

Quantitative and Qualitative Evaluation on Stored Carbons of Mangrove Ecosystems in Chumphon, Thailand

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Abstract: Abundant carbon content and a high carbon accumulation rate were quantitative characteristic of the mangrove mud layer, which was formed by the development of mangrove forests. As a qualitative characteristics, humic acids extracted and determined from mangrove ecosystems showed that mangrove had a relatively high amount of aliphatic component, while deltaic sediments underlying the mangrove mud layer showed a lower content of aliphatic and a higher content of carboxylic component. Humic acid components of the mangrove mud layer resemble to those of paddy soils, ascribed to soil formation with the influence of water. Stored carbons of mangrove ecosystems were not yet progressed in humification. However, aliphatic rich mangrove soils are susceptible to carbon decomposition due to its long chain structure. Land use changes that may cause dehydration should be avoided from the viewpoints of sustaining a certain level of carbon level in mangrove ecosystem.

Keywords: mangrove soils, ¹⁴C dating, carbon accumulation rate, humic acids

Introduction

Mangrove's role as carbon sink has been well documented and reported in the last few decades (Woodroffe et al. 1989; Fujimoto and Miyagi 1993; Matsui 1998, Matsui and Yamatani 2000) because their implication attracted much attention by growing concerns on global warming problems.

Tropical coastal region of the biosphere are the most biogeochemically active regions and represent potentially important sinks of carbon in the biosphere (Twilley et al. 1992). In the previous study, we estimated total stocks of sediment carbon considering stratigraphy of underlying mangrove forest (Matsui and Yamatani 2000). It was then revealed that 1,208 tC ha⁻¹ of carbon were stored to the basement rock at 8.5 m depth. And a significant portion of total carbon was stored in the mangrove mud layer that was formed by the development of mangrove forests. A capacity of storing carbon in the mangrove mud layer was significantly high if comparing to two other sub-layers (shell-dominated sand- and mud layer), which are deltaic sediments formed by terrestrial deposits supplied on the different time of sea-level change.

By adding the results of radiocarbon dating to those carbon stocks, sedimentation rate of each layer can be given to better understand the contribution of mangroves in carbon dynamics of coastal ecosystem. It also gives insights into understanding the time of mangrove development at the study region.

While quantitative aspects of organic carbon in mangroves were studied intensively, qualitative aspects

have not been quite investigated due partly to the difficulty of fractionation of organic matter (=humic) substances. Soil humus is formed immediately after fresh plant debris incorporated into the soil and metabolized by microorganisms. It plays roles not only as nutrient source for plants and microorganisms, but also as a slow-acting fertilizer due to its high cation exchange capacity. The quantity and quality of humic component are determined by environmental factors like soil temperature, soil moisture regime, vegetation type and clay contents. Moreover, humic component is positioned in dynamic equilibrium, whose components determined on the balance between input of fresh organic matter and output through humification. Composition of humic acids could indicate environmental condition under which humic acids were formed and source of organic matter from where humic acids derive. Thus studying of humic acid may provide another insight to understanding about how carbon stored by the influence of mangrove and also about the fate of organic matter accumulated by forests.

Adsorption chromatography using nonionic macroporous resin Amberlite XAD-8 made possible to separate into 4 different components which are 1) aromatic rings with short aliphatic substituents and many carboxyl groups, 2) phenolic groups, 3) relatively long aliphatic chains and 4) aromatic rings with long aliphatic substituents (Yonebayashi and Hattori 1990). With this developed separation technique, we attempted to clarify humic components of mangrove soils for understanding qualitative aspects of mangrove organic matter.

