CARBON DYNAMICS OF RECLAIMED COAL MINE SOIL: A CHRONOSEQUENCE STUDY IN THE GEVRA MINING AREA, KORBA, CHHATTISGARH, INDIA

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Abstract

Reclamation of mined soil improved soil quality and SOC sequestration. A chronosequence study consisting of 8 and 25years old reclaimed mine soils under Azadirachta indica, Gmelina arborea, Dalbergia sissoo and recently dumped soils in Gevra, Chhattisgarh, India was initiated to quantify the quality and quantity of carbon pools. MBC (microbial biomass carbon) showed highest value in case of Azadirachta indica (1468.45 ug C/g soil) followed by Dalbergia sissoo (1338.19 ug C/g soil) and Gmelina arborea (1160.61ug C/g soil) in surface soil after 25years of reclamation. Mean total soil C stock was estimated as 334.72,226.94 and 191.20 Mg C ha-1, under Azadirachta indicia, Dalbergia sissoo and Gmelina arborea plantation respectively. Carbon stock of the soil increased with an increase in year of reclamation. Among the four different pools of organic carbon, the carbon per cent was highest in the non-labile pool of carbon under Azadirachta indica (88.25%). Humic acid C content and C/N ratio had increased under Azadirachta indica, Dalbergia sissoo with an increase in the year of reclamation. FT-IR spectra in the case of Azadirachta indica, Dalbergia sissoo and Gmelina arborea indicated that relative proportions of aromatic groups along the chronosequence have increased. TOC (Total organic carbon) content was highest under Azardichta indica but aromaticity was highest under Gmelina arborea as obtained by E4/E6 and EET: EBZ ratio. These results indicated that different carbon pool and aromaticity of carbon improved with the increase in year of reclamation and significant relationships were present between spectroscopic indices and different soil carbon parameters.

INTRODUCTION

India produced 606.89 million tonnes of coal during 2017-18 (MOC, 2019), of which more than 92% was produced by open strip mining. During open strip mining process, entire vegetation cover is removed, and topsoil is scraped out to reach the coal seam. It results in extensive soil degradation, loss of microbial population, severe loss of soil organic carbon which leads to destruction of vast amounts of vegetative area. Indorante et al. observed that SOM (soil organic matter) content declined drastically in soils disturbed by mining (Indorante et al.,1981). With the adoption of appropriate reclamation strategies, post-reclamation land management practices, and increasing time since reclamation, reclaimed mine soils can sequester significant amounts of SOC (Jacinthe & Lal, 2007). Reclamation of mine soils could be done by physical and biological methods. Physical reclamation, which is costly, aims at creation of suitable landforms, compatible with the landscape. Biological reclamation is concerned with establishing and maintaining vegetation cover on the overburden dump, which is compatible with surrounding landscape, stable and self-sustainable. Revegetation is a useful way to reduce erosion and protect soils against deterioration and improving SOC stock during reclamation. Thus soil reclamation and re-establishment of vegetation cover on disturbed land could lead to C sequestration.

Trees, being efficient biomass generators, add more organic material (both above-and below-ground) to the soil. Their deep roots involve a greater depth of raw mine stones in the soil organic system (Singh et al., 2015). The restored site has a large potential to sequester atmospheric C that may vary with the climatic conditions and the plant species used for reclamation (Lal, 2005; Pietrzykowski & Daniels, 2014). Soil organic carbon is a useful indicator of soil quality and contributes largely to the global carbon pool. Recalcitrance indices can serve as an indicator of stable carbon in the soil (Datta et al., 2018). Soils hold one of the largest terrestrial reservoirs of organic carbon (OC), and while most of this pool cycles on very slow time scales (centuries to millennia), climate change and landscape disturbance can affect the proportion of soil organic carbon (SOC) with the atmosphere (Houghton et al., 2001). Since post-mining soils are depleted of carbon, chronosequence based approach to understand the effects of time since reclamation on development of different SOC pools can be easily studied under this condition.

SOC represents a complex assemblage of polyphenols, amino acids, ketones, esters, carbohydrates, and a wide variety of different moieties with highly variable and complex molecular properties (Chin et al., 1998). Spectroscopic techniques provide useful information about the structural and compositional characteristics of SOC molecules (Muñoz et al., 2009), based on the intensity and position of different absorption bands, diagnostic to the structure and composition of specific chromophores (functional groups) (Yu et al., 2010). A variety of ultraviolet-visible (UV- vis) (Jiang et al., 2011) and Fourier transform infrared (FT- IR) (Haberhauer et al., 2000) spectroscopic indices have been devised to relate molecular characteristics of SOC to its source, quality, and decomposition pathways. For spectroscopic techniques, sample requirement is less and sample preparation is easy.

