Variable carbon recovery of Walkley-Black analysis and implications for national soil organic carbon accounting

S. Lettens[a], B. De Vos[b], P. Quataert[b], B. van Wesemael[c], B. Muys[a] & J. van Orshoven[a]
[a]Department of Land Management and Economics, Katholieke Universiteit Leuven, Celestijnenlaan 200 E, BE-3001 Leuven,
[b]Research Institute for Nature and Forest, Gaverstraat 4, BE-9500 Geraardsbergen, and [c]Department of Geography,
Université Catholique de Louvain, Place Louis Pasteur 3, BE-1348 Louvain-la-Neuve, Belgium

Summary

There is considerable interest in the computation of national and regional soil carbon stocks, largely as the result of the provisions of the Kyoto Protocol. Such stocks are often calculated and compared without proper reference to the uncertainties induced by different analytical methodologies. We illustrate the nature and magnitude of these uncertainties with the present soil organic carbon (*SOC*) study in Belgium. The *SOC* recovery of the Walkley-Black method was investigated based on a database of 475 samples of silt loam and sandy soils, which cover different soil depths and vegetation types in northern Belgium. The organic carbon content of the soil samples was measured by the original Walkley-Black method and by a total organic carbon analyser. The recovery was computed as the ratio of these two results per soil sample. Land use, texture and soil sampling depth had a significant influence on the recovery as well as their three-way interaction term (land use × texture × sampling depth). The impact of a land use, texture and sampling depth dependent Walkley-Black correction on the year 2000 *SOC* inventory of Belgium was determined by regression analysis. Based on new correction factors, the national *SOC* stocks increased by 22% for the whole country, ranging from 18% for cropland to 31% for mixed forest relative to the standard corrected *SOC* inventory. The new recovery values influenced therefore not only C stocks in the year 2000, but also the expected *SOC* change following land use change. Adequate correction of Walkley-Black measurements is therefore crucial for the absolute and comparative *SOC* assessments that are required for Kyoto reporting and must be computed to take into account the regional status of soil and land use. 'Universal' corrections are probably an unrealistic expectation.

Introduction

Over the past 60 years, a range of analytical techniques has been used to measure soil organic carbon (*SOC*) content. Reasons to choose a certain technique are its reliability, reproducibility, time-efficiency, cost of equipment or chemicals and the possible environmental risk. The Walkley-Black method (Walkley & Black, 1934; Walkley, 1947) has been the most widely reported procedure for the past 50 years. It is rapid and requires minimum equipment compared to other wet or dry combustion methods (Nelson & Sommers, 1982). *SOC* is oxidized in a dichromate-sulphuric acid mixture and due to incomplete oxidation, the original method (without external heating) measures less than 100% of the *SOC* present in the soil sample. Therefore a correction factor has to be applied. Based on 20 samples, Walkley & Black (1934) decided that the recovery is on average 76%. Thus a correction factor of 1.32 was introduced for quantifying the total *SOC* content of a soil sample. Although the Walkley-Black methodology was originally carried out without applying external heat (Walkley, 1947), many variants exist with heating of various intensity and duration. Important modified dichromate oxidation techniques that involve extensive heating, like those of Tinsley (1950), Mebius (1960) and Allison (1960) do not require a correction factor because most of the organic C in the soil is oxidized to CO_2 (Kalembasa & Jenkinson, 1973). Methods that involve minimal heating, such as Schollenberger (1927), require a small correction factor (1.15) (Allison, 1960).

Since its publication, the validity of the 1.32 conversion factor or its equivalent 76% recovery rate has been debated. It has been confirmed by Walkley (1947) and Gillman *et al.* (1986), but it has been questioned as well, e.g. by Drover & Manner (1975). More recently, Diaz-Zorita (1999) and Brye & Slaton (2003) reported that the recovery of 76% is generally too large and that it may vary according to land use, soil type (soil texture in particular), sampling depth and climate. They recommend the use of differential recovery percentages that take into account these factors prior to the compilation and comparison of Walkley-Black based *SOC* inventories.

Driven mainly by the Kyoto Protocol, national or regional soil organic carbon inventories are compiled across the globe (e.g. Batjes, 1996; Batjes, 2002; Falloon *et al.*, 2002; Tate *et al.*, 2003; Bellamy *et al.*, 2005). The importance of absolute *SOC* assessments in this context is obvious. In Belgium, a spatially explicit approach was adopted (Lettens *et al.*, 2004; Lettens *et al.*, 2005a). In this approach, the territory is subdivided into landscape units (LSU) defined through the intersection of a land cover/use map and a soil association map. *SOC* measurements from various and heterogeneous sources were selected to estimate the *SOC* stocks of the LSU. Particular attention was devoted to the consistent quantification of variability and to the statistically sound testing of differences of *SOC* stocks between LSUs. The majority of the *SOC* measurements has been obtained using the standard Walkley-Black method (Walkley, 1947). Since the *SOC* inventories in Belgium differentiate between land use types, soil associations (defined mainly in terms of soil texture and drainage conditions) and depth, our objective was (i) to examine the effect of these class variables on *SOC* recovery by the Walkley-Black method by comparing it with an accurate dry combustion technique and (ii) to acknowledge this effect, if any, by re-computing and re-interpreting the Belgian *SOC* inventory of 2000. A differential recovery will indeed influence *SOC* stocks and their regional or national aggregation. In addition, land use dependent recoveries may affect the predicted *SOC* change after land use change.

Materials and methods

Sampling scheme and SOC measurements

Soil samples were collected at four locations. Table 1 provides a summary description of the sites. The locations within Belgium are indicated in Figure 1. At each of the four sites (two silt loam soils and two sandy soils), three land use types (forest, grassland and cropland) were sampled, as closely together as possible, at two fixed sampling depths (0–10 cm and 20–30 cm) and using 20 sample points. These 20 points were located on two parallel transects of 10 points each. The distance between the sample points was 10 m. Five samples were lost during sampling, leading to a total sample number of 475. Soil samples were air-dried, crushed and passed through a 2-mm mesh sieve. Organic carbon analysis was carried out by the Research Institute for Nature and Forest. Organic carbon was first determined in each soil sample by the standard Walkley-Black method (Walkley, 1947). No external heat was applied. All samples were analysed by dry combustion with the Shimadzu 5050 A (with SSM-5000 A Solid Sample Module, Shimadzu, Kyoto, Japan) total analyser as well. Dry combustion total analysers with infrared detectors measure the CO_2 generated by complete decomposition of organic material at temperatures at or above 900°C. These methods are currently considered as the most reliable, with recoveries close to 100%. There are small differences between dry combustion total organic carbon (TOC) systems, but as a group, their recovery performance is much better than wet oxidation methods (Brye & Slaton, 2003). The volume per cent of microaggregates (0–250 mm) versus macroaggregates (250–2000 mm) was determined by laser diffraction (Coulter LS200, Miami, FL, USA) for 72 samples, also by the Research Institute for Nature and Forest. Three samples were selected randomly for each combination of location, soil depth and land use. Particle-size distribution was determined for each site by a laser diffraction method (LDM), calibrated, and validated

Table 1 Description of the location, land use, soil type and textural composition (average volume percentage of clay, silt and sand) of the soil samples.

