

*Research Paper***Photochemical Oxidation of Soil Organic Matter by Sunlight**

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(Received on 12 June 2016; Revised on 08 August 2016; Accepted on 10 November 2016)

Although soils are considered as major carbon stores, rapid oxidation of soil organic carbon can contribute to CO₂ evolution and global warming on a large scale. Generally, microbial and climatic factors are thought to be mainly responsible for such oxidative losses. Another probable factor is photodegradation by sunlight. Cultivated soils of the tropics are left barren for a greater part of the year particularly during summer when sunlight is at its peak intensity. This could cause photodecomposition of soil organic constituents and account for rapid losses of soil organic carbon. Studies showed that 2-14% of organic carbon in soils could be oxidized within 3 years by sunlight. This amounts to 5000-47,000 kg of CO₂ for every hectare of soil. Oxidation is not only due to the effect of light itself but also due to the heating caused by sunlight. Oxidative losses are higher in soils with higher levels of organic carbon and in soils of higher pH. It is suggested that covering soils with mulches or green cover during the fallow period in summer may be adopted to reduce photodegradative CO₂ losses from soils.

Keywords: Sunlight; Photodecomposition; Soil Organic Matter; Carbon Dioxide; pH; Ultraviolet

Introduction

Soil Organic Carbon (SOC) is stored in soils mainly as humic substances and in undecomposed plant and animal residues. In this way, soils can sequester a huge amount of carbon which amounts to about twice that is present in vegetation or atmosphere (Bellamy *et al.*, 2005). However, extensive studies in recent years have indicated that SOC is reducing at an alarming rate from soils all over the world (Bond-Lamberty and Thomson, 2010). Bellamy *et al.* (2005) showed that carbon was lost from soils in England and Wales at a mean rate of 0.6% per year amounting to about 13 million tonnes of carbon annually. Such increased decomposition has been generally attributed to higher temperatures and other related factors such as water content, soil microorganisms (Bellamy *et al.*, 2005; Knorr *et al.*, 2005). However, there is no clear consensus on either temperature being a major driver of soil carbon losses or the extent to which labile and non-labile pools of SOC are temperature sensitive (Davidson and Janssens, 2006; Fang *et al.*, 2005).

Photochemical degradation has been proposed

as a plausible route for decomposition of dissolved organic carbon (DOC) in waters and in decomposition of litter. Moran and Zeep (2000) studied the long term photochemical degradation of estuarine dissolved organic matter and found that photodegradation closely followed 1st order kinetics. Photodegraded DOC could be further utilized by bacteria and partitioned between bacterial biomass and respired carbon (McCallister, 2002). A modeling study showed that ultraviolet B (uv-B) levels could affect short-term litter dynamics and yet have little effect on SOC due to alteration of microbial communities (Moorhead and Calloghan, 1994). Photodegradation of soil organic carbon (SOC) by solar radiation, was found to contribute substantially to the ecosystem scale CO₂ losses at both a bare peatland in New Zealand and a summer-dead grassland in California (Rutledge *et al.*, 2010).

Although, it appears that photochemical degradation of dissolved organic materials has been investigated extensively, photodecomposition of soil organic carbon has not been given adequate importance as a possible significant factor for carbon mineralization. In general perception, photodegradation losses of SOC is not expected to be

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substantial since UV-B radiation has very little penetrating power and soil minerals themselves can protect organic materials from the sunrays. However, the higher intensity and duration of sunlight in tropical regions and the fact that soils are often left barren for a greater part of the year, the susceptibility of soil organic components to decomposition by sunlight gets magnified. Forest soils in tropics are known to be rapidly depleted in organic carbon and reach low levels within a few years of clearing and cultivation (Saikh *et al.*, 1998a). This observation, together with the fact that cultivated soils of the tropical and equatorial regions have low organic carbon content, suggests that sunlight could be a causative agent for SOC mineralization.