Spectroscopic assessments of SOC in mine soils are relatively scarce as compared to those in undisturbed soils and also data on the quality and amount of carbon sequestration through reclamation of mine lands in Gevra coalfields and elsewhere in India were scanty. Therefore, the objectives of this study were to assess the different carbon pools in soil under three trees *Azadirachta indica, Dalbergia sisoo, Gmelina arborea* and quality of carbon sequestered in a chronosequence comprising two reclaimed mine soils having similar soil-forming conditions except for time (since reclamation) and compared with recently dump mine soil. Therefore, the objectives of the experiment were: (i) isolate different SOC pools in each year (8 and 25year) mine soil; (ii) characterize temporal changes in molecular properties of each SOC pools along the chronosequence; and (iii) identify interrelationships between SOC molecular properties and SOC sequestration. The governing idea was to gain insight into the different carbon pools present and broad classes of functional groups associated with the SOC molecules in these mine soils and present a qualitative assessment of the changes in molecular properties along the chronosequence. The indices were selected to obtain complementary information about the SOC molecular properties and thus to gain a holistic view of the overall structural and compositional details of the organic molecules. Outcomes of this study will provide clues to understanding the influences of time on the SOC molecular properties and on SOC pools to gain insight into SOC sequestration processes in reclaimed mine soils under three tree species.

Materials and Methods

Study Site

The study was conducted in the Gevra open cast coal mining project operated by South Eastern Coalfields Ltd., situated in Korba district of Chhattisgarh, India. The Gevra opencast project of South Eastern Coalfields Limited, Gevra, lies between Latitude 220 18'00" and 820 39'30". The elevation ranges from 288m to 328m above mean sea level. The climate of the area is dry to moist tropical. The temperature rises to 480C in May and drops to 70C in December. The average rainfall is 1265mm. Initial reclamation work at the Gevra Coalfields limited was performed in 1987. The mines were owned, mined, and reclaimed by the same company. The mines were all reclaimed to forest ecosystem following the guidelines of forest (Conservation) Act, 1980. During open-strip mining of coal, excavated subsoils were dumped in areas that have already been mined. These dumps are unstable due to the continuous dumping of excavated spoil material. The reclamation process involves plantation of tree saplings with fertilizer application to ensure high vegetative stand and quick ground cover. Predominant tree species used for reclamation include *Gravellia pteridifolia, Eucalyptus camaldulensis, Pongamia pinnata, Platanus occidentalis, Juniperus virginiana, Quercus macrocarpa, Azardicta indica, Acacia catechu, Delbergia sissoo, Emblica officinalis, Mangifera indica, Syzygium cumini, Ficus* religiosa, *Delonix regia, Gmelina arborea, etc.*Topsoil and other soil amendments have not been applied on the entire surface. Recently dumped soil consist of rock debris, soils and subsoil materials excavated from the different depths. These soils have not been revegetated. The reclamation work was initiated in 1987, and a chronological sequence of reclamation sites was selected i.e. 25 and 8years after reclamation under *Azadirachta indica, Dalbergia sisoo, Gmelina arborea* plantation and recently dumped soil without plantation. These tree species were selected because it was dominantly present in both the reclamation year i.e. 25 and 8 years and normally used for reclamation. Precautions were taken to select those sites with similar geology, landform, and management.

Soil Sampling and Processing

Soil samples were collected from different overburden dumping areas of the Gevra mining project that were under two stages of reclamation (8 and 25 years) under *Azadirachta indica, Dalbergia sisoo, Gmelina arborea* plantation and recently dumped spoil without plantation.

Bulk and core (7.5 cm diameter, 7.5 cm deep) soil samples were obtained using augers and backhoe for 0-15,15-30,30-45 and 45-60. Three representative replicates from each site were obtained by random sampling. The cores were used to measure soil bulk density (Blake and Hartge, 1986) and the whole soil samples were ground to pass through 0.5 mm sieve for determining TOC and carbon pools. Soil BD values were corrected for the gravel and roots present in the samples.

Soil TOC was obtained by treating 2ml of 4M HCl into 200 mg soil samples and then determined by Eltra CS80 carbon sulfur analyzer. Soil microbial biomass carbon was determined using the chloroform fumigation–extraction method for surface soil (Vance, 1987). Carbon stock of the study sites was calculated from their respective TOC (Total organic carbon) concentration, corrected bulk density, fine earth fraction and thickness of the soil layer as follows:

SOC stock (Mg ha^{-1}) = [C_{conc} (%) ×BD (Mg m^{-3}) x T(m) x 10^4($m^2 ha^{-1}$)] /100

where C_{conc} = Total organic carbon concentration; BD = corrected bulk density; T = thickness of the soil layer.

Different pool of carbon was determined by modified Walkley-Black method for 0-15 and 15-45cm depth (Chan et al., 2001). The determination of oxidizable carbon was done using 5 and 10 mL of concentrated sulphuric acid instead of the 20 mL specified by Walkley and Black (1934). The resulting three acid-aqueous solution ratios of 0.5:1, 1:1, and 2:1 (which corresponded respectively to 12 N, 18 N, and 24 N of H_2SO_4) allowed comparison of oxidizable organic carbon extracted under increasing oxidizing conditions (Walkley, 1947). The amount of oxidizable organic carbon determined using 5, 10, and 20 mL of concentrated sulphuric acid when compared with total carbon concentration allowed separation of total organic carbon into four fractions of decreasing oxidizability: Fraction 1 (12N H_2SO_4) – Very labile soil organic carbon; fraction 2 (18N – 12N H_2SO_4) – Labile soil organic carbon; fraction 3 (24N –18N H_2SO_4) – Less labile soil organic carbon., fraction 4(TOC-24N H_2SO_4)- Non-labile soil organic carbon. The recalcitrant index (RI) of SOC was derived in two ways for assessing different tree species effects on soil C stabilization (Datta et al., 2018).

