

## EFFECTS OF INITIAL SOIL CARBON AND METAL CONTENTS ON SORPTION OF DISSOLVED ORGANIC CARBON ON THE SOILS OF TROPICAL RAIN FOREST TRANSFORMATION SYSTEMS

Ngatijo<sup>1</sup>, Damris Muhammad<sup>1\*</sup>, Asmadi Saad<sup>2</sup>, Abu Bakar<sup>3</sup>, Wanda Hamidah<sup>4</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science and Technology, Jambi University

<sup>2</sup>Department of Agro-technology, Faculty of Agriculture, Jambi University

<sup>3</sup>Department of Chemistry Education, Faculty of Education, Jambi University

<sup>4</sup>Department of Biology Author Education, Faculty of Education, Jambi University

[damris@unja.ac.id](mailto:damris@unja.ac.id)

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### ABSTRAK

Karbon organik terlarut (DOC) dalam tanah memainkan peran penting dalam distribusi nutrisi dan konsentrasinya dapat dipengaruhi oleh keberadaan partikel mineral tanah. Kandungan karbon tanah awal dapat mengurangi kapasitas tanah untuk menyerap DOC karena adanya tolakan muatan negatif. Penelitian ini mengkaji pengaruh kandungan karbon dan logam tanah awal terhadap adsorpsi DOC yang ditambahkan pada tanah hutan tropis melalui percobaan *batch*. Kandungan logam berat tanah (Al dan Fe), total karbon organik dan kandungan DOC tanah ditentukan. Untuk menentukan apakah dan bagaimana variasi kandungan karbon tanah mempengaruhi adsorpsi DOC, maka dua tanah dengan kandungan logam dan karbon yang berbeda (tanah permukaan dan bawah permukaan) dari dua sistem transformasi (hutan tropis sekunder dataran rendah dan perkebunan sawit masyarakat digunakan). Karbon organik terlarut diekstraksi dari permukaan tanah yang kaya organik dengan air dan dipisahkan ke tingkat yang diperlukan dan digunakan dalam percobaan *batch*. Karbon organik terlarut berkorelasi negatif dengan kandungan logam tanah terutama pada sub permukaan tanah. Dengan kandungan organik karbon tinggi korelasinya tidak signifikan. Ini mungkin menjelaskan adanya tolakan DOC yang membawa perubahan negatif oleh partikel tanah kaya organik.

### ABSTRACT

Dissolved organic carbon (DOC) in soil plays a significant role water could be affected significantly due to absorption on soil mineral particles but initial soil carbon content might reduce the capacity of soil to absorb DOC due to repulsive negative bearing charges. This study investigated the effect of initial soil carbon and metal contents on adsorption of added DOC on the soil of tropical forest through batch experiments. Soil heavy metals (Al and Fe), total organic carbon and DOC contents in the soils were measured. In order to determine whether and to what extent variation in metal and carbon contents of the soil affect the DOC adsorption, two soils with different metal and carbon contents (top and sub surface soils) from two transformation systems (secondary lowland tropical forest and small holder palm oil plantation) were used. Dissolved organic carbon was extracted from organic-rich surface soil with water and concentrated to a required levels and used in batch experiments. Dissolved organic carbon correlates negatively with soil metal contents particularly at soil sub surface. In presence of high carbon organic contents the correlation is not significant. This may explain repulsion of DOC bearing negative charges by organic rich soil particles

## INTRODUCTION

Transformation of tropical rainforest is still undergoing and mainly driven by expansion of oil palm, rubber, mining and timber (Abood *et al.*, 2014; Laumonier *et al.*, 2010). Area of oil palm plantation has significantly increased in the last decade and reached 17 million hectares world wide. Indonesia contributed for 60% of this increase and is now the main producer of palm oil (FAO, 2014). It has been widely recognized that transformation of tropical forest to intensive agricultural plantation might result in modification of soils properties and processes (McGrath *et al.*, 2001; Ross, 1993) and thus affects soil organic carbon and dissolved organic carbon in soil water (Don *et al.*, 2011; Van Noordwijk *et al.*, 1997).

Dissolved organic carbon in soil water plays an important role in both carbon cycling and chemistry of soils, through its influence on acidity, nutrient availability, metal toxicity and transport. It is the most dynamic and mobile fraction of the soil carbon and interacts with soil solid through adsorption-desorption mechanisms or to be taken by soil biota and plant roots, along with heavy metals. Dissolved organic carbon could stay dissolved in the soil solution and involve in dissolution equilibria of metals in the soil solution and reduce metal adsorption. In this case, soil surfaces compete more effectively for the free metal ion with forming soluble organo-metallic complexes or being preferentially adsorbed onto the surfaces instead of the metals it is competing with. Types and amounts of minerals present in the soils are of considerable importance in determining whether DOC stays in the solution in the form of organo-metal complexes or be weakly adsorbed to the soil surface, or form strong inner-sphere complexes that are bound even more strongly than would the free metal ion.