This investigation was undertaken to comprehend the decomposition losses of soil organic matter by sunlight and the extent to which soil factors could influence such decomposition. We studied 42 different soils from different vegetative environments for up to three years under sunlight and in the laboratory under ultraviolet light. Here, we show that SOC in soils is significantly reduced when exposed to sunlight (2-14% reduction in 3 years). Losses of SOC are higher in soils with initially higher SOC content. Increase in pH of the soil also increases photodecomposition. Decomposition by sunlight is found to be a combined action of its heating effect as well as photolytic processes.

Materials and Methods

Surface soil samples (Ap; 0-15 cm) were collected from three types of agro-climatic regions in India, and also from within the Simlipal National Park, Mayurbhanj, Orissa, India (Table 1). Simlipal is a single compact block of forest (about 850 sq km) with least anthropogenic intervention, having a variety of vegetative zones including evergreen forests, deciduous forests, natural grasslands and cultivated lands adjoining these forest areas. Site details and soil details are available elsewhere (Saikh *et al.*, 1998a, b). Essentially three categories of samples were collected from cultivated lands and the corresponding adjoining forest lands from topographically similar locations. Soil samples were air dried and sieved through 2 mm. Mineralogy of the clay fraction of the Alfisol, Entisol and Mollisol samples were studied by XRD on a Philips PW 1140

instrument using Ni-filtered CuK_α radiation and at a scanning speed of $1^\circ 2\theta/\text{min}$.

For sunlight photodecomposition experiments, 1 g of each soil sample was placed in glass tubes with the open end covered with a film of permeable plastic for exchanges of gases and moisture. These samples were laid out horizontally in trays and placed in sunlight every day for up to three years (8 h/day x 6 days x 45 weeks x 3 years) (excludes 7 weeks of rainy season). Another set of samples was taken in glass tubes coated with black paint and similarly placed in sunlight. Therefore, samples in test tubes with black coating experienced only heating effect of sunlight whereas in test tubes without the coating, the samples were subjected to both effect of light rays (from sunlight) as well as heat. All experiments were conducted in triplicate. SOC content was determined at the beginning of the experiment, after two years and after three years. Organic carbon in soils was determined by dichromate oxidation using the modified Walkley-Black method (Nelson and Sommers, 1996). All analyses were repeated thrice and the average value was recorded.

For simulated experiments, 10 g of each soil sample was spread in a petridish and irradiated by UV-B source [Philips HPL-N, 125 W, high pressure mercury lamp of light intensity $4.75 \times 10^3 \text{ Lm.}$] up to a period of 250 h. For pH studies, soils were treated with dilute NaOH or HCl to adjust pH to desired levels, dried and sieved through 2 mm. SOC was determined as described above.

Results and Discussion

Photochemical losses of soil organic carbon

We studied SOC decomposition by sunlight and ultraviolet light in (i) three soil types collected from diverse agroclimatic regions and (ii) soils from a protected National Park under different vegetative cover and having wide variations in SOC. Our studies showed (Table 2, Fig. 1) that when exposed to sunlight for 2 years, SOC losses ranged from 0.5 to 5 g kg^{-1} (1% to 6%); after 3 years, losses ranged from 0.7 to 6.4 g kg^{-1} (2% to 14%). This amounts to an increase in atmospheric CO_2 in 3 years by around 5000-47,000 kg from 1 ha of soil. Percentage loss in SOC was highest for an Alfisol (ferruginous red soil) followed by an Entisol (recent alluvium) and least for a Mollisol