$RI_{1=}$ C_{NL}

C_{TOC}

RI_2 =C_{LL}+ C_{NL}

C_{VL} +C_L

where RI: recalcitrant index; C_{VL}: very labile C; C_L: labile C; C_{LL}: less labile C; C_{NL}: non labile C.

Humic acid(HA) was extracted for 25 and 8years old restored mine soil by the method of IHSS (1981). The C, H(hydrogen), and N(nitrogen) contents of HA samples were determined using an elemental analyzer (Flash EA 1112 series). The C/N and C/H atomic ratios were calculated by determining the ratio of C to N and C to H contents, respectively. UV-VIS absorption spectra of HA sols (prepared in 0.05M $NaHCO_3$ solution to contain 0.1 g dm^{-3} C, pH 8.3-8.4), in the 200-700 nm range were recorded using a UV-visible spectrophotometer (Evolution 60s, Thermo Fisher Scientific, USA) with 1 nm resolution. Following ratio were calculated- A_{253nm}/ A_{220nm} and A_{465nm}/ A_{665nm} (Chaudhary et al., 2015).

ATR-FTIR spectra of HAs in the 4000-400 cm^{-1} range were recorded by a Thermo Scientific Nicolet iS5 FT-IR Spectrometer(Spectral resolution: better than 0.8 cm^{-1}; better than 0.5 cm^{-1} using aperture). Air spectrum was used as background. Peak intensities were determined relative to the baseline dependant on the spectral region.

Statistical Analysis

Factorial Randomized block design was used to analyze the experimental data as per the procedure illustrated by Gomez and Gomez (1984). The tree species and year after reclamation were kept as two factors with three and two levels (some cases three) respectively. Finally, for pairwise comparisons, the Duncan's Multiple Range Test (DMRT)was used. All of this analysis was conducted on R-software with help of r-package "Agricola" (Mendiburu, 2020).

RESULTS

Microbial Biomass Carbon

Soil MBC had significant difference for all species after 25year of restoration from recent dump. Microbial biomass C was found in the range 57– 1480.8 ug C/g soil. MBC showed an increase of 150.31%, 585.92% and 295.97% with increased age of reclamation under *Azadirachta indica, Dalbergia sissoo,* and *Gmelina arborea* respectively in surface soil (Table 1). MBC showed the highest value in case of*Azadirachta indica* (1468 ug C/g soil) followed by *Dalbergia sissoo* (1338 ug C/g soil) and *Gmelina arborea* (1161 ug C/g soil) in surface soil after 25year of reclamation. MBC was higher in the reclaimed than the recent dump (Figure 1). Soil MBC showed an obvious increase in all plantation during the 8th and 25th year of reclamation.

Carbon Content of Mine Soil

Distribution of organic carbon (%), very labile pool of carbon was highest in the case of 25years of reclamation except in the case of*Gmelina arborea* (Table-2). It had increased non-significantly from 3.57 to 4.59%, 5.32 to 6.24% in *Azadirachta indica* and*Dalbergia sissoo* respectively but it had decreased significantly in the case of *Gmelina arborea* with the increase in year of reclamation from 17.09 to 7.51%. In case of labile carbon pool, it had increased non significantly from 3.06 to 3.44% and significantly from 3.08 to 8.10% in *Azadirachta indica* and *Dalbergia sissoo*respectively but in case of *Gmelina arborea* it had decreased significantly from 12.39 to 5.34% with the increase in year of reclamation in surface soil. In the case of less labile pool of carbon, it had increased from 8.41 to 15.24% and 6.00 to 28.72% in*Azadirachta indica* and *Dalbergia sissoo* but in case of*Gmelina arborea* with increase in year of reclamation in surface layer, it had decreased from 17.18 to 11.10%. In case of non-labile carbon pool, there was an increase under *Azadirachta indica* and*Gmelina arborea* except for *Dalbergia sissoo,* it had decreased significantly with the increase in year of reclamation. Among four different pools of organic carbon, the carbon per cent was highest in the non-labile pool of carbon and it had increased with an increase in year of reclamation except in the case of *Dalbergia sissoo* .

The recalcitrance index serves as an indicator of stable carbon in the soil (Datta *et al.,* 2017,2018). The recalcitrance index 1 (RI1) was in the order of *Azadirachta indica* >*Gmelina arborea* > *Dalbergia sissoo* at 0–15cm soil depth (Table-3). The recalcitrance index 2 (RI2) was in the order of *Azadirachta indica* > *Dalbergia sissoo*> *Gmelina arborea* at 0–15cm soil depth. There was a significant difference in bulk density(BD) for all species. BD decreased with an increase in year of reclamation from 0-25years (Figure 2). BD increased with increase in depth. BD was improved from 1.64 % to 1.40%, 1.33% to 1.22% and 1.49% to 1.46% over the year of reclamation in 0-15 cm depth(Table-5).