Municipality	Land use	N-Lat	E-Long	WRB^{a} soil type	Dominant texture class	Clay (0–2 mm) /%	Silt (2–63 mm) /%	Sand (63 m–2 mm) /%
Hoeilaart	broadleaf forest	50°46¢27²	4°25¢27²	Dystric Albeluvisol	Silt loam	17	73	10
	grassland	50°46¢ 07²	4° 25¢ 59²	Luvisol				
	cropland	50°44¢18²	4°24¢55²	Luvisol				
Brakel	broadleaf forest	50° 49¢ 13²	3° 44¢ 58²	Haplic Luvisol	Silt loam	25	71	4
	grassland	50° 49¢ 03²	3° 44¢ 54²	Haplic Luvisol				
	cropland	50° 49¢ 00²	3° 44¢ 55²	Haplic Luvisol				
Lommel	coniferous forest	51° 10¢ 27²	5° 18¢ 47²	Haplic Podzol	Sand - Loamy sand	4	11	85
	grassland	51° 10¢ 48²	5° 18¢ 42²	Haplic Podzol				
	cropland	51°10¢49²	5°18¢40²	Haplic Podzol				
Brasschaat	coniferous forest	51°18¢28²	4°31¢18²	Anthric Podzol	Loamy sand	3	7	90
	grassland	51°18¢35²	4°31¢11²	Anthric Podzol				
	cropland	51°18¢34²	4°31¢08²	Anthric Podzol				

[a] WRB ¼ World Reference Base soil classification (FAO 1998).

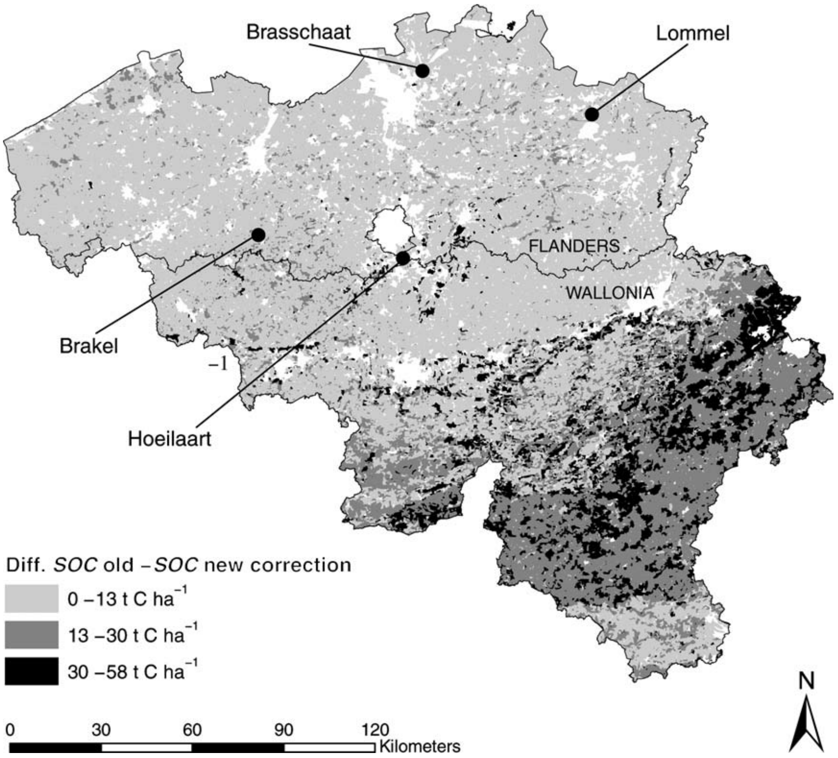


Figure 1 Spatial distribution of the increase in *SOC* content in 2000 for Belgium (0–30 cm) due to the new correction methodology. The four sample locations are indicated.

with standard pipetting and sieving procedures (ISO 11277) after application of the same pre-treatment.

Computation of recovery and test statistic

The percentage recovery (*WBR*) obtained by the Walkley-Black method compared to the dry combustion method is computed as:

$$WBR \text{ ¼ } 100\,\frac{SOC_{\mathrm{WB}}}{\mathrm{TOC}}; \qquad \text{ð1Þ}$$

where SOC_{WB} ¼ *SOC%* by Walkley-Black not corrected with the traditional factor 1.32; *TOC* ¼ total organic carbon or the *SOC%* by dry combustion.

In order to detect possible significantly different recoveries between the factor levels of land use type, soil type, sampling depth or their interaction terms, we made an ANOVA with Tukey's pair-wise comparison. For each of the significantly different factor levels, a regression equation between SOC_{WB} and *TOC* is derived. Grouping the factor levels that are not significantly different increases the number of observations per regression equation. Measurement error is present in both X and Y axes, in which case ordinary least square (OLS) regression is still appropriate for predicting Y from X. However, due to the measurement error in X, the regression coefficient is not the best estimator of the parameter b in an underlying law-like relationship Y ¼ a þ bX where X is TOC and Y is SOC_{WB} (Webster, 1997). Webster (1997) advises the use of structural analysis, or Deming regression, to correct the regression coefficients by taking into account the observed error in X. We quantified the relative importance of the error in X compared to the error in Y for our dataset by estimating the factor k ¼ ex^2=ey^2, where ex^2 and ey^2 are the error variances of X and Y. It appeared that when k was less than 0.5, the effect on slope and intercept of the OLS was negligible. The average k, based on duplicate measurements, was estimated as 0.046. Hence, the error in X was sufficiently small to justify the use of OLS regression.

Re-computing the Belgian SOC inventory for 2000

We re-computed the Belgian *SOC* inventory for 2000, as described by Lettens *et al.* (2005a). The elementary spatial unit is the landscape unit (LSU), which consists of several polygons and is characterized by a unique combination of land use and soil association. The 289 LSUs considered cover 24 042 km^2, which is 79% of the Belgian territory. The uncharacterized 21% consists of 19% urban land and military zones and 2% fallow land, heath land, excavated soil and inland marshes. Since no measurements are available for these land use types, they are excluded from the analysis. The land use type of the LSU is derived from the Corine Land Cover map (1990 version, resolution 250 × 250 m^2; European Commission, 1993) and includes cropland, grassland, broadleaf forest, coniferous forest and mixed forest. The soil type corresponds to one of the 65 soil associations of the Belgian Soil Association map (Tavernier & Mare´ chal, 1972; published at a scale of 1:500 000).