Table 1: Soils and their SOC contents

Location	Initial SOC (g kg ⁻¹)	Location	Initial SOC (g kg ⁻¹)
Baruipur West Bengal [Cultivated, Entisol]	16.8	Kukurbhuka, Simlupal [Decidious, 16D]	15.5
Vishnupur West Bengal [Cultivated, Alfisol]	9.2	Kukurbhuka, Simlupal [Cultivated, 16C]	7.8
Auli Uttaranchal [Cultivated, Mollisol]	87.7	Matughar, Simlupal [Evergreen, 12E]	58.3
Gitilpi, Simlupal [Decidious, 1D]	49.0	Matughar, Simlupal [Grassland, 12G]	34.1
Gitilpi, Simlupal [Cultivated, 1C]	8.7	Gurguria, Simlupal [Cultivated, 14C]	6.5
Astakumar, Simlupal [Decidious, 2D]	30.7	Simlupalgarh, Simlupal [Cultivated, 15C]	15.4
Astakumar, Simlupal [Cultivated, 2C]	10.3	Barmakabari, Simlupal [Decidious, 17D]	43.1
Burhabalang, Simlupal [Decidious, 3D]	33.9	Kapatgai, Simlupal [Cultivated, 18C]	9.5
Burhabalang, Simlupal [Cultivated, 3C]	17.4	Tindiha, Simlupal [Grassland, 20G]	19.2
Ligirda, Simlupal [Decidious, 4D]	21.0	Jenabil-Kapatgai, Simlupal [Decidious, 21D]	34.8
Ligirda, Simlupal [Cultivated, 4C]	15.4	Barheipani, Simlupal [Decidious, 24D]	29.8
Makabari, Simlupal [Decidious, 5D]	30.2	Nawana, Simlupal [Cultivated, 25C]	17.2
Makabari, Simlupal [Cultivated, 5C]	19.3	Balarampur, Simlupal [Cultivated, 26C]	12.1
Bakua, Simlupal [Evergreen, 6E]	62.4	Jenabil-Bakua, Simlupal [Evergreen, 28E]	71.3
Bakua, Simlupal [Cultivated, 6C]	13.5	Jenabil-Deothali1, Simlupal [Evergreen, 29E]	59.0
Nuagaon, Simlupal [Evergreen, 7E]	58.6	Jenabil-Deothali2, Simlupal [Evergreen, 30E]	53.5
Nuagaon, Simlupal [Cultivated, 7C]	26.2	Bhanjabasa-UBK, Simlupal [Evergreen, 35E]	62.4
Jamuna, Simlupal [Decidious, 8D]	33.8	Bhanjabasa-Meghasani1, Simlupal [Evergreen, 36E]	52.5
Jamuna, Simlupal [Cultivated, 8C]	21.0	Bhanjabasa-Meghasani2, Simlupal [Evergreen, 37E]	61.4
Tarinibila, Simlupal [Evergreen, 10E]	64.7	Bhanjabasa-Meghasani3, Simlupal [Evergreen, 38E]	42.3
Tarinibila, Simlupal [Grassland, 10G]	23.7		
UBK, Simlupal [Evergreen, 11E]	34.9		
UBK, Simlupal [Grassland, 11G]	26.2		

Table 2: Photodecomposition of soil organic matter

Soil type	Initial SOC(g kg ⁻¹)	SOC losses after 2 yrs exposure to sunlight in g kg ⁻¹ (% loss of SOC)*			SOC losses after 3 yrs exposure to sunlight in g kg ⁻¹ (% loss of SOC)*			SOC losses after exposure to UV light for 250 h in g kg ⁻¹ (% loss of SOC)*
		Total loss	Loss due to heat effect	Loss due to light effect	Loss due to heat effect	Loss due to heat effect	Loss due to light effect	
Entisol	16.80	0.35(2.1)	0.21(1.2)	0.14(0.8)	0.96(5.7)	0.48(2.8)	0.48(2.8)	3.10(18.4)
Alfisol	9.18	0.27(2.9)	1.50(1.6)	1.20(13.1)	0.60(6.5)	0.32(3.5)	0.28(3.0)	3.50(38.1)
Mollisol	87.72	0.90(1.0)	7.20(0.8)	1.80(0.2)	1.40(1.6)	1.16(1.3)	0.24(0.3)	8.20(9.3)

*Differences due to treatments significant at P = 1%

(organic rich mountain soil). However, decomposition of SOC in terms of amount lost, was highest in Mollisol; this was followed by Entisol and Alfisol. Thus in 3 years, 1.4 g kg⁻¹ SOC was photodecomposed from

Mollisol whereas 0.6 g kg⁻¹ SOC was photodecomposed from Alfisol (Table 2). Amount decomposed appears to be related to initial levels of SOC – Mollisol had the highest content of SOC,