An increase in organic carbon content of the soil was found along the re-vegetation age gradient. An increase in organic carbon content of soil by two times occurred along the re-vegetation age gradient of 0 to 25years (Figure 3). Significant difference in TOC was observed in surface soil between 25 and 8years of reclamation. With increasing depth from 0–15 to 30-45cm, there was a decline in soil organic carbon content of 76%, 79% and 59% in *Azadirachta indica* ,*Dalbergia sissoo,* and *Gmelina arborea* tree, respectively in 25yeras of reclamation (Figure 3). Soil total organic carbon (SOC) was 2.16,1.67 and 6.96 times higher in surface soil of the oldest reclaimed site than the young reclaimed mines under *Azadirachta indica, Dalbergia sissoo* and *Gmelina arborea* respectively (Table 5); maximum accumulation of SOC was observed under *Azadirachta indica* followed by *Dalbergia sissoo* and *Gmelina arborea* . TOC content was higher in surface than subsurface soil which was probably due to leaf litterfall and its conversion to humus in the surface soils.

Total soil C stock in restored mine soil under different tree plantation was given in Table-4 and 5. Mean total C stock was estimated as 334.72,226.94 and 191.20 Mg C ha^{-1}, in*Azadirachta indica* , *Dalbergia sissoo,* and *Gmelina arborea* plantation respectively. Carbon stock of the soil increased with increase in year of reclamation.

Humic Acid Elemental Composition and Ratios

Carbon content of humic acid was highest in the case of*Azadirachta indica* followed by *Dalbergia sissoo* and*Gmelina arborea* . It had increased from 34.95% to 41.96%, 16.31% to 28.65% and 18.50% to 21.16% under *Azadirachta indica, Dalbergia sissoo* and *Gmelina arborea* with increase in year of reclamation for surface soil(Table-6). Humic acid nitrogen content was highest in the case of *Azadirachta indica* followed by*Dalbergia sissoo* and *Gmelina arborea* . C/N ratio had increased with increase in year of reclamation except in case of*Gmelina arborea* . Highest C/N ratio was observed in case of*Gmelina arborea* . C/H ratio was highest in case of

Azadirachta indica.

Quality of Soil Carbon Sequestered

The average E_{ET}: E_{Bz} ratios increased significantly ($p< 0.05$) along the chronosequence following the order *Gmelina arborea* > *Azadirachta indica* > *Dalbergia sissoo* (Table-7) . The average E_{ET}: E_{Bz} ratios were higher at*Gmelina arborea* in both reclamation years. Average E_4: E_6 ratios of HAs decreased along the chronosequence for all three tree species.

The FT-IR spectra are capable of identifying the major functional groups and broad classes of biomolecules present in the SOM, such as carbohydrates, lignins, cellulose, and amino acids, through the vibrational characteristics of their structural bonds. In the present study, the FT-IR spectral methods were mainly intended to improve the overall understanding of the SOC molecular characteristics in the mine soils. Also, the FT-IR method was used to estimate the "relative abundances" of broad classes of functional groups in the mine soils rather than to quantify the absolute of their amounts. The FT-IR spectral patterns identified following absorption bands in the mine soils (Figure 4), namely broadband between 2983 and 3000 cm^{-1}, corresponding to CH_3, CH_2, and NH_3 stretch; a peak at 1862–1820 cm^{-1} arising from C=O stretching of cyclic anhydrides and mixed anhydrides; peaks at > 3400 cm^{-1} corresponding to O-H and N-H stretch; and a peak at 1695 cm^{-1} for COOH vibrations; a peak at 1500-1490 cm^{-1}representing aromatic carbonyl group;873-728 cm^{-1} corresponds to aromatic C-H group and peak around 1500 cm^{-1} represents N-H, C=N(amide II band), and C=C.

The FT-IR spectral patterns appeared similar for the mine soils (Figure 5). Relative absorbance intensities of certain bands differed between the mine soils (Figure 5). For example, in the case of *Azadirachta indica, Dalbergia sissoo* and *Gmelina arborea* relative proportions of aromatic groups along the chronosequence increased(Figure 5(a, b, c)). In case of *Dalbergia sissoo* and *Gmelina arborea* COO^{-}, -C-NO_2, C=C, and aromatic C-H group were highest in 25years old reclaimed soil than in 8 years old reclaimed soil.

DISCUSSION

Chronosequence-based approaches are useful ways of addressing rates and direction of changes in various pedologic characteristics including SOC dynamics (Brentley, 2008). Mine soils included in the present study were characterized by similar mining and post-reclamation land management history, climatic conditions, bedrock geology, and topographic characteristics and differed only by their respective times since reclamation. Temporal changes in carbon pools along the chronosequence under *Azadirachta indica, Dalbergia sissoo,* and *Gmelina arborea* were studied under this experiment.