As described in the above, this study has the objectives

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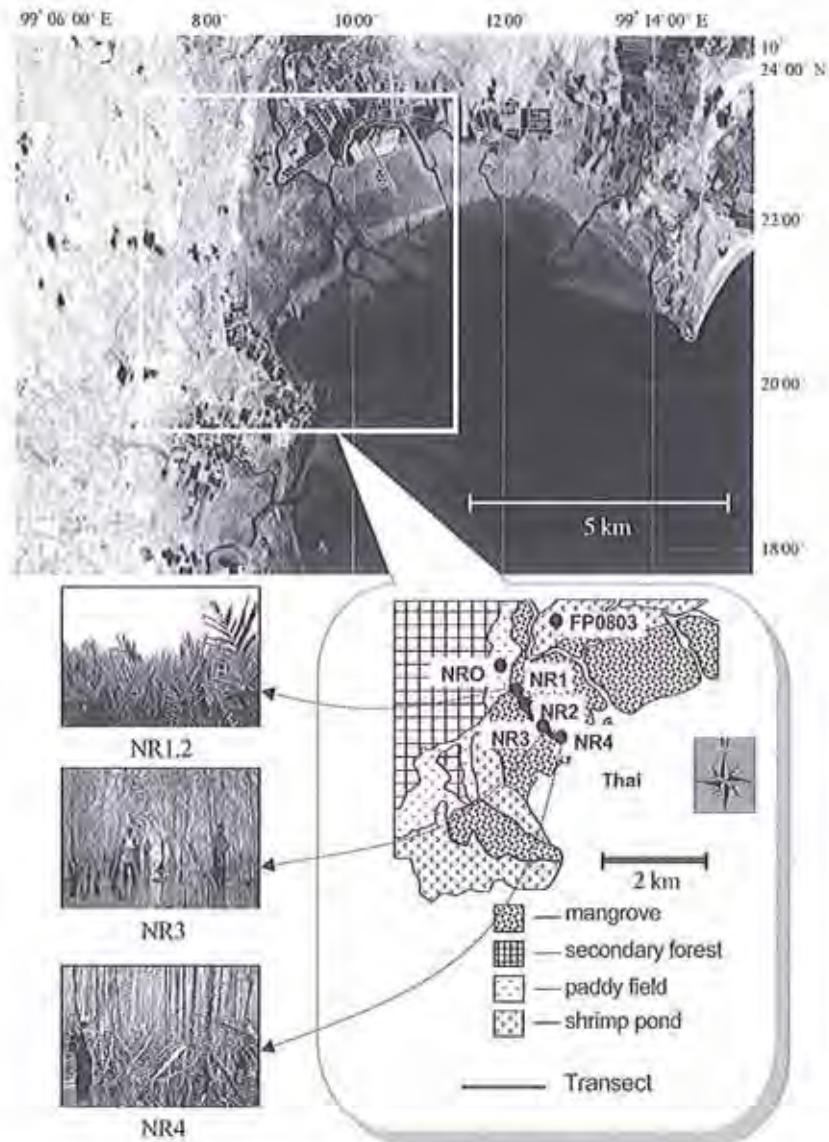


Fig. 1. Locations of sampling sites

1) to understand quantitatively carbon stocks in mangroves from the viewpoints of space and time, 2) to clarify characteristics of mangrove humic acids comparing to those of other ecosystem, and 3) to consider proper carbon management in tropical coastal ecosystem judging from qualitative and quantitative characteristics of mangrove carbons.

Materials and methods

1. Study site

The transect across different mangrove zones was made in Tungka Bay, Chumphon, Thailand (Matsui and Yamatani 2000). 4 sampling points (NR1-NR4) were established in mangrove areas along the transect, and

2 point (NR0, FP0803) were made in paddy field, and in abandoned shrimp pond, respectively (Fig. 1). Study site was affected by anthropogenic activity, especially by shrimp aquaculture. There were some traces of human activity even in the midst of mangrove forests (NR3, NR4). In NR1, NR2 located nearby the village, conversion from natural mangrove ecosystem is significant. In which a high frequency of cutting trees from 1980's made changes into *Acrostichum* spp. dominated field.

Relative dominance of mangrove species was measured in each sampling point. In the plot of 10 x 10 m, diameter and tree height of each specie were determined after the species identification.

Table 1 Information on the samples for radiocarbon dating analysis

Site	Layer	Code no.	Depth*	Type of sample	Pre-treatment
NR1	Mangrove mud	Beta-150281	105-115	organic sediment	acid washes
NR2	Mangrove mud	Beta-147659	100-104	organic sediment	acid washes
	Shell dominated Mud	Beta-147660 Beta-147661	400-404 530-540	organic sediment shell	acid washes acid etch
NR3	Mangrove mud	Beta-150282	105-112	organic sediment	acid washes
	Shell dominated Mud	Beta-150283 Beta-150284	385-393 535-542	organic sediment organic sediment	acid washes acid etch
	Mangrove mud	Beta-147663	174-176	shell	acid etch
NR4	Shell dominated Mud	Beta-147665 Beta-150285	387 700-710	shell organic sediment	acid etch acid washes

*Depth where the sample was taken

2. Methods

2.1 Soil sampling and measuring soil properties

Soil samples were collected by Soil Check Simplification Consortium (SCSC). SCSC is the boring machine equipped with engine, developed for collecting undisturbed soil samples from the deeper depths. Three phase distribution, bulk density were determined from undisturbed soils removed by 100cc stainless cylinder. EC was measured from 0.5 ml of pore water diluted 20 times by adding distilled water with TOA Electronics, Conductivity meter TOA CM305. Total carbon and nitrogen were measured by combustion method at 800 °C using a Sumitomo-Kagaku sumigraph NC-800-13N.