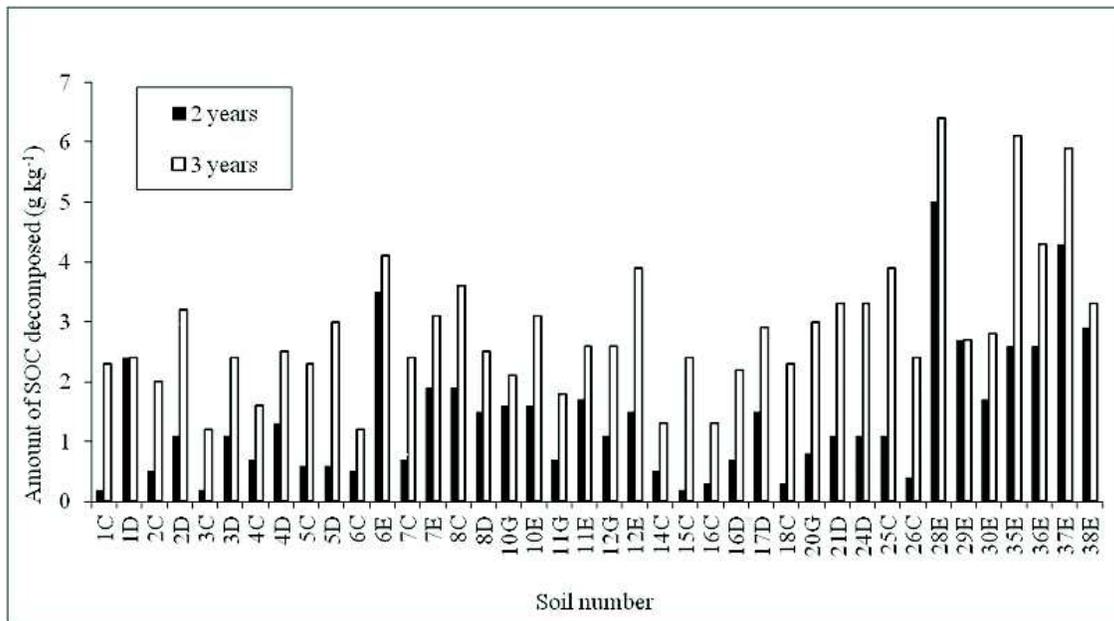


Fig. 1: SOC losses by photodecomposition after 2 and 3 years. Soil numbers with C, D, E and G refer to soils under cultivation, deciduous forest, evergreen forest and natural grassland, respectively. Soils with the same numeral are paired samples from adjoining area but under different vegetative covers

followed by Entisol and then Alfisol. Reduction in SOC levels was statistically significant at the 1% probability level.

In the 3rd year of exposure to sunlight, SOC losses nearly doubled over that during the first 2 years. Thus in Entisol, there was a 174% increase in oxidation of SOC in the 3rd year compared to the total of first 2 years. A probable explanation is that initial decomposition observed after 2 years would cause breakdown to smaller molecules, which might then be oxidized at faster rates during the 3rd year. Soils from cultivated lands showed, on an average, higher percent increases in SOC losses in the 3rd year over the first 2 years in comparison to soils from forested areas (Fig. 1). This was also true for paired samples such as 1C-2C, 1D-2D, etc. – the cultivated soil of the pair showed more rapid increase in SOC loss over time compared to its adjacent forest soil.

Simulated photodecomposition by UV light (Table 2) revealed similar patterns of SOC decomposition as with sunlight. Percentage losses were highest in Alfisol and least in Mollisol. However, Mollisol lost the highest amount of SOC. Rate of SOC decomposed by UV was also highest for Mollisol; it was marginally lower in Entisol than in Alfisol (Fig. 2). The differences between oxidation kinetics in