Soil associations represent fragmented zones with similar texture (according to the eight textural classes of the Belgian texture triangle, see Lettens *et al.*, 2004) and drainage class. *SOC* values have been calculated for incremental depth layers (0–10 cm, 0–20 cm, . . ., 0–100 cm). *SOC* values from various datasets are attributed to LSUs in a process called geo-matching (Lettens *et al.*, 2005b).

The new recovery values are applied to the *SOC* datasets that use standard Walkley-Black analysis to measure percentage *SOC*. All *SOC* datasets but one contain standard Walkley-Black measurement values. The exception is the dataset containing *SOC* concentrations of forested LSUs in Flanders (the administrative region covering northern Belgium, see Figure 1) in 2000 that were obtained by loss-on-ignition (LOI) (De Vos *et al.*, 2005). According to the Corine Land Cover geodataset, 82% of the Belgian forests are situated in Wallonia (the administrative region covering southern Belgium), while forests occur on 21% of the Belgian territory. Therefore, the *SOC* concentration of 96% (= 100%-0.18 × 21%) of the total LSU area considered is obtained with the standard Walkley-Black method and corrected according to the newly derived recovery equations.

In order to apply the recovery equations, the *SOC* percentages that are based on the standard Walkley-Black method are back-converted to the original measurement values by dividing by 1.32. The correction methodology is then applied for each LSU-depth combination. In order to remain in line with the sample dataset, no distinction is made between measurements under deciduous, coniferous or mixed forest. Only cropland, grassland and forest are retained. Similarly, all measured samples are considered to have either sand or silt loam texture. The correction equation for 0–10 cm is applied to the upper 20 cm of soil and the correction equation for 20–30 cm is applied to the 20–30 cm layer of soil. Deeper soil layers are not considered in this exercise.

For each newly computed C concentration $\hat{X}_{\mathrm{new}}$, the model uncertainty is estimated by the model variance, VAR_{M}, according to

$$VAR_{\mathrm{M}} = \sigma^2 \left[1 + \frac{1}{N} + \frac{(\hat{X}_{\mathrm{new}} - \bar{X})^2}{\sum_{i=1}^{N} (X_i - \bar{X})^2} \right]; \qquad (2)$$

where N is the number of observations per WB recovery group, $\bar{X}$ is the average C concentration per WB recovery group and σ^2 is estimated by $SDEV_{\mathrm{pred}}{}^2$, with $SDEV_{\mathrm{pred}}$ the standard deviation of the prediction:

$$SDEV_{\mathrm{pred}}{}^2 = \frac{\sum_{i=1}^{N} (Y_i - \hat{Y}_i)^2}{N-2}; \qquad (3)$$

where $\hat{Y}_i$ is the predicted C concentration.

Several of the datasets that underlie the computations for the 2000 inventory contain average *SOC%* values per municipality and not individual measurements. This is corrected by multiplying $SDEV_{\mathrm{pred}}$ with the factor $1/\sqrt{n}$, with n the number of observations for each of the average *SOC%* values.

The *SOC* percentages per profile or per municipality are scaled to a *SOC* stock (t C ha^{-1}) of a landscape unit. This procedure is described in Lettens *et al.* (2004, 2005a). The confidence interval around the average *SOC* stock of an LSU, $\overline{SOC}_{\mathrm{LSU}}$, is:

$$\overline{SOC}_{\mathrm{LSU}} \pm z(1-\alpha/2) \times \sqrt{VAR_{\overline{SOC}_{\mathrm{LSU}}}};$$

where $z(1-\alpha/2)$ is the cumulative probability of the standard normal distribution for a confidence level $1-\alpha$; $VAR_{\overline{SOC}_{\mathrm{LSU}}} =$ the total variance for $\hat{X}_{\mathrm{new}} = SOC_{\mathrm{LSU}}$.

The *SOC* change following land use change is estimated by comparing the LSUs with an identical soil type but different land use type. The observed difference in space can be considered as an estimate of the expected *SOC* change in time for the soil association, given the corresponding land use change. This approach is comparable to using chronosequence data instead of measuring the same site at successive moments in time. When applied to predict future *SOC* stock changes, it implies that *SOC* stocks are in equilibrium at both times and that future climate and management conditions remain equal (Lettens *et al.*, 2005b).

Results

Walkley-Black SOC recovery (WBR)

Table 1 shows general characteristics of the sampling sites. According to Table 2, soil organic carbon percentage measured by dry combustion ranges from 0.8% in the 20–30 cm layer of grassland on silt loam to 6.3% in the upper 10 cm layer of forest on silt loam. Soil inorganic carbon ($CaCO_3$) content is not shown in Table 2, but is less than 1% for all sites. The dependent factor of the ANOVA is the Walkley-Black recovery and the explanatory factors are land use class, soil texture class and soil sampling depth class. The recovery values are homoscedastic and, although slightly skewed, normally distributed for the 12 possible combinations of the factor levels (see Table 2). The ANOVA shows that the three main factors, land use (probability $P < 0.0001$), texture ($P < 0.0001$) and depth ($P = 0.004$), as well as the two-way interaction terms land use × depth ($P < 0.0001$) and soil texture × depth ($P = 0.0005$) and the three-way interaction term land use × texture × depth ($P = 0.01$) are significant. The average recovery is least for forest (61%), then grassland (64%) and the greatest recovery is found for cropland (66%). Sandy soils have a greater recovery (66%) than silt loam soils (61%). Although the difference is significant, the recoveries for the 0–10 cm and 20–30 cm layer do not differ strongly: 63% and 64%,

Table 2 Summary statistics of the Walkley-Black recovery values (*WBR*) per land use type, texture and soil sampling depth (cm)

Land use	Texture	Soil sampling depth /cm	Number of observations	TOC /%	Average *WBR* /%	Minimum *WBR* /%	Maximum *WBR* /%	Variance *WBR*	Standard deviation *WBR* /%	Skewness *WBR*
Forest	Silt loam	0–10	39	6.3	58	44	72	36.3	6.0	0.15
		20–30	39	1.1	60	44	74	31.9	5.7	-0.26
	Sand	0–10	40	5.7	59	38	92	94.4	9.7	0.71
		20–30	40	2.2	67	46	90	77.9	8.8	0.16
Grassland	Silt loam	0–10	40	2.3	62	54	69	11.5	3.4	-0.52
		20–30	40	0.8	59	52	66	10.7	3.3	0.47
	Sand	0–10	39	2.4	66	54	79	23.6	4.9	-0.01
		20–30	39	1.9	68	61	74	13.0	3.6	0.05
Cropland	Silt loam	0–10	40	1.3	63	53	73	21.7	4.7	-0.11
		20–30	39	0.9	64	52	72	23.3	4.8	-0.45
	Sand	0–10	40	2.3	68	60	80	18.1	4.3	0.29
		20–30	40	2.3	68	61	83	27.8	5.3	0.86

respectively. All these averages must be treated with caution since interaction exists between the three factors.

