vast spreads of fresh and unrolled stone-artefacts, variously[10–12,16] encountered in the sub-Himalayas in open-air context, could be the handiwork of hominines during these last phases.

It may not be out of context to mention here that recently, several Palaeolithic type stone artefacts were found by the present authors, from around the already excavated archeological mound of Bara[17] (5 km south of Ropar in Punjab plains), which also appears to underlie a geological formation (these artefacts have been deposited with the Superintending Archaeologist, Simla Circle, Simla, Himachal Pradesh, India). If similar stone artefacts also emerge in the stratified context therefrom, the presently identified Holocene lithic industry might telescope into the early Harappan stage.

This is just a preliminary report about a recent excavation which deems to initiate a new perception about sub-Himalayan stone-age research; a detailed article on this will be communicated elsewhere.

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Quantifying the underestimation of soil organic carbon by the Walkley and Black technique – examples from Himalayan and Central Indian soils

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Soil organic carbon (SOC) is an important indicator of soil quality and productivity. The present study focuses on the comparative evaluation of the ‘wet digestion’ and ‘oxidative combustion–infrared analysis’ methods for determination of SOC with examples from parts of the Himalayan and Central Indian soils. It is found that the commonly used wet digestion (Walkley and Black) method underestimates the SOC significantly. The study estimates a correction factor quite different from the standard adopted in most of the investigations. Considering the importance of SOC stock and dynamics being used as inputs in models predicting global climate change and future global carbon cycle, it is emphasized that appropriate correction factors need to be developed for Indian soils, and applied to the SOC estimates obtained from the Walkley and Black method to improve the accuracy.

Keywords: Oxidative combustion–infrared analysis, soil organic carbon, TOC analyser, Walkley and Black method.

THE quantification of soil organic carbon (SOC) has recently attracted the attention of many researchers as it is the largest terrestrial carbon (C) pool in addition to be-

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*For correspondence. (e-mail: gopal@iirs.gov.in) ing an important indicator of soil quality and productivity. Its spatial variability, pool and dynamics are important inputs in the models being used to understand the present and future global C cycle and to predict the global climate change. A large source of uncertainty in the results of these models is due to the uncertainty in the distribution and dynamics of the SOC reservoir[1].

The most widely used techniques for determination of SOC fall in two categories[2,3]: (1) wet digestion method followed by titration or measurement of evolved CO_2, and (2) dry combustion at high temperatures followed by detection of evolved CO_2. In the wet digestion method, the Walkley and Black (WB)[4] technique is used in most of the soil-testing laboratories as a standard method because of its simplicity and minimal time and equipment requirement[5]. In this method, the C present in the soil organic matter is measured by the titrimetric method using a strong oxidizing agent ($K_2Cr_2O_7$) in the presence of H_2SO_4. In the dry combustion method, the sample is heated to elevated temperatures, and the evolved CO_2 is measured either by titrimetric, gravimetric, manometric, spectrophotometric or gas chromatographic techniques[3]. Nowadays, the automated dry combustion instruments, such as elemental carbon, hydrogen, nitrogen (CHN) analyser, total organic carbon (TOC) analyser and gas chromatograph are being increasingly used for better precision[3,6].

In the present study, a comparative evaluation has been made between the wet digestion method of WB and an oxidative combustion–infrared analysis method using TOC analyser for determination of SOC in the loamy soils of the Himalayan landscape and clayey soils of Central India. A total of 50 samples from the eastern part of Dehradun Valley (Himalayan landscape) and 44 samples from six districts (Dewas, Hoshangabad, Indore, Raisen, Sehore and Ujjain) of Madhya Pradesh (Central India) have been used in the analysis. These samples represent different horizons of 30 soil profiles (up to 1 m depth), 15 each for the Himalayan landscape and Central India.