Although many adsorption studies have confirmed of such possible of DOC- metals interaction in soil solution, a lack of information concerning the influence of initial carbon and heavy metal contents of the soils on the added-DOC adsorption needs more study. We investigated the effect of in situ initial organic carbon and heavy metal contents in the soils on adsorption of DOC added to the soils in lab experiments. We used soils collected from tropical rainforest and the transformed oil palm plantation in Jambi. We hypothesized that adsorption of DOC on the soils decreases with total carbon content but increase with heavy metal in the soils. Nevertheless, the DOC sorption would be mainly pronounced in mineral soils rather than organic-rich soils. We assume that the C content and the soil composition in the subsoil under

the plantations were similar to the C content and the soil composition in the subsoil of the forest before the conversion.

## **METHOD**

### **Materials and Reagents**

Plastic spoon was used to collect soil samples, plastic bag and boxes holder for transportation of soil samples, 2-mm sieve, freezer for sample storage in the lab, mortar and pestle for soil graining, centrifuge for separation water-extractable organic carbon, analytical balance, hot plate, magnetic stirrer, 0.45- $\mu\text{m}$  glass membrane filter, UV-VIS spectrophotometer, LECO CHN-1000 and Atomic Absorbance Spectrophotometer (AAS). Chemicals used in this study were  $\text{KMnO}_4$ , deionized water,  $\text{FeCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{H}_2\text{SO}_4$ .

### **Preparation of soil samples**

Soil samples were collected from a small holder of palm oil plantations in Muaro Jambi, Jambi Province. The top organic soil (10 cm) and sub soils (30-50 cm) were collected from a number of randomly selected points (3 points) across the site and placed into clean plastic bags and sealed. Upon return to the laboratory, the soil was sieved through a 2-mm mesh and then stored in freezer at  $-5^\circ\text{C}$ . Soils collected from secondary forest proximate from the palm oil plantation were also treated as above.

### **Total C content**

Total C content in the soils was determined by dry combustion. Approximately 200 mg of the grained soil samples was covered in tinfoil before the analysis. The samples were combusted and the C was oxidized to  $\text{CO}_2$  which was measured by infrared light (Leco CHN-1000). The data was reported on dry basis.

### **Extraction of soil DOC**

Dissolved organic carbon was prepared by aqueous extraction of organic rich soil from secondary forest near the small holder palm oil plantation in Muaro Jambi. The extraction was performed by adding 200 g soils to 1 liter of deionized water. The suspension was stirred for 24

h at 180 rpm. The suspensions were centrifuged at 14.000 rpm for 10 min at 25 ° C. The supernatants were filtered over a 0.45- $\mu\text{m}$  glass fibre membrane filter. Five soil extracts were combined together and concentrated to obtain 150 mg  $\text{CL}^{-1}$  as stock solution. The resulted DOC solution was stored in freezer at -5 °C until used for other experiments within 2 weeks. Otherwise, new DOC solution was made.

### **Analysis of DOC**

Dissolved organic carbon was analyzed with indirect method of  $\text{KMnO}_4$  as oxidizing agent. The solutions of DOC were added with an excess of  $\text{KMnO}_4$  and left over for 10 min to ensure complete DOC oxidation. Absorbances of unreacted  $\text{KMnO}_4$  solution were determined with UV-VIS Spectrophotometer at  $\lambda_{\text{max}}$  565 nm. The absorbance difference between before and after the reaction was used to estimate DOC concentrations in the solution.

### **Analysis of soil metal contents**

Total Fe and Al contents in the soils were determined on grinded and oven-dried soil using destructive method of AAS. Accurately weighted solids (2 gr) were added to 100-ml beaker glass containing 10-ml concentrated  $\text{H}_2\text{SO}_4$  covered by watch-glass on a hot plat. The suspension was slowly heated up to 230°C while dropwise  $\text{HNO}_3$  was added repeatedly until clear solution was obtained. The suspension was filtered off Whatman-41 paper to a 50-ml measuring glass and diluted with distilled water to the mark. The Fe and Al contents were determined by AAS.