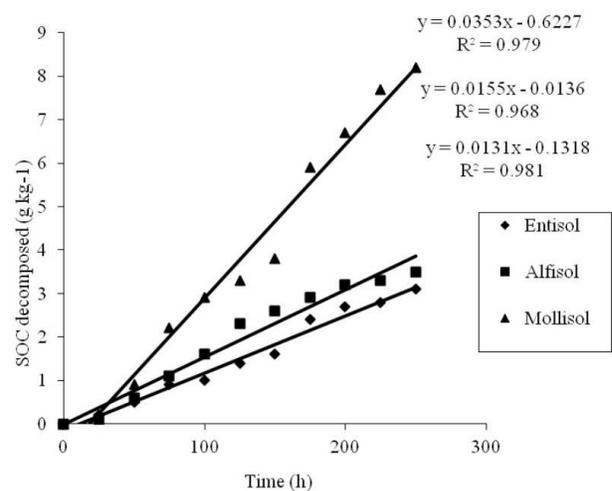


Fig. 2: Decomposition of SOC by UV radiation

Entisol and Alfisol suggests soil mineralogical influence on SOC complexation that could affect humus stability (Ahmed *et al.*, 2002a, 2002b). Mineralogical differences are evident in the three soils with the Entisol clay showing smectite and illite clays, the Alfisol showing kaolinite and the Mollisol showing kaolinite, illite and chlorite. Rates of decomposition were essentially linear. Data suggest that (a) amount of carbon oxidized is related to the initial organic carbon level in soil and (b) other soil parameters (like

mineralogy) probably also influence SOC decomposition.

Relationship to Initial Soil Organic Carbon Content and pH

To investigate relations between SOC content and amount photodecomposed, we studied soil samples collected from a National Park that has wide variations in SOC levels due to differences in vegetation. This includes evergreen and deciduous forests, natural grasslands and small patches of cultivations by indigenous tribes employing primitive methods. Trends indicate (Fig. 3) that SOC losses were higher in soils with initially higher levels of SOC (correlation coefficients, $R^2=0.52$). Amount of SOC lost followed the order, evergreen forest soils > deciduous forest soils > grassland soils > cultivated soils (Fig. 3); this is the same as the trend in the initial organic carbon content of the soil, with evergreen forest soils having highest SOC and cultivated soils the lowest. For every hectare of soil, the CO_2 evolved from evergreen forest soils when cleared and exposed to sunlight, is in the range of 19,000 to 47,000 kg whereas for cultivated soils (inherently poor in SOC), CO_2 evolution is about 9000 to 29,000 kg.

Soils adjusted to different pH and exposed to UV light showed an overall increase in decomposition with increase in pH. Although pH increase from 6 to 7.5 produced only marginal differences in decomposition rates, there was a steeper increase in decomposition on increasing the pH from 7.5 to 9. Alkaline pH appeared to make SOC particularly

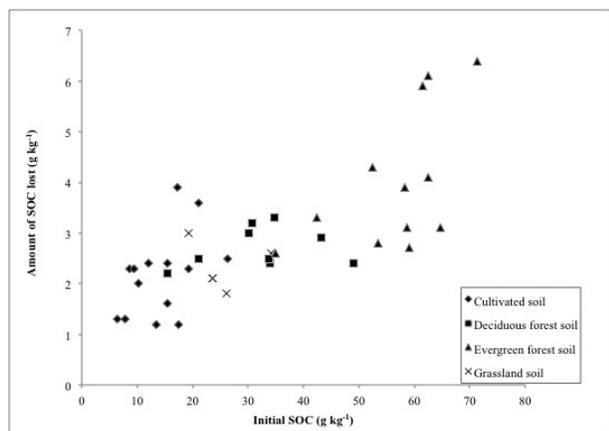


Fig. 3: SOC lost by photodecomposition after 3 years exposure to sunlight with soils from different vegetative zones

susceptible to photochemical decomposition (Fig. 4). Increase in soil pH might weaken the bonding with clay (Ahmed *et al.*, 2002a) and the SOC would be more easily oxidizable.