Prior to analysis, the soil samples were air-dried, ground and sieved to < 0.2 mm diameter. For determining SOC using WB method, a known weight of soil sample was treated with standard $K_2Cr_2O_7$ in the presence of concentrated H_2SO_4. The sample was slowly digested at low temperature, and the excess of $K_2Cr_2O_7$ not reduced by the organic matter was titrated back against a standard solution of $Fe(NH_4)_2(SO_4)_2$ in the presence of NaF and H_3PO_4 as flocculating agents, and diphenylamine as an indicator. The end-point of the titration was recorded based on visual colour change from violet to light green. For determining SOC using dry oxidative combustion method, Shimadzu-make TOC analyser (model $V_{CPH/CPN}$) with a solid sample module (SSM-5000A) was used. SOC was determined by the difference method, where difference of total carbon (TC) and inorganic carbon (IC) was taken. For TC analysis, the sample was heated to 900°C in the presence of oxidation catalyst, and the evolved CO_2 was carried by synthetic air to the non-dispersive infrared (NDIR) gas analyser for detection. The NDIR outputs an analog detection signal that forms a peak, and the peak area was measured by the TOC–Control V software. For IC measurement, the sample was acidified with a small amount of orthophosphoric acid (85%) and heated to 200°C, and the evolved CO_2 was detected by NDIR. The calibration curves that mathematically express the relationship between peak area and TC/IC concentration were generated by analysing various concentrations of TC/IC standard solutions. Potassium hydrogen pthalate (KHP) and sodium carbonate (Na_2CO_3) were used as chemicals for making standard solutions for TC and IC respectively. The calibration curves for TC and IC are shown in Figure 1. These calibration curves would give a maximum error of 0.67% for TC and 1.51% for IC. The calibration curves and the performance of the instrument were also validated using chemicals of known concentrations.

A summary of SOC results obtained from the WB method (after applying standard correction factor of 1.32)[6] and TOC analyser for both the study areas is given in Table 1. SOC varied from 0.44 to 4.81% (average 1.15%) in Himalayan soils and from 0.22 to 2% (average 0.87%) in Central Indian soils, as estimated using the WB method; whereas the TOC analyser-based measurements indicated that SOC varied from 0.75 to 8.39% (average 2.1%) in case of Himalayan soils and from 0.46 to 2.71% (average 1.28%) in the case of the Central Indian soils. SOC estimates obtained from both the methods provided consistent results ($R^2 = 0.99$ for Himalayan soils and $R^2 = 0.78$ for Central Indian soils). The higher scatter found in the case of the Central Indian soils may be attributed to more stable organic carbon in the mineral fraction[7] and stabilization of soil organic matter by forming strong clay–humus complexes[8]. As shown in Figure 2, the WB method underestimates SOC significantly, despite applying standard correction factor. The underestimation varied between 33.5 and 49.5% with an average of about 45% for the Himalayan soils, and between 12.2 and 66.5% with an average of about 33% for the Central Indian soils. If the standard correction factor of 1.32 was not applied, then it varied between 49.6 and 61.7% (average 58%) for the Himalayan soils, and between 33.5 and 74.7% (average 49%) for the Central Indian soils.

It is well established that about 60–86% of SOC is only oxidized in the WB method[9], and therefore, a standard correction factor of 1.32 (considering recovery of 76% OC) is used to obtain the corrected SOC value. However, the actual recoveries vary depending upon the site and the method used. For example, Allison[10] reported recoveries ranging from 59 to 94%; De Vos *et al.*[6] reported actual recoveries for forest soils ranging from 27 to 105%. In order to find the appropriate correction factors for the soils of the two study areas, SOC estimates obtained using the TOC analyser and the WB method

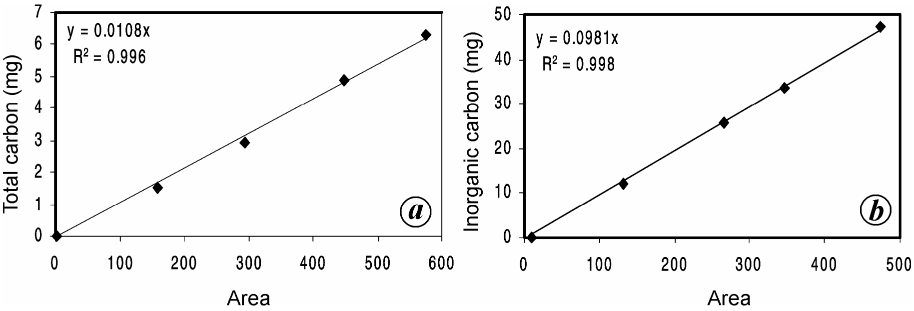

Figure 1. Calibration curves for (***a***) total carbon and (***b***) inorganic carbon.

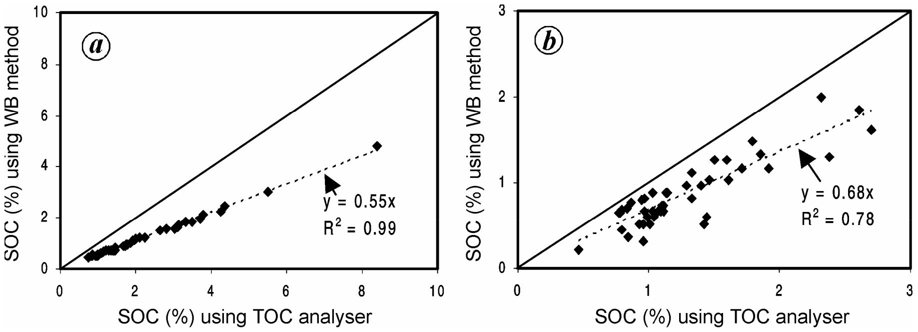

Figure 2. Comparison of soil organic carbon (SOC) estimates obtained using Walkley and Black (WB) method (after applying standard correction factor of 1.32) and TOC analyser for (***a***) Himalayan soils ($n = 50$), and (***b***) Central Indian soils ($n = 44$).