2.2 Determination of radiocarbon dating and sedimentation rate

Table 1 shows sample information for ¹⁴C dating referring the depth of sample collection and determination method.

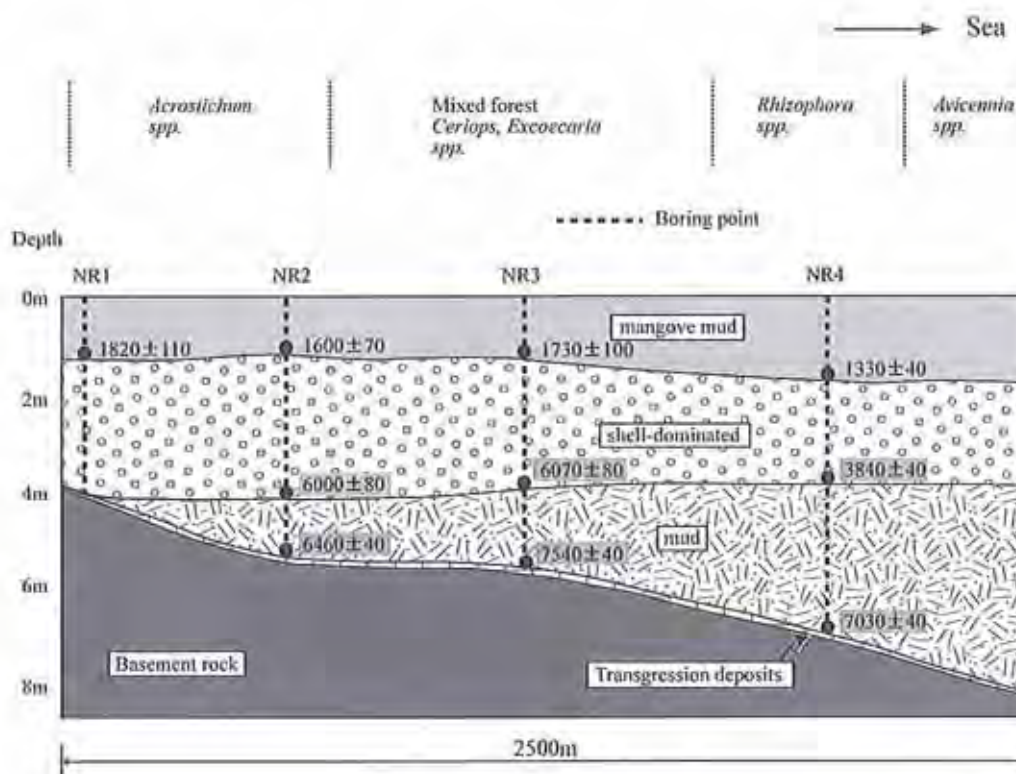
For the radiocarbon dating, two different types of samples were used. One is shell, which was pre-treated by acid etch, then measured by AMS (Accelerator Mass Spectrometry) method. Shell is likely to be ideal sample since it is autochthonous fossil showing more accurate time of sedimentation wherein shell is buried. Not large amount of shell were obtained in the sampling, however radiocarbon dating was possible since AMS method requires just a few grams of sample. Another is organic sediment, pre-treated by acid wash, measured by radiometric-standard method, which is standard method being widely used in radiocarbon dating.

Sedimentation rate was calculated from the results of radiocarbon dating for the mangrove mud layers previously identified by stratigraphic survey. For which samples were collected just above the boundary of each layer in order to know the starting time of each layer formation (Fig. 2).

2.3 Humic acid determination

Humic acids were determined from the samples of the mangrove mud layer (NR2, NR3, NR4 0-5), the shell dominated layer (NR4 305-310) and the mud layer (NR4 490-495), and from paddy field (NR0) and abandoned shrimp pond (FP0803).