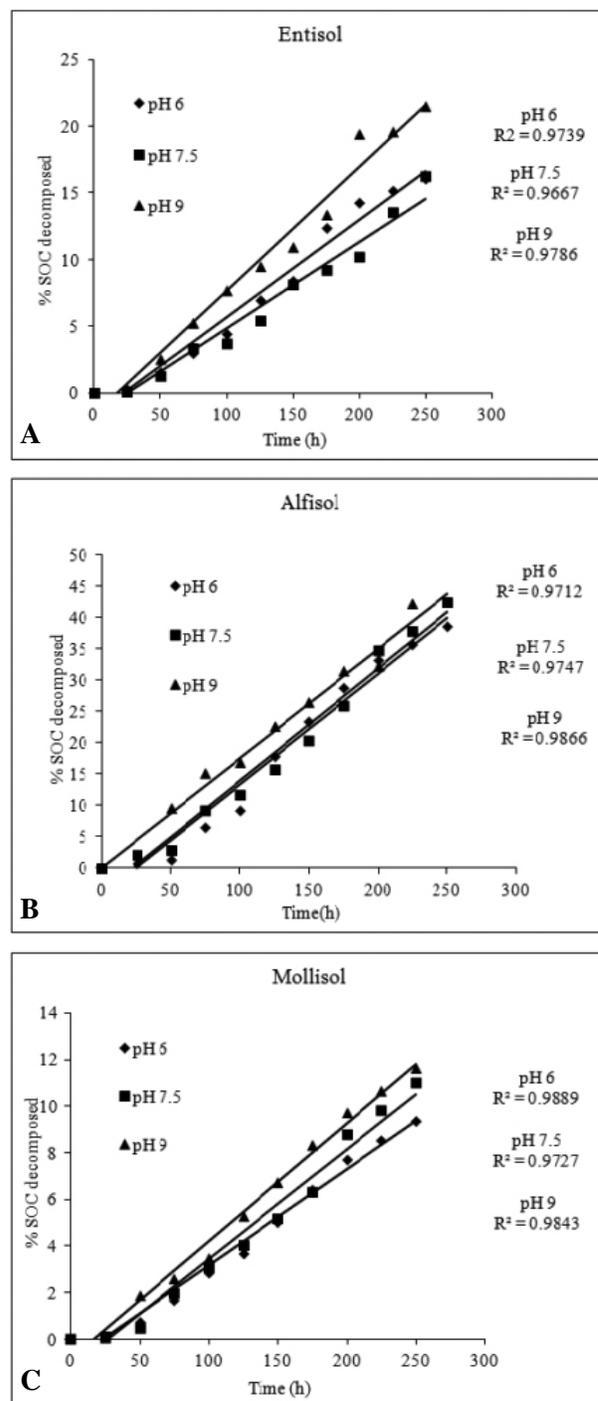


Fig. 4: Rates of photodecomposition of SOC by UV radiation with variation in soil pH in (A) Entisol, (B) Alfisol (C) Mollisol

Photooxidation losses from Alfisol were in the range of 40-45% after 250h of UV exposure. This was lower in Entisol (at about 15-20%) and least in Mollisol. As mentioned earlier, this suggests the influence of soil mineralogy and clay-humus bonding on SOC oxidation.

Effect of Heat Versus Light

To understand the relative influences of decomposition due to 'heat effect' of sunlight *versus* 'light effect', we compared losses in SOC kept in darkened tubes with SOC losses in samples kept in clear glass tubes (both exposed to sunlight for upto 3 years). Significant SOC losses also occurred in soil samples kept in darkened tubes ('heat effect' of sunlight, Fig. 5). The difference between SOC losses in samples kept in clear glass tubes and those kept in blackened tubes provides losses due to photochemical processes alone ('light effect' of sunlight, Fig. 5). Broadly, the effects of heat and light are comparable in most soils and it appears that both contribute to SOC oxidation. There was no observable difference in SOC losses from different vegetative zones in regard to the amount decomposed by heat *versus* light. Some soils from evergreen forests lost significantly more carbon due

to heating effect of sunlight whereas losses due to light effect were higher in some soils of natural grasslands and deciduous forests. The effect of light on photodegradation can be attributed to UV-B radiation (Rutledge *et al.*, 2010), with the consequent breakdown to smaller molecules like CO_2 , N_xO_y , etc. However, oxidation due to heating effect alone would occur in the absence of UV radiation and may be attributed to atmospheric oxidation with increasing rates at higher temperatures.