### **Equilibria experiments**

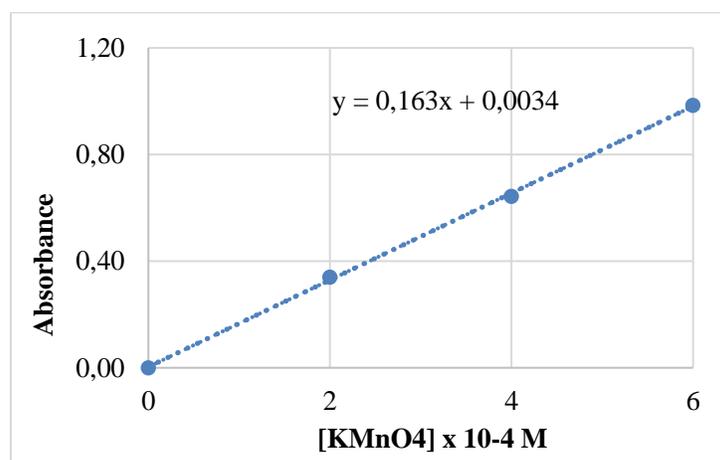
The DOC adsorption experiments conducted on duplicates of 0, 20, 40, 80 dan 150 mg  $\text{C L}^{-1}$  were prepared by diluting the stock DOC solution (150 mg  $\text{CL}^{-1}$ ). The initial DOC solution (30 mL) and 3 g of soil were added to a 100 mL glass bottle on a magnetic stirrer and agitated for 24 hours (100 cycles/min), at 4 °C. The final solution was filtrated off a 0.45  $\mu\text{m}$  glass fibre membrane filter and analysed for DOC. Six standards of  $\text{KMnO}_4$  were used (0,  $1 \times 10^{-4}$ ,  $2 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $4 \times 10^{-4}$ ,  $5 \times 10^{-4}$  and  $6 \times 10^{-4}$  M) to construct a standard curve. The amount DOC adsorbed was estimated by taking the difference between the concentration before and after adsorption

equilibrium by assuming that each 1 mole  $\text{KMnO}_4$  reacted with 0.75 mole carbon. The procedure was repeated for all other solutions.

## RESULTS AND DISCUSSION

### Calibration curve of $\text{KMnO}_4$

The calibration curve for determination of  $\text{KMnO}_4$  absorption were determined by measuring absorbance of the five standard solutions ( $0$ ,  $2 \times 10^{-4}$ ,  $4 \times 10^{-4}$  and  $6 \times 10^{-4}$  mole  $\text{L}^{-1}$ ) at max wavelength (Figure 1). The result shows that Figure 1. It shows that good sensitivity and linearity of the UV-VIS instrument used to measure absorbances of  $\text{KMnO}_4$ . The straight line equation of  $A=0,163[\text{KMnO}_4] + 0,0034$  and  $r^2 0,997$ .



**Figure 1.** Calibration curve of  $\text{KMnO}_4$

### Characteristics of the soils

The data given in table 1 shows total Fe, total Al, total C and DOC in top and bottom soils of small holder palm oil plantation and secondary forest. the soils correlated with Al total in the small holder palm oil significantly, but in the secondary forest soil. Total Fe in both soils is higher than Al. Carbon total of top soils palm oil plantation and secondary forest is not significantly different ( $P < 0.05$ ).

Sample A showed in general a low content of both Al and Fe sesquioxides (Table 2); however, the variation between field replicates was high. The contrasting soil B had a high Fe

content, while the Al content was not higher than for A. In comparison, sample C had a larger Al content and a much lower Fe content. Sample C was rich in amorphous Al, approximately five times higher than the average. Sample B showed a higher content of amorphous and crystalline Fe than the two other soils. Sample A had in general low clay content; most field replicates had a clay fraction lower than 10%, and as for other properties, the variability was high. The soil C content was  $1.7 \pm 0.8\%$  for P1, 1.3% for P3, and 2.3% for B. There was not seen any great differences in pH between the three soils. The calculated hydrophobicity index (HI) for the B-horizons ranged between 9.5 and 12 and from 2.3 to 3.8 for the O-horizon samples.

P significantly; and the available K pool of PMF in the primary succession stage was lower as compared to MEBF forest type in the climax succession stage. This was consistent with the results of a study of a tropical wet forest soil in Costa Rica (Gunina, *et al.*, 2014). Plant cover type and its considerable influence on soil properties has been reported in earlier studies (Islam, *et al.*, 2000; Garten, *et al.*, 2006), with lowland tropical forests having less P returned to the soil through litterfall. In stable environments, however, soil nutrient loss is gradual under relatively humid conditions as reported in Hawaiian ecosystems. Differences between soil quality indexes is mainly caused by various biotic and abiotic conditions such as forest soil litter, microbial biomass and their associated activities, and the initial soil properties. In tropical forest ecosystems, soil property is very complex due to having a closer relationship with succession. Our results for this lower subtropical forest are consistent with studies reporting complicated changes of soil properties with forest succession, but long term monitoring should be implemented for a more complete understanding. The pattern for available Zn, Cu, Fe and B shows an increasing tendency in forest succession which is explained by the increase in organic matter that provides more exchangeable sites for cations, or the influence of the pH value, because H ions are released by the decomposition of organic matter and by direct root exudation. All four elements favour leaching of nutrient cations because of competition for the exchange sites. The pattern of the four elements was consistent with our hypothesis.