When comparing the least square means of the recovery for the interaction term land use × texture × sampling depth with Tukey pair-wise comparison, it appears that not all pairs of soil-land use-depth combinations are significantly different. Those that are not significantly different from each other but are significantly different from the remaining recoveries are gathered into one group. This results in three groups (see Figure 2), mutually significantly different at a significance level, a, of 0.05 and characterized by the following average recovery value:

1 WBR1 ¼ 67% for sandy cropland 0–10 cm, sandy cropland 20–30 cm, sandy forest 20–30 cm, sandy grassland 0–10 cm and sandy grassland 20–30 cm;

2 WBR2 ¼ 63% for silt loam cropland 0–10 cm, silt loam cropland 20–30 cm and silt loam grassland 0–10 cm;

3 WBR3 ¼ 59% for sandy forest 0–10 cm, silt loam forest 0–10 cm, silt loam forest 20–30 cm and silt loam grassland 20–30 cm.

Effect on the 2000 Belgian SOC inventory

The computation of the new 2000 *SOC* inventory is based on the three regression functions derived for each group (see Figure 2 and Table 3). The intercept is not significant for any of the *WBR* groups. The effect of the new correction methodology on the results is quite strong, especially for the forested LSUs (Figure 3). Figure 4 clearly shows that the impact of the Walkley-Black correction on forested LSUs in Wallonia is stronger than in Flanders. Figure 1 shows that the geographical distribution of the *SOC* stock increases due to correction. The largest net increases occur in southern Belgium. The total *SOC* stock in the upper 30 cm amounts to 157 Mt C based on the standard recovery value of 76% and 191 Mt C based on the new, differential recoveries and amounts to a 22% increase in total *SOC* storage in Belgian soils in 2000.

Effect on expected SOC change following land use change

Although the original inventory predicts largely the same trends, the net increases and decreases change proportionally to the new Walkley-Black correction. Converting cropland on soil association 50 (stony loam soils with texture B horizon and an admixture of schist and slate) to coniferous forest for example, is expected to sequester 47 t C ha^{-1} (80–127 t C ha^{-1}) in the upper 30 cm as derived from the corrected inventory instead of 28 t C ha^{-1} (67–94 t C ha^{-1}) as derived from the original inventory (see Table 4). The absolute changes are more pronounced when the new recovery values are applied.

Discussion

Walkley-Black recovery

The three Walkley-Black recovery groups are quite diverse. The first group (WBR1) could be interpreted as the sandy soil group under agricultural land use for all soil depths. WBR2 is valid mainly for silt loam soils under arable and grassland, whereas WBR3 refers mostly to forest soils. It may also be concluded that recovery does not change with increasing depth under cropland and that the two agricultural land use types have an equal recovery factor on sandy soils.

The literature available on Walkley-Black recovery is extensive. When investigating the dependence of the recovery on physical factors, authors come up with apparently conflicting results. In some cases, no correlation at all is observed between recovery and land use (Mikhailova *et al.*, 2003), texture (Bornemisza *et al.*, 1979; Rhodes *et al.*, 1981; Ulmer *et al.*, 1992) or soil sampling depth (Diaz-Zorita, 1999; Hussain & Olson, 2000; Mikhailova *et al.*, 2003). In the present study, the recovery appears to be less than the standard value of 76% and additionally it depends upon land use, soil texture and soil sampling depth. Recovery under cropland is on average significantly greater than under grassland. However, a detailed examination