Followed to fractionation method of Yonebayashi and Hattori (1990), humic components were separated as follows. Amberlite XAD-8 resin was pulverized and the 50-200µm range was isolated. The sieved particles were washed with ethanol, acetonitrile, again with ethanol, and packed into a column (20cm × 1.8cm i.d.) which was conditioned with 0.1 M sodium hydroxide followed by the universal buffer taken to pH 3 with sodium hydroxide. Humic acid was dissolved in 0.1 M NaOH and treated with Amberlite IR-120 resin to make the H⁺-saturated form. Five mg of humic acid dissolved in 2 ml of aqueous solution was loaded onto the column packed with XAD-8 resin. A pH-gradient solution was prepared by titrating 200 ml of 0.02 M universal buffer, contained in an air-tight flask, with 0.1 M NaOH using a peristaltic pump, and passed through at a flow rate of 1.5 ml min⁻¹. The pH of the column effluent was measured with a pH electrode. A water-ethanol gradient was generated by mixing 200 ml of distilled water, contained in an air-tight flask, with ethanol using a peristaltic pump. Elution was at a flow rate of 1.5 ml min⁻¹. The elution profile was determined by measuring the optical density at 400 nm after the effluent was alkalinized above pH 12 by addition of 10 M NaOH. Stepwise elution was run with universal buffer solutions adjusted to pH 7 and pH 11, distilled water, and 50 % ethanol. The elution profile was determined in the same way as for the pH gradient chromatography. Each effluent was precipitated with sulfuric acid and dissolved in 0.1 M NaOH. Since the humic fraction eluted at pH 7 was not precipitated by acidification, it was adsorbed on a small XAD-8 column at pH 3 and eluted with the NaOH solution. Each of the four eluates was dialyzed against distilled water and freeze dried.



● indicates the point where a sample for c14 determination was taken from.

Fig. 2. Stratigraphy of the studied soils

Table 2 General characteristics of the studied soils

	Soil depth (cm)	Three phase distribution (%)			Bulk density (g/ml)	Root debris ¹⁾ (%)	EC (dS/m)	Total-C (%)	Total-N (%)	CN ratio
		Air	Liquid	Solid						
FP 0803	0~5	8.4	36.4	55.2	1.44	0.29	0.48	0.52	0.04	14.7
NR0	0~5	44.4	14.6	41.0	1.12	0.28	3.49	0.38	0.02	16.0
NR1	0~5	18.8	58.2	23.0	0.56	0.76	37.5	9.64	0.62	15.6
NR2	0~5	16.9	69.7	13.4	0.29	0.98	40.0	14.2	0.87	16.3
NR3	0~5	11.1	65.2	23.7	0.58	2.17	45.0	3.41	0.18	18.9
NR4	0~5	15.4	64.6	20.0	0.48	1.16	39.4	4.84	0.22	22.1
NR4	305~310	9.0	46.2	44.9	1.21	0.03	48.4	0.79	0.02	33.0
NR4	490~495	4.4	48.4	47.2	1.25	-	52.6	1.13	0.02	51.2

¹⁾ - (minus) indicates no root debris was collected.

Results

1. Vegetation characteristics in the sampling points

In the each sampling point, mangrove species composition was determined. For arboreal composition, *Excoecaria agallocha* occupied 100% in NR1, NR2. The total D2H of NR1, NR2 were 3.9 and 22.9, respectively. For forest floor vegetation in NR1, NR2, >90% was occupied by *Acrostichum spp.* In NR3, relative dominance was *Excoecaria agallocha* 69.7%, *Ceriops tagal* 30.3% with total D2H of 263.7 and 114.9, respectively. *Rhizophora apiculata*,

Rhizophora mucronata were present in NR4 with a relative dominance of 90%, 10%, and with total D2H of 421.5 and 46.8.

In NR1, NR2, *Acrostichum spp.* were notably extended in the area. *Acrostichum spp.* normally distribute in small area, however distribution in this area had more than a few ha which is quite unusual (personal communication with Prof. Dr. Suzuki, Yokohama National Univ.)