Microbial Biomass Carbon

The microbial biomass could provide a satisfactory estimate of the soil microbial population reclamation (Ross et al., 1990). MBC increased with increase in year of reclamation, similar results were reported by others (Singh et al., 2015b). Accumulation of labile carbon during reclamation promotes a rapid increase in MBC and associated soil biological activity (Mukhopadhyay et al., 2014). In this study, climate, relief and parent material were the same for all species, therefore, difference of soil properties (including soil organic carbon) found can ascribe to the increase in MBC with increase in year of reclamation.

Plant-microbe interaction and C, N cycles also play a major role in soil carbon sequestration (Macdonald et al., 2011). Microbial biomass, while a small portion of SOC, mediates the transfer of SOC among inputs, low fraction organic carbon and organo-mineral high fraction organic carbon. MBC increased in all plantations during 8 and 25 years of reclamation indicates soil redevelopment and improvement in restored coal mine soil after plantation establishment in our study. The MBC and Cstock were significantly positively correlated with the TOC ($p < 0.01$). This suggests with an increase in organic carbon content microbial activity also improved as organic carbon provides food and energy to microbes.

Carbon Content of Mine Soil

Among four different pools of organic carbon, the carbon per cent was highest in the non-labile pool of carbon and it had increased with increase in year of reclamation except in the case of *Dalbergia sissoo* . Chaudhary et al. study, the average per cent resistant SOC pool increased significantly ($p < 0.05$) along the chronosequence (Chaudhary et al., 2015). This gave an early indication of the presence of a higher proportion of humic-like substances in the older mine soils. From the result of different pool of carbon, we can conclude that mean non-labile carbon pool was highest under *Azadirachta indicia* and mean very labile, labile carbon pool was highest under *Gmelina arborea.*

The recalcitrance index 1 showed variations among the three tree species. RI 1 decreased with increase in year of reclamation suggesting decline in quantity of less labile carbon under *Azadirachta indicia* and *Dalbergia sissoo* but increase of less labile carbon pool in case of *Gmelina arborea.* The recalcitrance index 2 decreased with increase in year of reclamation except in the case of*Gmelina arborea* . Recalcitrance index 2 was highest in the case of*Azadirachta indica* followed by *Dalbergia sissoo* and*Gmelina arborea* which suggested more stability of SOC in case of*Azadirachta indica* .

The decrease in bulk density with increase in year of reclamation was mainly due to root system development, addition of biomass, and improvement in soil structure (Mukhopadhyay et al., 2014., Singh et al., 2015). In all three tree species bulk density was higher in lower layer as compared to surface soil and also the bulk density decreased with increase in age of reclamation. These results indicated that if there is no post reclamation management to restore the loose topsoil, this layer is vulnerable to heavy erosion and exposed the compact subsurface soil layer over time. Bi & Zhang (2014) reported that soil bulk density of surface soil decreased. The bulk density of soil can be used to calculate the total quantities of carbon sequestered at a particular time and soil depth. Correlation analysis (Table-6) showed that the MBC of the reclaimed soils was negatively correlated with the BD(Mg/m^3). This indicates high BD decreases microbial activity. The TOC of reclaimed soil was significantly negatively correlated with BD ($p < 0.05$). Among three tree species decrease in BD was highest under *Gmelina arborea* .

Tripathi et al. reported that mine soil can act as a significant sink for atmospheric CO_2 through revegetation

(Tripathi et al.,2013). In the present study, the TOC content was found to gradually increase with the reclamation age. This indicates that in similar pedogenetic conditions, time has a positive effect on the evolution of the TOC in reclaimed soils. Several chronosequence studies have shown that SOC constantly accumulates in reclaimed soils over time, which shows great potential for carbon sequestration (Singh et al., 2015b). The low TOC content of recently reclaimed mine land was mainly due to increase in SOC mineralization, soil erosion due to low soil aggregation and high soil compaction, and leaching of SOC (Shrestha & lal,2006). Maximum accumulation of SOC was observed under *Azadirachta indica*followed by *Dalbergia sissoo* and *Gmelina arborea*indicating high carbon accumulation potential of *Azadirachta indica.* It also suggests significant accumulation of organic residues has occurred in restored mine soils and presence of a higher proportion of humic-like substances in older mine soils.