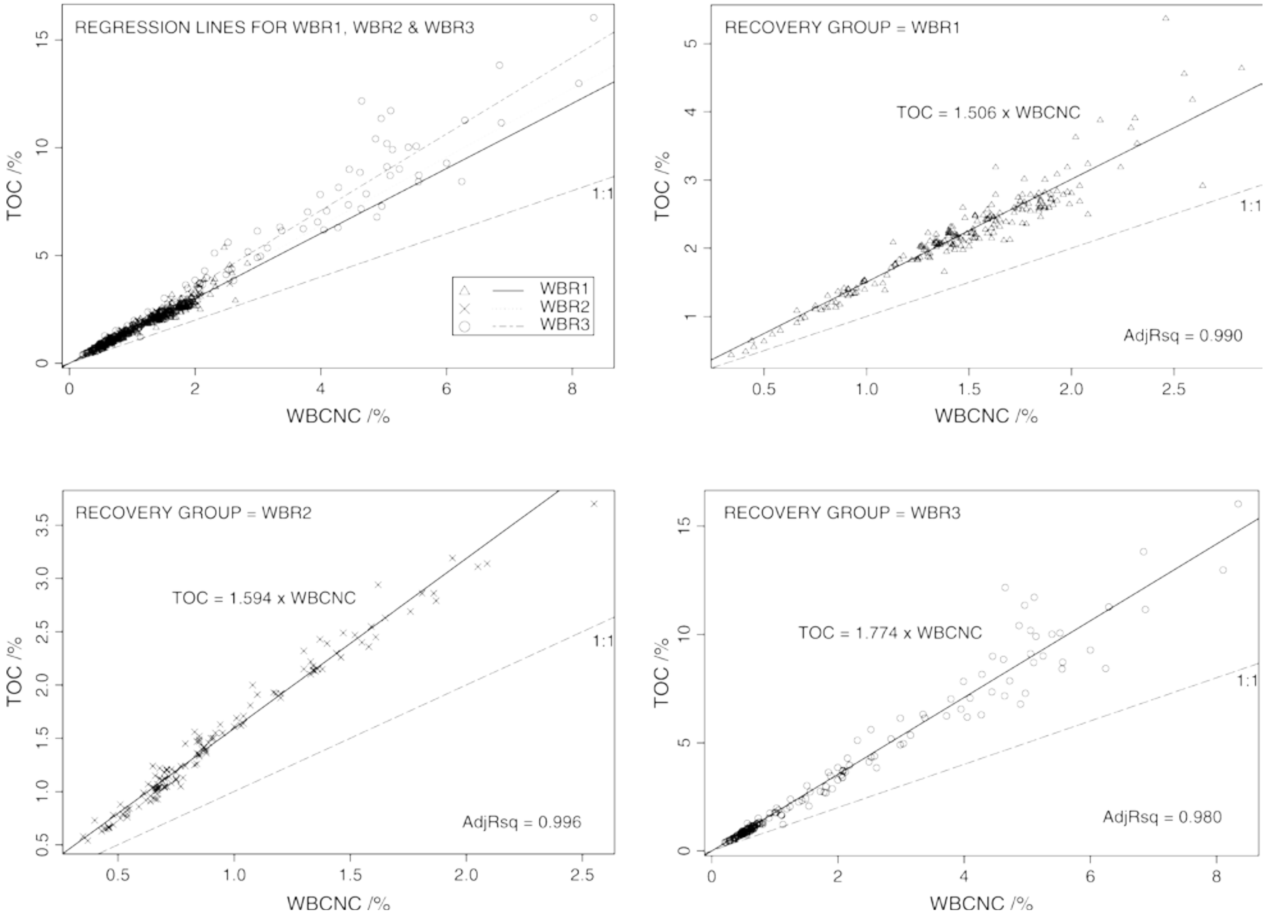


Figure 2 Regression lines for the three recovery groups WBR1, WBR2 and WBR3. The regression equations and the adjusted R^2 (AdjRsq) are indicated (WBCNC ¼ organic carbon content measured by Walkley-Black, without correction factor (%); TOC ¼ total organic carbon content, measured by dry combustion (%)).

of the three recovery groups WBR1, WBR2 and WBR3, reveals that grassland recovery is only less than cropland recovery for the 20–30 cm soil layer of silt loam soils. For the 0–10 cm of soil on silt loam and for both depths on sandy soil, grassland recovery is not significantly different from cropland recovery. Diaz-Zorita (1999) reports that the recovery is less under pasture (59%) than under any of the cultivation systems (tillage with moldboard plow or chisel plow or no-tillage: 73%) on a loam soil in the subhumid Argentinean Pampa (0–15 cm). The author explains this result by the presence of phenolic and lignin compounds under graminaceous perennial pastures that resist oxidation at the temperatures obtained

Table 3 Number of observations *N*, average percentage *SOC* according to Walkley-Black (without correction factor: SOC_{WB}) and dry combustion (TOC), average recovery (*WBR*), intercept (b_0), linear regression coefficient of TOC (b_1), standard error (*SE*) of this coefficient and standard deviation of the prediction ($SDEV_{pred}$) for the regression equations derived for the three recovery groups WBR1, WBR2 and WBR3

	N	Average SOC_{WB} /%	Average TOC /%	Average *WBR* /%	b_0	b_1	*SE of* b_1	$SDEV_{pred}$
WBR1	198	1.47	2.21	67	not significant	1.506	0.011	0.23
WBR2	119	0.95	1.52	63	not significant	1.594	0.009	0.69
WBR3	158	1.98	3.48	59	not significant	1.774	0.020	0.11

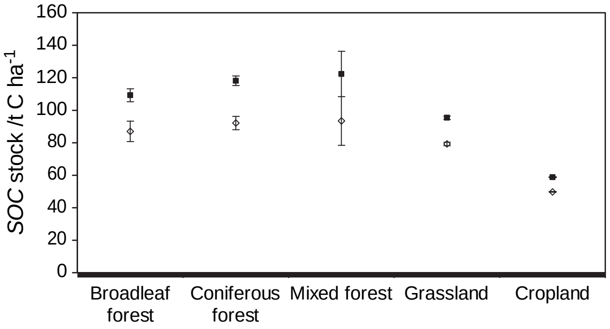
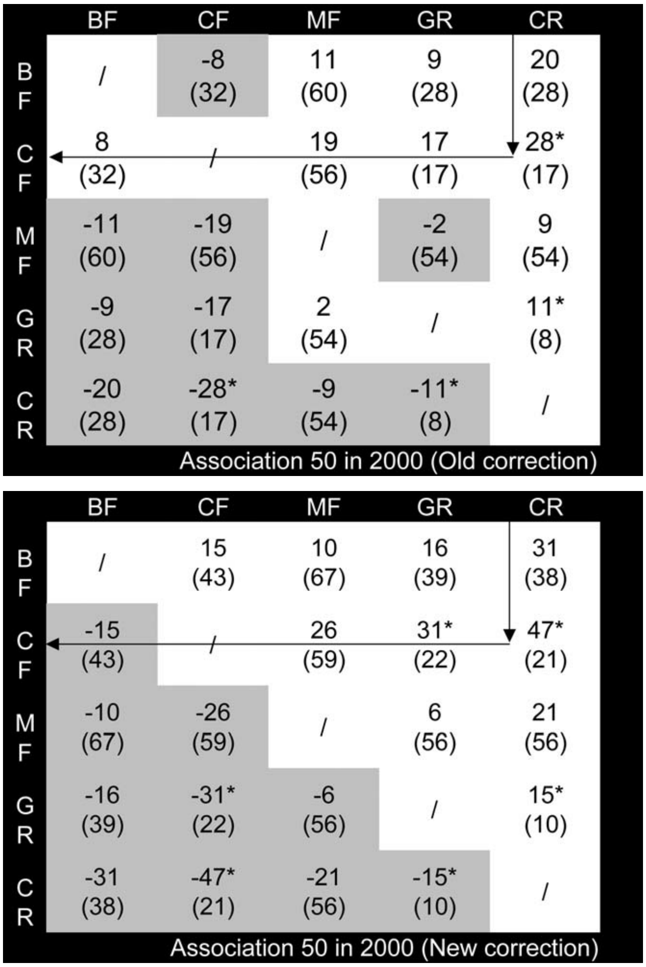


Figure 3 Average (t C ha^{-1}) soil organic carbon stock and 95% confidence intervals for five land use types in 2000 for the upper 30 cm of mineral soil, based on the old (*e*) and the new (j) carbon recoveries for Walkley-Black analysis.

Table 4 Expected *SOC* change in 0–30 cm (t C ha^{-1}) following land use change, for association 50 in the year 2000, based on the old (upper) and the new (lower) correction factors. The matrix must be read in the direction of the black arrow. The 95% confidence intervals are shown between brackets, significant changes are indicated by '*', decreases are in grey (BF ¼ broadleaf forest; CF ¼ coniferous forest; MF ¼ mixed forest; GR ¼ grassland; CR ¼ cropland)



	BF	CF	MF	GR	CR
BF	/	-8 (32)	11 (60)	9 (28)	20 (28)
CF	8 (32)	/	19 (56)	17 (17)	28* (17)
MF	-11 (60)	-19 (56)	/	-2 (54)	9 (54)
GR	-9 (28)	-17 (17)	2 (54)	/	11* (8)
CR	-20 (28)	-28* (17)	-9 (54)	-11* (8)	/

Association 50 in 2000 (Old correction)

	BF	CF	MF	GR	CR
BF	/	15 (43)	10 (67)	16 (39)	31 (38)
CF	-15 (43)	/	26 (59)	31* (22)	47* (21)
MF	-10 (67)	-26 (59)	/	6 (56)	21 (56)
GR	-16 (39)	-31* (22)	-6 (56)	/	15* (10)
CR	-31 (38)	-47* (21)	-21 (56)	-15* (10)	/

Association 50 in 2000 (New correction)

with H_2SO_4 in the Walkley-Black analytical procedure. The effect of lignin is also recorded in earlier research. Baker (1936) describes that Walkley-Black recovery of starches, hemicelluloses and celluloses (easily decomposable non-lignin fractions) is almost 100% and therefore the lignin and lignin-like materials must account for the average *SOC* recovery of 76%. Research on Walkley-Black recovery under forest is rare. Similar to our results, Drover & Manner (1975) found a poorer recovery under forest than under grassland.