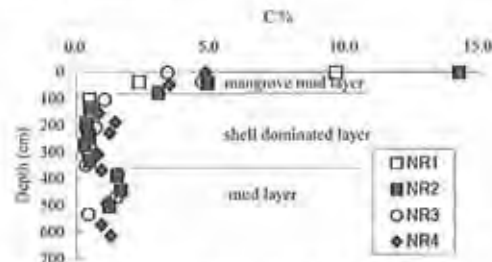
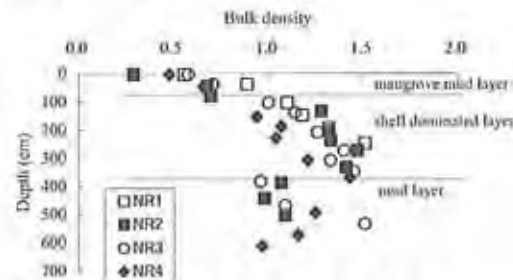
2. General characteristics of soil properties

Non-mangrove soils were characterized by a low

Table 3 Results of radiocarbon dating analysis

Site	Layer	Depth*	Measured ^{14}C age (yr BP)	$\delta^{13}\text{C}$ (‰)	Conventional ^{14}C age (yr BP)	Sedimentation rate (mm/yr)
NR1	Mangrove mud	105-115	1820±110	-25.00	1820±110	0.60
NR2	Mangrove mud	100-104	1610±70	-25.70	1600±70	0.63
	Shell dominated Mud	400-404	6020±80	-25.90	6000±80	
NR3	Mud	530-540	6070±40	-1.40	6460±40	0.62
	Mangrove mud	105-112	1730±100	-24.40	1730±100	
	Shell dominated	385-393	6080±80	-25.90	6070±80	
NR4	Mud	535-542	7530±40	-24.20	7540±40	1.32
	Mangrove mud	174-176	1020±40	-5.80	1330±40	
	Shell dominated	387	3400±40	1.80	3840±40	
	Mud	700-710	7050±40	-26.20	7030±40	

* Depth where the sample was taken

**Fig. 3.** Changes of C% in the depth**Fig. 4.** Changes of bulk density in the depth

EC value (Table 2). However, abandoned shrimp pond (FP0803) showed even lower EC, indicating that salts were washed away after the abandonment of shrimp pond. The studied abandoned shrimp pond was located away from tidal influence. Therefore, precipitation may have lowered salinity without additional salt input from seawater after the abandonment in 1980's.

Surface soils in the mangrove areas showed a relatively high content of organic matter comparing to non-mangrove areas such as abandoned shrimp pond (FP0803) and paddy field (NR0) (Table 2, Fig. 3). This fact would indicate a comparatively high organic matter productivity of mangrove ecosystem. In *Acrostichum* area (NR2), total carbon showed a highest value, 14.2 %. Since the other *Acrostichum* area (NR1) also had a high total carbon content, it is plausible that *Acrostichum* area is capable to produce a high organic matter. Low carbon content in abandoned shrimp pond (FP0803) where it was mangrove

before 1980's may indicate that a decline of carbon content was caused by land use change. As a large part of mangrove was converted into shrimp pond in the study area, a significant amount of carbon was certainly lost from coastal ecosystem.

CN ratio of topsoil tends to decrease seawards from NR1 to NR4 (Table 2), and from the upper layer (NR1 0-5) to lower layer (NR4 490-495). Since biological activity generally lowers CN ratio, this tendency indicates higher biological activity in inland zone and in the surface layer.

In general, sub-layers (the shell dominated layer, the mud layer) were more compacted comparing to the mangrove mud layer as shown in a relatively high percentage of bulk density and solid phase (Table 2, Fig. 4). In the sub-layers, the mud layer was less compacted as was shown by bulk density (Fig. 4). This fact might be related with higher carbon content of the mud layer (Fig.

Table 4 Carbon stocks (tC ha⁻¹) and carbon accumulation rate (tC ha⁻¹ year⁻¹)

Layer	NR1		NR2		NR3		NR4	
	Stocks	Accum.rate	Stocks	Accum.rate	Stocks	Accum.rate	Stocks	Accum.rate
Mangrove mud	370	0.21	440	0.35	373	0.22	553	0.50
Shell dominated			245	0.12	305	0.11	332	0.27
Mud			104	0.14	109	0.10	162	0.15

3). Carbon content was higher and bulk density was lower in the mud layer comparing to the shell dominated layer (Fig. 3).

3. Radiocarbon dating

The mud layer started to form around 6460 - 7030 ¹⁴C B.P as were shown in the radiocarbon dating of the mud layer bottom (NR2, 6462; NR3, 7540; NR4, 7030 ¹⁴C B.P.) (Table 3), the mud layer formed. As Fujimoto et al. (1999) reported the first regression occurred before 7200 year B.P in the Southwestern coast of Thailand, the mud layer could be formed during the transgression period.