According to Shukla & Lal, 2005, reclamation increased soil organic C stock. The lower soil organic C stock for newer reclaimed soils as compared with older sites showed the unfilled C-sink capacity of newer sites. An increase in organic matter usually is accompanied by a reduction of a soils bulk density (Tunstall, 2010; www.eric.com.au). In present study also we found as the age of reclamation increased the BD decreased. Soil organic matter plays a major role in soil development process as it influences other soil properties, such as nutrient accumulation, water-holding capacity, cation exchange capacity (CEC), and microbial activity (Vinduskova & Frouz,2013). Among three tree species, carbon stock was highest under *Azadirachta indicia.*

Humic Acid Elemental Composition and Ratios

Carbon content of humic acid was significantly higher under*Azadirachta indica* plantation. Increase in TOC leads to increase in humic acid and hence carbon content. Carbon content increased with increase in year of reclamation. Abakumov et al. also reported increase in carbon content of humic acid with increase in year of reclamation (Abakumov et al.,2012). This increase probably due to increasing in TOC content with an increase in year of reclamation. Moreover, the humic acid C was positively correlated with less labile carbon(Table-8). We can conclude, the less labile pool of carbon had a significant contribution to humic acid formation. Humic acid nitrogen content was highest in the case of *Azadirachta indica* followed by*Dalbergia sissoo* and *Gmelina arborea* . This may be due to presence of nitrogen-containing functional group in humic acid. C/N ratio had increased with increase in year of reclamation. This increase was attributed due to increase in carbon content with increase in year of reclamation. Highest C/N ratio was observed in case of *Gmelina arborea* indicating a high proportion of carbon than nitrogen under

Gmelina arborea.

Quality of Soil Carbon Sequestered

Higher E_{ET}: E_{Bz} ratios observed in the HAs fractions in older mine sites indicated that SOM molecules became more enriched in polar functional groups as mine soils aged along the chronosequence and probably became more reactive over time. A vast majority of the chromophores that absorb light in the ultraviolet region (l < 400 nm) are aromatic groups comprising phenols and various aromatic acids with varying degrees of substitution (Chin et al., 1994). According to Weishaar et al. absorption features between the 200 and 380 nm are indicative of conjugated systems, commonly associated with aromatic moieties (Weishaar et al., 2003)). The magnitude of the E_{ET}: E_{Bz} ratio also offers an insight into the type of substitution occurring in the aromatic C species. The E_{ET}: E_{Bz} represents the ratio of absorption intensities of the electron in the transfer band (around 250 nm) and the benzenoid band (around 220 nm). The intensity of the former band is primarily affected by the presence of hydroxyl, carbonyl, carboxyl, and ester moieties and therefore indicates the extent of substitution in the benzene nucleus by these polar functional groups (Fuentes et al., 2006). For unsubstituted benzene, E_{ET}: E_{Bz} is low and increases with increasing substitution by polar functional groups (Kim & Yu, 2005).

The absorbance intensities at 465 nm correspond to organic carbon molecules of intermediate structural complexity including carbohydrate and proteins, whereas the band at 665 nm arises from more structurally complex and humified biomolecules (D'Orazio & Modelli, 2010). The magnitude of E_4: E_6 is inversely related to the extent of aromatic C=C absorption, with a low ratio corresponding to a higher degree of aromaticity, molecular condensation, and high molecular weight (Chen et al., 2002). In present study, we found higher E_4/E_6 ratio in 8years restored soil than in 25years of reclamation. It represents high aromaticity and molecular weight in 25 years old restored soil. The result obtained indicated that TOC content was highest under *Azardichta indica* but aromaticity was highest under *Gmelina arborea* .

FT-IR spectra of restored mine soil in the case of *Azadirachta indica, Dalbergia sissoo* and *Gmelina arborea* indicated that relative proportions of aromatic groups along the chronosequence increased indicating higher proportion of resistant SOC components in the older mine soils. This probably was due to fresh litter input in the younger mine soils that comprised of more labile organic matter. In case of *Dalbergia sissoo* and *Gmelina arborea* $COO^{-,}$ -C-NO_2, C=C and aromatic C-H group were highest in 25years old reclaimed soil than in 8 years old reclaimed soil which was in agreement with the results obtained from the UV- vis spectroscopic methods. SOC molecules became increasingly enriched in aromatic C species with higher degree of substitution by quinones and ketonic moieties in older mine soils.

The spectroscopic indices used in this study used to obtain complementary information about the structure and composition of the broad classes of functional groups associated with the organic molecules in the mine soils and gain a holistic view of the overall SOC molecular characteristics in the chronosequence. Results indicated that the SOC molecules in the older mine soils were comprised of highly humified polyaromatic and polycondensed species with higher proportions of O-containing and N-containing functional groups. Significant ($p<0.05$) positive relationships were found between the spectroscopic index E_{ET}: E_{Bz} and carbon stock indicating that humification of SOC molecules probably has progressed with increase aromatization of the SOC molecules(Table-8).