**Table 1.** Concentrations of Fe (%), Al (%), C total (%) and DOC (ug g<sup>-1</sup>) in the top soil (0-10 cm) and bottom soil (30-50 cm) of small holder palm oil plantation and secondary forest, Muaro Jambi (n=3)

Soil of Palm Oil Plantation	Mean ± SD			
	Fe (%)	Al (%)	C Total (%)	DOC (ug g <sup>-1</sup> )
• Top 10 cm	0,26 ± 0,05	0,18 ± 0,11	4,17 ± 0,50	13,25 ± 2,00
• Bottom 30-50 cm	2,67 ± 0,46	2,30 ± 0,92	1,73 ± 0,46	5,93 ± 1,53
Soils of Secondary Forest				
• Top 10 cm	2,03 ± 0,40	1,30 ± 0,17	7,25 ± 0,46	26,75 ± 3,03
• Bottom 30-50 cm	2,83 ± 0,55	1,76 ± 0,50	1,92 ± 0,31	10,05 ± 2,00

**Table 2.** Correlation coefficients between Fe, Al, C total and DOC at top and bottom of the soil samples collected from small holders of the palm oil plantation (top) and secondary forest (bottom) in Muara Jambi, Jambi Province.

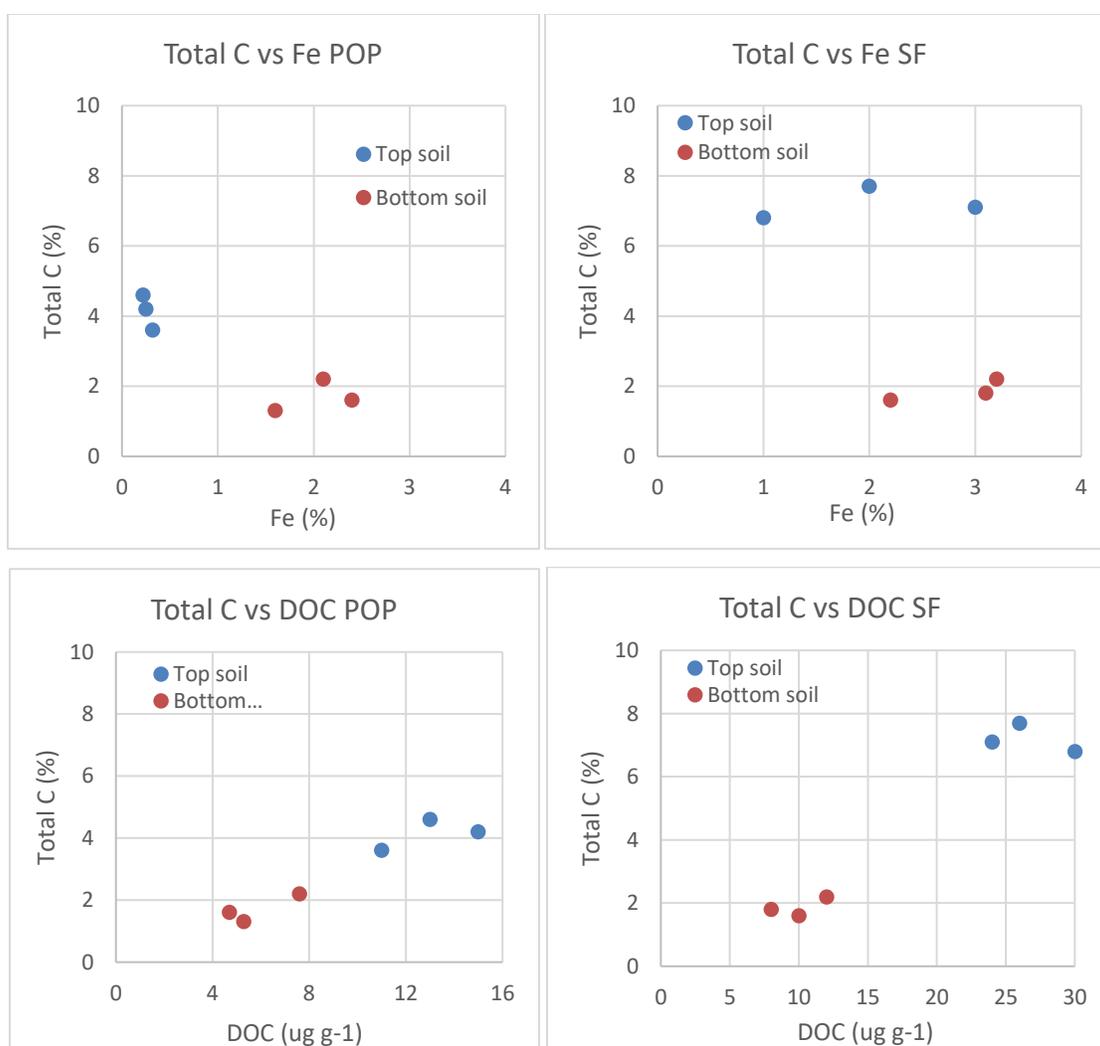
Palm oil Plantation	Fe top	Al top	C total Top	DOC top	Fe Bottom	Al Bottom	C total Bottom	DOC Bottom
Fe Top								
Al Top	0,941**							
C total Top	-0,994**	-0,898**						
DOC top	-0,682**	-0,888**	0,596**					
Fe Bottom	0,932**	0,756**	-0,967**	-0,371				
Al Bottom	0,225	0,539**	-0,115	-0,866**	-0,143			
C total Bottom	0,106	-0,235	-0,217	0,655**	0,459	-0,945**		
DOC Bottom	-0,412	-0,694**	0,307	0,307	-0,054	-0,981**	0,862**	