The organic-rich mangrove mud layer has started to deposit around 1330 - 1820 years B.P. These quite resembled with the reported times in the Southwestern coast of Thailand (Fujimoto et al. 1999). Sedimentation rates of the mangrove mud layer were quite similar except for one of NR4 (Table 3). The higher sedimentation rate at NR4 in *Rhizophora spp.* is supposedly due to the location since NR4 situated most seaward.

If comparing carbon dating results among the different locations in the mangrove mud layer, sedimentation is likely to start earlier in inland than offshore. This would agree to the belief that mangrove ecosystem is developing into the direction of offshore. Moreover, quite different carbon accumulation rate of topsoil among the locations shall reflect different forest productivity depending on mangrove species (Table 4).

Carbon accumulation rate was relatively high in the mangrove mud layer and the highest in the zone of *Rhizophora spp.* (Table 4). Since the formation of the mangrove mud layer was greatly affected by mangrove forests, its vigor productivity contributed to higher carbon accumulation rate comparing to underlying sub-layers (the shell dominated layer and the mud layer).

4. Characteristics of humic acids

The distribution of humic acid components was illustrated in a three-axial diagram (Fig. 5). In order to compare mangrove humic acids with ones of other ecosystems, the data was cited from the study conducted by Yonebayashi (1992). From the viewpoints of humic substances distribution, topsoils of NR0, NR1, NR3 and

NR4, which belong to the mangrove mud layer, were grouped into the same group. Carboxylic content in mangrove humic substances was between paddy soils and volcanic soils, and aliphatic content was relatively high. These facts indicate that humification of mangrove humic substances were not so yet progressed. Mangrove ecosystem is generally influenced by tidal water so that humification is retarded from progressing.

NR2 was notably characterized by a quite high amount of semi-aliphatic and aliphatic component, which resembled to chemical characteristic of sea-bottom or lake-bottom sediments. Highly dominance of *Acrostichum spp.* in NR2 and high organic matter content in surface soils may have influenced to this humic composition, but the exact reason still remained unclear.

In NR4, carboxyl components were higher and aliphatic components were lower in the sub-layers. An increase of carboxyl and a decrease of aliphatic components, are related with structural changes caused by humification process. If dehydration occurs, demethylation proceeds in aliphatic components, increases carboxyl which is resistant component, hence advances humification. Sediments of sub-layers were supposed to be transported from the land, partly incorporated with marine origin deposits. Terrestrial organic matter is susceptible to humification since terrestrial condition is generally drier than aquatic condition. Humic components in the sub-layers therefore were rich in carboxyl components and less in aliphatic components. In an abandoned shrimp pond, FP 0803 where water is stagnant inside the pond, humification did not occur strongly due to its prolonged wet condition.

Aliphatic rich mangrove soils are susceptible to decomposition. Change of land use such as conversion from mangrove to shrimp pond may cause structural changes of mangrove humic components. Specially, aliphatic components are easily broken by microbial activity since it holds a long aliphatic chain in their structure (Yonebayashi 1992). Carbon decomposition will be accelerated by a decrease of moisture regime and by an increase of soil temperature. Therefore, it is worth studying a fate of mangrove organic carbons caused by land use change, with water/soil condition monitoring

from the viewpoints of humic substances,

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- 松井 直弘¹⁾・小崎 隆²⁾: タイ国チュンボン県のマングローブ生態系に蓄積した炭素の定量的、定性的評価
- マングローブとその隣接した生態系の合計8地点から土壌中の腐植酸を抽出し、その特徴を明らかにした。マングローブ泥層は他の層に比べて蓄積炭素量が多く、脂肪族性の腐植酸が多く含まれていた。一方、マングローブ泥層下部のデルタ堆積物層では脂肪族性腐植酸が少なく、カルボキシル性腐植酸が多かった。マングローブ泥層が水田土壌に近い腐植酸構成を持っていることから、マングローブ泥層が水の影響を強く受けて生成されたことがわかった。長期的に水が停滞する地点ではミミモチシダが繁茂しており、土壌中腐植酸は海底や湖底の堆積物に近似した、脂肪族性腐植酸に富む腐植酸構造を示した。脂肪族性腐植酸は長側鎖構造を持っていることで好気的な環境下で分解されやすい特徴を持っている。そのため水分率を低下させ、土壌を酸化的環境に導く土地利用はマングローブ生態系から多量の炭素を消失させる可能性がある。

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