The results of this study suggest that soils exposed to sunlight lose a significant amount of SOC by photochemical and thermal decomposition. Therefore, fields left fallow and without a crop or mulch cover, would contribute significantly to atmospheric carbon dioxide due to the oxidative processes triggered by sunlight. Forests that have been cleared for cultivation would be huge sources of carbon dioxide with organic rich soils oxidizing more carbon. Sunlight appears to oxidize soil carbon by a direct photochemical effect as well as by the indirect effect of heating. It is recommended that when the soil is fallow, measures to reduce photochemical carbon dioxide production, by the use of mulches, be comprehensively implemented.

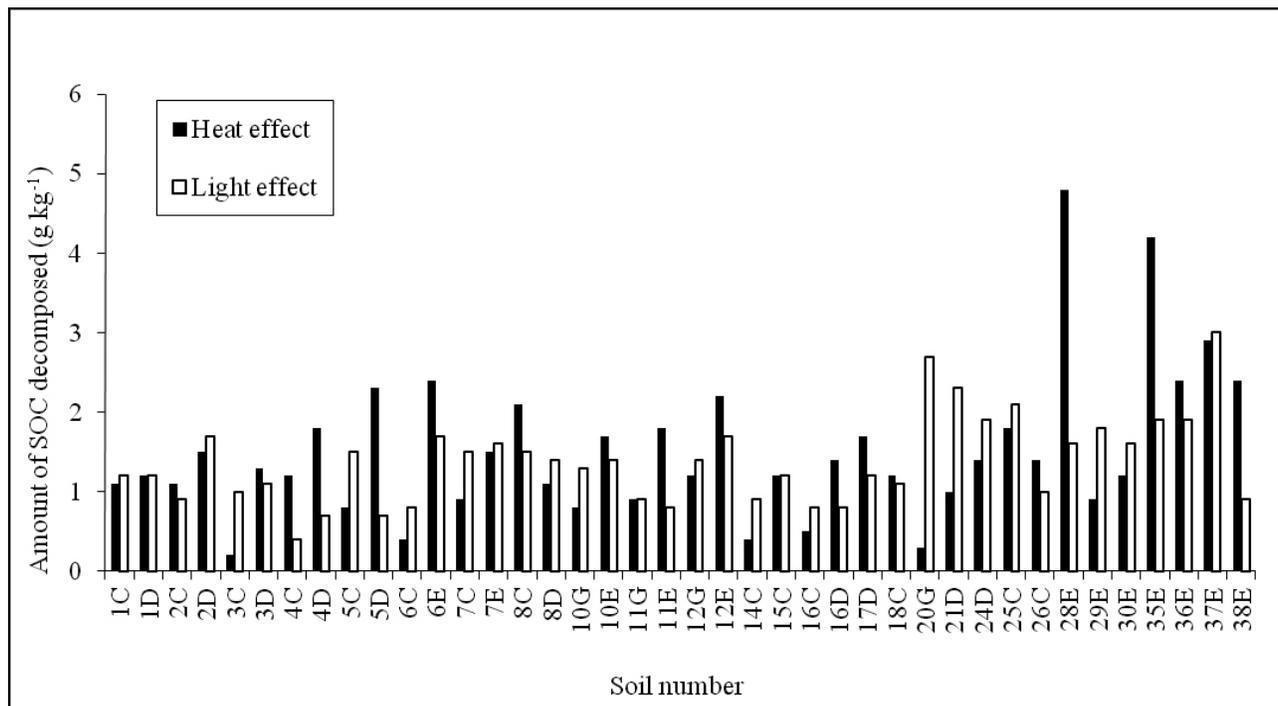


Fig. 5: SOC losses due to 'heat effect' of sunlight and 'light-effect' of sunlight after 3 years exposure to sunlight. Soil numbers with C, D, E and G refer to soils under cultivation, deciduous forest, evergreen forest and grassland, respectively. Soils with the same numeral are paired samples from adjoining areas but under different vegetative covers

Acknowledgement

The authors are grateful to the Indian National Science Academy, New Delhi for support.

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