12.3
AK	Haplic Luvisol	Silt loam	K	[a]	83.1	26.9	74.3	73.6	9.5

[a] Mound covering material, made of thermally altered soil mixed to charcoal residues.

stage of SOC may also have an influence on the estimate as the calculation of SOC content assumes that C^0 is completely oxidized to C^{IV} (Walkley, 1947). An average oxidation stage of zero for SOC is generally acceptable (Tiessen and Moir, 1993), but it may vary to some extent from one soil organic compound to another (Masiello et al., 2008).

Dichromate oxidation is also used to discriminate between SOC and black carbon (BC) in soil and sediments because BC is supposed to be more resistant to chemical oxidation than uncharred SOC, related to its fused aromatic ring structure. By definition, BC includes all forms of solid carbonaceous residues from biomass burning or pyrolysis and fossil fuel combustion (Schmidt and Noack, 2000), which corresponds to a broad molecular continuum with no clear-cut chemical boundaries (Hammes et al., 2007). Despite its relative resistance, BC is not totally inert to dichromate oxidation, even in its most refractory form (Masiello et al., 2002). Resistance to dichromate oxidation depends on the initial feedstock (Ascough et al., 2011; Bird and Gröcke, 1997; Hammes et al., 2007; Knicker et al., 2007; Skjemstad and Taylor, 2008), the conditions of production (Ascough et al., 2011; Bird and Gröcke, 1997; Naisse et al., 2013) and the size of BC particles (Skjemstad and Taylor, 2008). Many charcoals contain fractions of distinct oxidative resistance (Bird and Gröcke, 1997), which stresses the complexity of BC quantification. Therefore, quantification protocols rely on the difference in the kinetics of degradation between BC and other uncharred SOC when soil or sediment is incubated in 2 M sulfuric acid with an excess of dichromate. Some authors derive the fraction of BC in the sample from multiple components exponential models fitted on mass or carbon loss over digestion time (Bird and Gröcke, 1997; Hammes et al., 2007; Lim and Cachier, 1996; Masiello et al., 2002; Wolbach and Anders, 1989), whereas others define BC as the amount of carbon remaining after a defined digestion time, which is a conservative, operational definition of BC (Hammes et al., 2007; Knicker et al., 2008; Rumpel et al., 2006; Song et al., 2002). Most protocols include pretreatment of the sample with HCl to remove carbonates and with a mixture of concentrated HF and HCl to liberate carbonaceous material possibly trapped in the sheets of phyllosilicates (Lim and Cachier, 1996). The Walkley-Black oxidation, much easier to implement, was also proposed to quantify charcoal in soil. Based on standard additions of charcoal to soil, Kurth et al. (2006) reported that about 80% of charcoal was resistant to the Walkley-Black oxidation, which is a relatively effective discrimination between BC and uncharred SOC.

In this work, the aim was to assess whether dichromate oxidation by the Walkley-Black procedure, a routine protocol used worldwide for the determination of soil organic carbon, discriminates between charcoal and uncharred soil organic matter in the topsoil of pre-industrial charcoal kiln sites of Wallonia, Belgium. These sites are circular