\*\* Significant at 0,05 level

Secondary Forest	Fe top	Al Top	C total Top	DOC Top	Fe Bottom	Al Bottom	C total Bottom	DOC Bottom
Fe Top								
Al Top	0,140							
C total Top	-0,756**	0,756**						
DOC top	-0,189	-0,945**	-0,500**					
Fe Bottom	0,891**	-0,577**	-0,971**	0,277				
Al Bottom	-0,999**	0,115	0,737**	0,219	-0,878**			
C total Bottom	0,459	-0,945**	-0,929**	0,786**	0,812**	-0,434		
DOC Bottom	-0,371	-0,866**	-0,327	0,982**	0,091	0,397	0,655**	

\*\* Significant at 0,05 level

Table 1 shows the concentration of Fe and Al, C total and DOC in soils of the small holder palm oil plantation and secondary forest of Muaro Jambi. Iron and Al are two heavy metals that are found in significant amount compared to other heavy metals. Both metals could be found in the amorphous forms of oxides, oxyhydroxides and hydroxides. The important of these elements in the soils due to high adsorption capacities and specific surface area (Yukselen and Kaya, 2008). While in the forms of inorganic crystalline forms are gibbsite ( $\text{Al}(\text{OH})_3$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and goethite ( $\text{FeOOH}$ ). Gibbsite is the most common Al found in soils, which is usually formed by silica removal from kaolinite.



**Figure 2.** Contrasting behavior among soil parameters at top and bottom soils between C total and Fe (top) and C total and DOC between palm oil plantation (POP) and secondary forest (SF).

Table 2 shows correlation coefficients among Fe, Al, C total, DOC at top and bottom of the soil samples collected at small holders palm oil plantation and secondary forest in Muaro Jambi Jambi Province.

Soil of palm oil plantation show a strong correlation between Fe and Al at top soil but not at the bottom soil. Fe and C total show a strong negative correlation at top soil but not at the bottom one. C total has a strong correlation with the DOC at both top and bottom soils. However, secondary forest shows that Fe and Al has no significant correlation at top and bottom soils. C total at top soil show a strong negative correlation with Fe and a strong positive correlation with Al. Figure 2 show a contrasting behavior among soil parameters at top and bottom soils between palm oil plantation (POP) and secondary forest (SF).

## CONCLUSIONS

1. Conversion of lowland tropical rainforest to tree plantations decreases SOC stocks in the top soil. Extensive land use such as jungle rubber leads to lower decrease of SOC than intensive land uses such as oil palm and rubber plantations.
2. The vertical distributions of C content follow a power function with soil depth and a linear function with the log-transformed C content in Harapan and, to a lesser extent, in Bungku landscape.
3. Oil palm and intensive rubber plantations have similar impacts on SOC losses and erosion. However, the C enrichment of SOC suggests that the leaf litter is the main source of C for microorganisms in rubber plantations.

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