The data do not show a clear trend between recovery and depth. For cropland in general, for grassland on sandy soil and for forest on silt loam soil, the recovery appears to be independent of depth. For cropland, this could be explained by the homogenization through ploughing. For grassland on silt loam soil, recovery decreases with depth while for forest on sandy soil, a strong increase in recovery is observed for the deeper soil layer. On average, the recovery increases with increasing depth. Bornemisza *et al.* (1979) sampled Andept soil profiles with a loam, silt loam or clay loam texture under forest in Costa Rica up to 95 cm deep. They found a greater recovery in the deeper layers (between 82.7 and 95.3%) than in the surface layer (75%). They argue that the easier oxidation of organic C in deeper layers is caused, at least partly, by a larger fulvic acid fraction, with lower molecular weights that are more easily oxidizable. Poor recovery in surface samples is probably due to the presence of fresh plant residues.

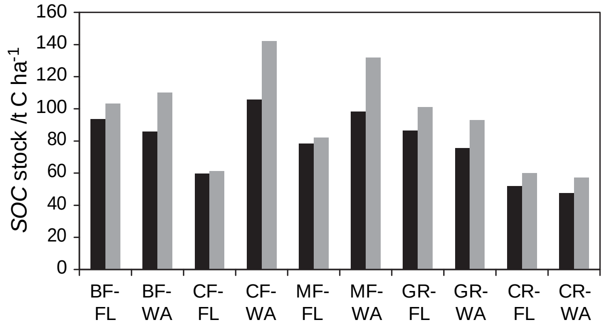


Figure 4 *SOC* content (t C ha^{-1}) for five land use types in the regions Flanders (FL) and Wallonia (WA), for the 0–30 cm soil layer and for the year 2000 with the old (j) versus the new (▨) correction methodology (BF ¼ broadleaf forest; CF ¼ coniferous forest; MF ¼ mixed forest; GR ¼ grassland; CR ¼ cropland.

A number of authors have observed that Walkley-Black recovery decreases in soils that contain reactive silicate clays or allophanic material (Richter *et al.*, 1973; Bornemisza *et al.*, 1979; Olayinka *et al.*, 1998; Diaz-Zorita, 1999; Chacon *et al.*, 2002). Based on 50 soil surface samples, Bornemisza *et al.* (1979) conclude that the type of clay mineral has a larger effect on the efficiency of Walkley-Black oxidation than the total clay content. Reactive silicate clays may stabilize organic matter through adsorption, thus decreasing recovery (Wiseman & Püttmann, 2005). In our results, silt loam soils with 17–20% clay indeed have poorer recoveries than sandy soils with 3–4% clay. This is especially clear for grassland and cropland, where the effect is independent of depth. In the soils of northern Belgium, clay with 2:1 mineralogy dominates. Illite is most common, though montmorillinite may occur in the region of the sampling location in Brasschaat. Since the soil samples of Brasschaat contain little clay (3%, see Table 1), clay mineralogy probably did not exert a large influence on our results. Six *et al.* (1999) state that in undisturbed soils, small (250–2000 mm) and large (> 2000 mm) macroaggregates are not disrupted and therefore, more C can be incorporated in the more stable microaggregates (53–250 mm) that are formed within the macroaggregates. Surface layers of soils under natural vegetation contain therefore more C in microaggregates or in small macroaggregates than in cultivated soils (Six *et al.*, 1999; Martens *et al.*, 2003; Degryze *et al.*, 2004; Leifeld & Kögel-Knaber, 2005). These aggregates may resist oxidation by Walkley-Black. Figure 5 shows that forest soils indeed contain a larger proportion of macroaggregates than cropland or grassland soils, especially in the 0–10 cm soil layer. These macroaggregates could protect the OC contained against Walkley-Black oxidation.

The presence of charcoal in forest soils could explain part of the poor recovery. Skjemstad & Taylor (1999) report that the rate of recovery of charcoal C by the Walkley-Black method depends on the nature of the material from which it is derived and its particle size. For woody material they find very poor recoveries ranging from 4% to 30% and this decreases with increasing particle size. These poor recoveries are confirmed by other authors (Walkley, 1947; Bremner & Jenkinson, 1960; Kerven *et al.*, 2000).

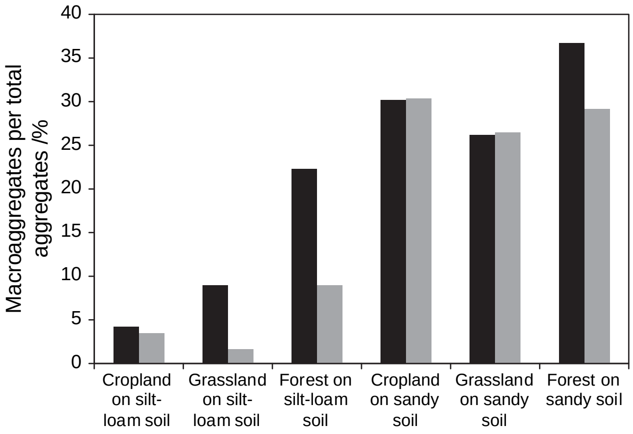


Figure 5 Proportion (%) of the volume of macroaggregates (250–2000 mm) to the total aggregate volume in 0–10 cm (j) and 20–30 cm (▨) for the land use types cropland, grassland and forest and for the textures sand and silt loam.

Finally, apparently small analytic details of the Walkley-Black procedure may have an important influence on the results. Skjemstad *et al.* (2000) found that the use of smaller flasks during Walkley-Black analysis resulted in higher reaction temperatures, which increased recovery and rendered the correction factor superfluous. Additionally, De Leenheer & Van Hove (1958) show that Walkley-Black analysis has little potential for soil samples with more than 7.5–10% C. If OC concentration exceeds 10%, the quantities of H_2SO_4 and $K_2Cr_2O_7$ need to be very large and the colour change during titration will be difficult to detect. Moreover, the high concentration of sulphuric acid and dichromate increases temperature, thus influencing recovery rates. In our dataset, for 25 forested surface soil samples (14 on silt loam and 11 on sand), TOC exceeds 7.5%. Recovery is least for the group with greatest TOC values (WBR3) (Table 3). Possibly, this is the result of applying an inappropriate method.