Table 1. Summary of soil organic carbon (SOC) results obtained from Walkley and Black method and TOC analyser for Himalayan soils ($n = 50$), and Central Indian soils ($n = 44$)

	SOC (%)	
	Walkley and Black method	TOC analyser
Himalayan soils		
Minimum	0.44	0.75
Maximum	4.81	8.39
Average	1.15	2.10
Standard deviation	0.80	1.41
Central Indian soils		
Minimum	0.22	0.46
Maximum	2.00	2.71
Average	0.87	1.28
Standard deviation	0.39	0.51

(without applying standard correction factor) are plotted in Figure 3. The correction factor, inverse of the slope of linear regression, for the Himalayan soils was found to be 2.4 (corresponding to average recovery of 41.6%) and that for the Central Indian soils was found to be 1.95 (corresponding to average recovery of 51.2%). Low recovery in the Himalayan soils may be attributed to incomplete oxidation of OC by the WB method in soils with high organic matter[6].

Like previous studies[6,10–13], the present study also observed the underestimation of SOC content in the WB method. However, for soils of the Dehradun Valley and Central India, the underestimation was found to be much higher than the standard assumption. The difference in correction factors obtained for the soils of the two study areas points out that in addition to the limitation of the WB method itself, the site characteristics, including physiography, parent material, soil and climatic conditions, and presence of stable organic carbon compounds in the mineral fraction[6,12] exercise an important role in causing the variability in the underestimation of SOC. The manual method adopted in the WB method would have also introduced some errors in SOC estimation. Thus, there is a strong need to develop appropriate correction factors for Indian soils to improve the SOC estimates obtained using the WB technique. Agro-climatic zones and variability in land use–land cover in addition to soil type could be considered as important factors for quantifying the underestimation of SOC by the WB method and for finding appropriate correction factors for Indian soils. The recently initiated study on ‘soil carbon pool assessment’ within the framework of the ‘National Carbon Project’ under the ISRO–Geosphere Biosphere Programme will address this issue. The present study is an effort in this direction.

The results of the present study have implications in SOC-related research, e.g. the estimated pool size and temporal change could be much higher. This is especially pertinent to SOC stocks estimated for Indian soils[14],

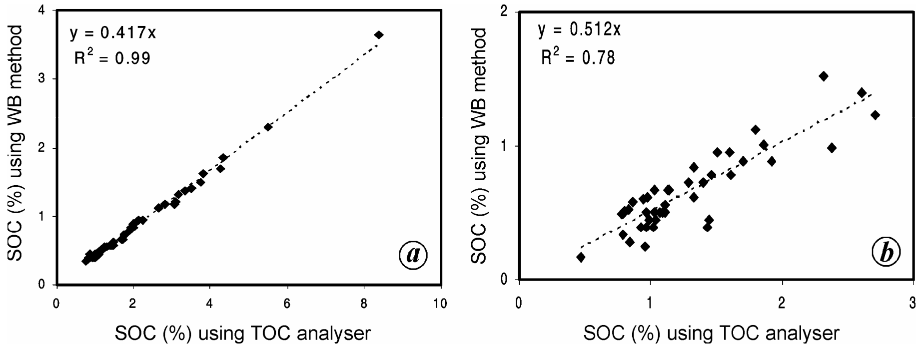

Figure 3. Comparison of SOC estimates obtained using WB method (without applying standard correction factor) and TOC analyser for estimating correction factor applicable for (***a***) Himalayan soils (*n* = 50), and (***b***) Central Indian soils (*n* = 44).

forest soils of India[15], and for parts of the Eastern and Western Ghats of southern India[16,17]. Recently, Bhattacharyya *et al.*[18] have quantified the change in SOC stock in the Indo-Gangetic plains and the black soil region in the semi-arid tropics of India for a period of 25 years (1980–2005). The overall increase in SOC stock (25–395%) indicated by them could be even higher in light of the present study. Further, estimation of uncertainty of SOC should consider the site characteristics as an additional factor if WB method is adopted.

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