Conclusion

Soil MBC increased in all plantations during the $8^{th}$and 25^{th} year of reclamation and was much higher under*Azadirachta indica* plantation than recently dumped soil. Among four different pools of organic carbon, the carbon per cent was highest in the non-labile pool of carbon and it had increased with increase in year of reclamation except in the case of *Dalbergia sissoo* . Non-labile carbon pool was highest under *Azadirachta indicia* and very labile, labile pool of carbon was highest under *Gmelina arborea* . Reclamation increased soil organic C stock of soil under all tree species, highest in case of *Azadirachta indica* . Recalcitrance index 2 was highest in case of *Azadirachta indica*and recalcitrance index 1 was lowest under *Azadirachta iindica*which suggested more stability of SOC in case of *Azadirachta indica* . Carbon content and C/N ratio of humic acid were significantly highest under *Azadirachta indica* plantation. TOC content was highest under *Azardichta indica* but aromaticity was highest under*Gmelina arborea* as obtained by E_4/E_6 and E_{ET}: E_{BZ} ratio. FT-IR spectra of restored mine soil indicated that in the case of *Azadirachta indica, Dalbergia sissoo* and*Gmelina arborea* relative proportions of aromatic groups along the chronosequence increased indicating higher proportions of resistant SOC components in the older mine soils. Overall, the results indicated that with the increase in year of reclamation accumulation of SOC and improvement of SOC pools took place and its highest under*Azadirachta indica* . Spectroscopic methods results were also clearly able to distinguish improvement in reclamation process with increase in year of reclamation.

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Conflicts of interest statement

The authors declare no conflict of interest.

Authors' contribution

Preeti Singh; Designed and performed experiments, analysed data and co-wrote the paper

A.K. Ghosh; Supervised the research, designed experiments and co-wrote the paper

Santosh Kumar; Performed statistical analysis

S.L. Jat; Seema; S.N Pradhan and Manoj Kumar- Helped in humic acid extraction, FT-IR analysis and interpretation.

REFERENCES

Abakumov, E.V., Cajthal, T., Brus, J., & Frouz, J. (2012). Humus accumulation, humification, and humic acid composition in soils of two post-mining chronosequences after coal mining. *Journal of soils sediments* .DOI 10.1007/s11368-012-0579-9

Bi, Y., & Zhang, Y. (2014). Role of the different planting age of seabuckthorn forests to soil amelioration in coal mining subsidence land. *International Journal of Coal Science Technology* , 1(2),192–197. DOI 10.1007/s40789-014-0029-y

Blake, G.R., & Hartge, K.H. (1986). Bulk density. In Methods of Soil Analysis Part 1-Physical and Mineralogical Methods, Klute A (ed.). Soil Science Society of America, Inc, Madison, WI; 364–367.

Brentley, S.L. (2008). Understanding soil time. *Science,* 321, 1454–1455. DOI: 10.1126/science.1161132

Chan, K.Y., Booowman, A., & Oates, A. (2001). Oxidizible organic carbon fractions and soil quality changes in an oxic paleustalf under different pasture leys. *Soil Science* , 166,61- 67. DOI: 10.1097/00010694-200101000-00009

Chaudhuri, S., Pena-Yewtukhiw, E.M., McDonald, L.M., & Skousen, J. (2015). Soil organic carbon molecular properties: effects of time since reclamation in a minesoil chronosequence. *Land degradation and Development,* 26, 237–248. DOI 10.1002/ldr.2202

Chen, J., Gu, B., Leboeuf, E.J., Pan, H., & Dai, S. (2002). Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere,* 48, 59–68. DOI:10.1016/s0045-6535(02)00041-3

Chin, Y.P., Alken, G., & O'Loughlln, E. (1994). Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environmental Science and Technology*,28,1853–1858.DOI: 10.1021/es00060a015

Chin, Y.P., Traina, S.J., Swank, C.R., & Backhus, D. (1998). Abundance and proper- ties of dissolved organic-matter in pore waters of a fresh-water wetland. *Limnology and Oceanography* , 43, 1287. DOI:10.4319/lo.1998.43.6.128

D'Orazio, V., & Modelli, D. (2010). Dissolved organic matter (DOM) evolution during the composting process of coffee by-products. In*15th International Humic Substances Society Meeting Proceedings* , Canary Islands.

Datta, A., Mandal, B., Basak, N., Badole, S., Krishna Chattanya, A., Majumder, S.P., Thakur, N.P., Kumar, P., & Kachroo, D. (2018). Soil carbon pools under long-term rice-wheat cropping system in Inceptiols of Indian Himalayas. *Archives of Agronomy and Soil Sciences* , 64(9),1315-1320. DOI:10.1080/03650340.2017.1419196

Felipe de Mendiburu. (2020). Agricolae: Statistical Procedures for Agricultural Research. R package version 1.3-2.

Fuentes, M., Gonzales-Gaitano, G., & Garcia-Mina, J.M. (2006). The usefulness of UV-visible and fluorescence spectroscopies to study the chemical nature of humic substances from soils and composts.*Organic Geochemistry,* 37,1949–1959.

Gomez, K.A., &Gomez, A.A. (1984). Statistical procedures for agricultural research. Wiley Interscience, New York.

Haberhauer, G., Feigl, B., Gerzabeck, M.H., & Cerri, C. (2000). FT-IR spectroscopy of organic matter in tropical soils: changes induced through deforestation. *Applied spectroscopy,* 54,221-224. DOI: 10.1366/0003702001949131

Houghton, J. T. et al. Climate change 2001: The Scientific Basis. Contributions of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (Cambridge Univ. Press, 2001).

Indorante, S. J., Jansen, I. J., & Boast, C. W. (1981). Surface mining and reclamation: Initial changes in soil character. *Journal of Soil and Water Conservation* , 36, 347-350.