Implications for national soil carbon inventories

Our data show an important impact of the new recovery values on the resulting *SOC* stocks. Figures 3 and 4 show that the land use type forest, in particular, gains much carbon after correction. The predicted *SOC* stocks increase most under forest in Wallonia. Since the original Walkley-Black method is not applied for Flemish *SOC* measurements in forest soils, the effect of the new correction factors is absent in most Flemish forest LSUs. This is illustrated in Figure 1, where the largest changes occur in forest-rich Wallonia. The predicted C sequestration after establishing forest on agricultural soils would have been underestimated if the standard Walkley-Black correction factor were used.

The exact reason for the observed differential Walkley-Black recovery is interesting, since it determines the error introduced by using the standard correction factor for the computation of the expected *SOC* change after land use change. For example, if the presence of recalcitrant compounds reduces the recovery, the predicted *SOC* change after land use change towards grassland (rich in lignin) or forests (rich in lignin and often charcoal) will be underestimated. If rather the formation of stable microaggregates causes poor recovery, certain management practices (e.g. reduced tillage or application of farmyard manure) or land use changes (e.g. towards forest or grassland), will not receive the carbon credits they deserve when using standard Walkley-Black correction. On the other hand, if the main cause is stabilization through adsorption on reactive silicate clays, then the underestimation is restricted to soil types with significant amounts of such materials, and, for the affected soils, the error before and after land use change will be similar. Finally, if small variations of the analytical procedure bring about the differential recovery, the impact on *SOC* stock prediction following Land Use, Land Use Change and Forestry (LULUCF) activities of the Kyoto Protocol becomes entirely unpredictable.

Quite a few regional, national or global *SOC* inventories use Walkley-Black measurements to determine *SOC* stocks per soil type (Batjes, 1996) or per soil type and land use/land cover type (Howard *et al.*, 1995; Arrouays *et al.*, 2001; Bernoux *et al.*, 2002). A pan-European protocol that describes how the Walkley-Black correction factors should be determined thus appears useful. The applied correction factors need to reflect the specific conditions of the soil sampling locations in order to interpret Walkley-Black measurements correctly. The formulation of a 'universal' correction factor is advised against. If the correction factor is, for example, derived for a specific soil type, it is valid for this soil type only and will lack accuracy for other soil types. If it is derived for a broad range of soil types, it will lack precision, since large variations occur between the different soil types.

Conclusion

This study assessed differential carbon recovery by Walkley-Black and analysed its impact on a national *SOC* inventory. It became clear that the results of a Walkley-Black analysis must be treated carefully. Soil sample characteristics such as land use, soil texture and sampling depth must be taken into account. In many countries Walkley-Black analysis is being replaced by more accurate measurement methods, but for studying the evolution of *SOC* stocks over time, where absolute *SOC* assessments are required, the correct interpretation of historic soil sampling results, most often obtained by methods based on Walkley-Black, is an important issue. In this study, we found an overall increase of 22% of soil carbon content when LSU and depth specific correction factors are applied to the Belgian *SOC* inventory of 2000. The recovery was least (59% compared to the standard recovery of 76%) for the group with the greatest OC content (mostly forested sites). An intermediate value (63%) was obtained for agricultural land on silt loam soil and the greatest recovery (67%) occurred generally under agricultural land on sandy soils. The three factors land use, texture and sampling depth all contributed significantly to the explanation of the recovery variability, but interaction existed, especially between soil depth and the two other factors. This complicates the explanation for the recoveries observed and further research is required in this field. It is recommended to use experimentally derived correction factors related to the characteristics of the samples when using Walkley-Black measurements for assessment of *SOC* stocks and stock changes.

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References

Allison, L.E. 1960. Wet-combustion apparatus and procedure for organic and inorganic carbon in soil. *Soil Science Society of America Proceedings*, 24, 36–40.

Arrouays, D., Deslais, W. & Badeau, V. 2001. The carbon content of topsoil and its geographical distribution in France. *Soil Use and Management*, 17, 7–11.

Baker, G.O. 1936. A study of the practicability of the Walkley-Black method for determining soil organic matter. *Soil Science*, 41, 47–51.

Batjes, N.H. 1996. Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science*, 47, 151–163.

Batjes, N.H. 2002. Carbon and nitrogen stocks in the soils of central and eastern Europe. *Soil Use and Management*, 18, 324–329.

Bellamy, P.H., Loveland, P.J., Bradley, R.I., Lark, R.M. & Kirk, G.J.D. 2005. Carbon losses from all soils across England and Wales 1978–2003. *Nature*, 437, 245–248.

Bernoux, M., Carvalho, M.D.S., Volkoff, B. & Cerri, C.C. 2002. Brazil's soil carbon stocks. *Soil Science Society of America Journal*, 66, 888–896.

Bornemisza, E., Constenla, M., Alvarado, A., Ortega, E.J. & Vasquez, A.J. 1979. Organic-carbon determination by the Walkley-Black and dry combustion methods in surface soils and Andept profiles from Costa-Rica. *Soil Science Society of America Journal*, 43, 78–83.

Bremner, J.M. & Jenkinson, D.S. 1960. Determination of organic carbon in soil. I. Oxidation by dichromate of organic matter in soil and plant materials. *Journal of Soil Science*, 11, 394–402.

Brye, K.R. & Slaton, N.A. 2003. Carbon and nitrogen storage in a Typic Albaqualf as affected by assessment method. *Communications in Soil Science and Plant Analysis*, 34, 1637–1655.

Chacon, N., Dezzeo, N., Folster, H. & Mogollon, P. 2002. Comparison between colorimetric and titration methods for organic carbon determination in acidic soils. *Communications in Soil Science and Plant Analysis*, 33, 203–211.

Degryze, S., Six, J., Paustian, K., Morris, S.J., Paul, E.A. & Merckx, R. 2004. Soil organic carbon pool changes following land-use conversions. *Global Change Biology*, 10, 1120–1132.

De Leenheer, L. & Van Hove, J. 1958. Détermination de la teneur en carbone organique des sols. *Pédologie*, 8, 39–77.

De Vos, B., Vandecasteele, B., Deckers, J. & Muys, B. 2005. Capability of loss on ignition as a predictor of total organic carbon in non-calcareous forest soils. *Communications in Soil Science and Plant Analysis*, 36, 2899–2921.

Diaz-Zorita, M. 1999. Soil organic carbon recovery by the Walkley-Black method in a Typic Hapludoll. *Communications in Soil Science and Plant Analysis*, 30, 739–745.

Drover, D.P. & Manner, H. 1975. Comparison between Walkley-Black and a dry combustion method for determining organic carbon in a humic brown soil, Papua-New-Guinea. *Communications in Soil Science and Plant Analysis*, 6, 495–500.

European Commission 1993. *Corine Land Cover, Technical Guide*. Directorate-General Environment, Nuclear Safety and Civil Protection EUR 12585, Luxembourg.

Falloon, P., Smith, P., Szabo, J. & Pasztor, L. 2002. Comparison of approaches for estimating carbon sequestration at the regional scale. *Soil Use and Management*, 18, 164–174.

FAO 1998. *World Reference Base for Soil Resources*. FAO, ISRIC and ISSS, Rome.

Gillman, G.P., Sinclair, D.F. & Beech, T.A. 1986. Recovery of organic-carbon by the Walkley and Black procedure in highly weathered soils. *Communications in Soil Science and Plant Analysis*, 17, 885–892.

Howard, P.J.A., Loveland, P.J., Bradley, R.I., Dry, F.T., Howard, D.M. & Howard, D.C. 1995. The carbon content of soil and its geographical distribution in Great-Britain. *Soil Use and Management*, 11, 9–15.

Hussain, I. & Olson, K.R. 2000. Recovery rate of organic C in organic matter fractions of Grantsburg soils. *Communications in Soil Science and Plant Analysis*, 31, 995–1001.

Kalembasa, S.J. & Jenkinson, D.S. 1973. Comparative study of titrimetric and gravimetric methods for determination of organic carbon in soil. *Journal of the Science of Food and Agriculture*, 24, 1085–1090.

Kerven, G.L., Menzies, N.W. & Geyer, M.D. 2000. Soil carbon determination by high temperature combustion a comparison with dichromate oxidation procedures and the influence of charcoal and carbonate carbon on the measured value. *Communications in Soil Science and Plant Analysis*, 31, 1935–1939.

Leifeld, J. & Kö gel-Knabner, I. 2005. Soil organic matter fractions as early indicators for carbon stock changes under different land-use. *Geoderma*, 124, 143–155.

Lettens, S., Van Orshoven, J., van Wesemael, B., De Vos, B. & Muys, B. 2005a. Stocks and fluxes of soil organic carbon for landscape units in Belgium derived from heterogeneous data sets for 1990 and 2000. *Geoderma*, 127, 11–23.

Lettens, S., Van Orshoven, J., van Wesemael, B. & Muys, B. 2004. Soil organic and inorganic carbon contents of landscape units in Belgium derived using data from 1950 to 1970. *Soil Use and Management*, 20, 40–47.

Lettens, S., Van Orshoven, J., van Wesemael, B., Muys, B. & Perrin, D. 2005b. Soil organic carbon changes in landscape units of Belgium between 1960 and 2000 with reference to 1990. *Global Change Biology*, 11, 2128–2140.

Martens, D.A., Reedy, T.E. & Lewis, D.T. 2003. Soil organic carbon content and composition of 130-years crop, pasture and forest land-use managements. *Global Change Biology*, 10, 65–78.

Mebius, L.J. 1960. A rapid method for the determination of organic carbon in soil. *Analytica Chimica Acta*, 22, 120–124.

Mikhailova, E.A., Noble, R.R.P. & Post, C.J. 2003. Comparison of soil organic carbon recovery by Walkley-Black and dry combustion methods in the Russian Chernozem. *Communications in Soil Science and Plant Analysis*, 34, 1853–1860.

Nelson, D.W. & Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, 2nd edn (eds A.L. Page *et al*.), pp. 539–579. ASA-SSSA, Madison, WI.

Olayinka, A., Adebayo, A. & Amusan, A. 1998. Evaluation of organic carbon oxidation efficiencies of a modified wet combustion and Walkley-Black procedures in Nigerian soils. *Communications in Soil Science and Plant Analysis*, 29, 2749–2756.

Rhodes, E.R., Kamara, P.Y. & Sutton, P.M. 1981. Walkley-Black digestion efficiency and relationship to loss on ignition for selected Sierra Leone soils. *Soil Science Society of America Journal*, 45, 1132–1135.

Richter, M., Massen, G. & Mizuno, I. 1973. Total organic carbon and oxidizable organic carbon by Walkley-Black procedure in some soils of Argentine pampa. *Agrochimica*, 17, 462–473.

Schollenberger, C.J. 1927. A rapid approximate method for determining soil organic matter. *Soil Science*, 24, 65–68.

Six, J., Elliott, E.T. & Paustian, K. 1999. Aggregate and soil organic matter dynamics under conventional and no-tillage systems. *Soil Science Society of America Journal*, 63, 1350–1358.

Skjemstad, J.O., Spouncer, L.R. & Beech, A. 2000. *Carbon Conversion Factors for Historical Soil Carbon Data*. CSIRO, Land and Water, Adelaide, Australia.

Skjemstad, J.O. & Taylor, J.A. 1999. Does the Walkley-Black method determine soil charcoal? *Communications in Soil Science and Plant Analysis*, 30, 2299–2310.

Tate, K.R., Scott, N.A., Saggar, S., Giltrap, D.J., Baisden, W.T., Newsome, P.F., Trotter, C.M. & Wilde, R.H. 2003. Land-use change alters New Zealand's terrestrial carbon budget: uncertainties associated with estimates of soil carbon change between 1990–2000. *Tellus Series B-Chemical and Physical Meteorology*, 55, 364–377.

Tavernier, R. & Maré chal, R. 1972. *Atlas Van België (Atlas of Belgium), Soil association map 1: 500,000, sheets 11A and 11B*. Nationaal Comité voor Geografie, Brussel, Belgium.

Tinsley, J. 1950. *Determination of organic carbon in soils by dichromate mixtures*. International Congress of Soil Science, Trans. 4, Amsterdam, 1, 161–164.

Ulmer, M.G., Swenson, L.J., Patterson, D.D. & Dahnke, W.C. 1992. Organic-carbon determination by the Walkley-Black, Udy Dye, and dry combustion methods for selected North-Dakota soils. *Communications in Soil Science and Plant Analysis*, 23, 417–429.

Walkley, A. 1947. A critical examination of a rapid method for determining organic carbon in soils – effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*, 63, 251–264.

Walkley, A. & Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science*, 37, 29–38.

Webster, R. 1997. Regression and functional relations. *European Journal of Soil Science*, 48, 557–566.

Wiseman, C.L.S. & Pü ttmann, W. 2005. Soil organic carbon and its sorptive preservation in central Germany. *European Journal of Soil Science*, 56, 65–76.