IHSS.(1981).Retrieved from http://humic-substances.org/isolation-of-ihss-soil-fulvic-and-humic-acids/.

Jacinthe, P.A., & Lal, R. (2007). Carbon storage and minesoils properties in relation to topsoil application techniques. *Soil Science Society of America Journal* , 71,1788-1791. DOI: 10.2136/sssaj2006.0335

Jiang, J., Yu, H., Xi, B., Meng, F., Zhou, Y., Liu, H. (2011). UV-visible spectroscopic properties of dissolved fulvic acids extracted from salined fulvo-aquic soils in the Hetao irrigation district, China.*Soil Research,* 49, 670–679.

Kim, H.C., & Yu, M.J. (2005). Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. *Water Research* , 39, 4779–4789. DOI: 10.1016/j.watres.2005.09.021

Lal, R. (2005). Forest soils and carbon sequestration. *Forest Ecology Management* , 220,242–258.DOI: 10.1016/j.foreco.2005.08.015

Macdonald, C.A., Anderson, I.C., Bardgett, R.D., & Singh, B.K., (2011). Role of nitrogen in carbon mitigation in forest ecosystems.*Current Opinion in Environmental Sustainability* , 3 (5), 303–310.

Ministry of Coal, India. (2019). Retrieved from https://www.coalindia.in/DesktopModules/DocumentList/documents/Annua
19.pdf

Mukhopadhyay, S., & Maiti, S.K. (2014). Soil CO_2 flux in grassland, afforested land and reclaimed coalmine overburden dumps: a case study. *Land Degradation Development* , 25,216–227.DOI: 10.1002/ldr.1161

Munoz, C., Monreal, C., Schnitzer, M., & Zagal, Z. (2009). Analysis of soil humic acid in particle size fractions of an alfisol from a Mediterranean-type climate. *Geoderma ,* 151, 199–203. DOI: 10.1016/j.geoderma.2009.04.006

Pietrzykowski, M., & Daniels, W.L. (2014). Estimation of carbon sequestration by pine (Pinus sylvestris L.) ecosystems developed on reforested post-mining sites in Poland on differing mine soil substrates. *Ecological Engineering* , 73, 209-218. DOI: 10.1016/j.ecoleng.2014.09.058

Ross, D.J., Hart, P. B. S., Sparling, G. P., & August, A. (1990). Soil restoration under pasture after topsoil removal: some factors influencing C and N mineralization and measurements of microbial biomass. *Plant and Soil* ,127, 49-59. DOI: https://doi.org/10.1007/BF00010836

Shresthra, R.K., & Lal, R. (2006). Ecosystem carbon budgeting and soil carbon sequestration in reclaimed minesoils. *Environment International,* 32,781-796. DOI:10.1016/j.envint.2006.05.001

Shukla, M.K., Lal, R., & Ebinger, M.H. (2005). Physical and chemical properties of a minesoil eight years after reclamation in northeastern Ohio. *Soil Science Society of America Journal,* 69,1288-1297. Doi:10.2136/sssaj2004.0221

Singh, P., Ram, S., & Ghosh, A.K. (2015). Changes in physical properties of mine soils brought about by planting trees. *Ecology Environment and Conservation* ,21, (S293-S299).

Singh, P., Ram, S., Jayant, H., & Ghosh, A.K.(2015b). Redevelopment of Soil Carbon Pools and Biological Properties on Restored Mine Spoils Under Plantation. *Journal of pure and applied microbiology* , 9(4),3031-3037.

Tripathi, N., Singh, R.S., & Nathanail, C.P. (2013). Mine spoil acts as a sink of carbon dioxide in Indian dry tropical environment.*Science of Total Environment* , 468,1162–1171. DOI: 10.1016/j.scitotenv.2013.09.024

Tunstall, B. (2010). Measuring soil carbon. http://www.eric.com.au/docs/research/soil/eric measuring soil carbon.pdf.

Vance, E.D., Brookes, P.C., & Jenkinson, D.S. (1987). An extraction method for measuring soil microbial biomass C. *Soil Biology Biochemistry* , 19,703–707. doi:10.1016/0038-0717(87)90052-6

Vinduskova, O., & Frouz, J. (2013). Soil carbon accumulation after open-cast coal and oil shale mining in northern hemisphere: a quantitative review. *Environmental Earth Science,* 69,1685–1698. DOI: 10.1007/s12665-012-2004-5

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, 251-263. DOI: http://dx.doi.org/10.1097/00010694-194704000-00001

Walkley, A., & Black, I.A. (1934). An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science* , 63, 251-263.DOI: https://doi.org/10.1097/00010694-194704000-00001

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fuji, R., Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science and Technology,* 37, 4702–4708. DOI:10.1021/es030360x

Yu, H., Xi, B., Su, J., Ma, W., Wei, Z., He, X., Guo, X. (2010). Spectroscopic properties of dissolved fulvic acids—an indicator for soil salinization in arid and semi-arid regions, China. *Soil Science,* 175, 240–245. DOI: 10.1097/SS.0b013e3181e055b4

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