J. Mar. Sci. Eng. **2015**, *3*, 1404-1424; doi:10.3390/jmse3041404

OPEN ACCESS

Journal of
Marine Science and Engineering
ISSN 2077-1312
www.mdpi.com/journal/jmse

Article

Soil Organic Carbon in Mangrove Ecosystems with Different Vegetation and Sedimentological Conditions

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Academic Editors: Joseph M. Smoak and Christian Joshua Sanders

Received: 1 June 2015 / Accepted: 12 November 2015 / Published: 19 November 2015

Abstract: A large number of studies have been conducted on organic carbon (OC) variation in mangrove ecosystems. However, few have examined its relationship with soil quality and stratigraphic condition. Mangrove OC characteristics would be explicitly understood if those two parameters were taken into account. The aim of this study was to examine mangrove OC characteristics qualitatively and quantitatively after distinguishing mangrove OC from other OC. Geological survey revealed that the underground of a mangrove ecosystem was composed of three layers: a top layer of mangrove origin and two underlying sublayers of geologic origin. The underlying sublayers were formed from different materials, as shown by X-ray fluorescence analysis. Despite a large thickness exceeding 700 cm in contrast to the 100 cm thickness of the mangrove mud layer, the sublayers had much lower OC stock. Mangrove mud layer formation started from the time of mangrove colonization, which dated back to between 1330 and 1820 ^{14}C years BP, and OC stock in the mangrove mud layer was more than half of the total OC stock in the underground layers, which had been accumulating since 7200 ^{14}C years BP. pH and redox potential (Eh) of the surface soils varied depending on vegetation type. In the surface soils, pH correlated to C% ($r = -0.66$, $p < 0.01$). C/N ratios varied widely from 3.9 to 34.3, indicating that mangrove OC had various sources. The pH

and Eh gradients were important factors affecting the OC stock and the mobility/uptake of chemical elements in the mangrove mud layer. Humic acids extracted from the mangrove mud layer had relatively high aliphatic contents, in contrast with the carboxylic acid rich sublayers, indicating that humification has not yet progressed in mangrove soil.

Keywords: mangrove; soil OC; redox potential; C/N ratio; humic acid; leaf analysis

1. Introduction

Mangrove ecosystems are recognized to have OC stocks equal to or higher than terrestrial tropical forests [1–5]. Mangroves are some of the most biogeochemically active regions on Earth and represent important carbon sinks in the biosphere [6–8]. However, mangrove ecosystems have been vastly exploited for anthropogenic uses; the rate of mangrove loss is 0.7%–7% annually, which is four times higher than the rate of rainforest loss [9–13].

To assess the carbon sink capacity of mangrove ecosystems, OC stock in mangrove ecosystems should be distinguished according to mangrove and non-mangrove origin to further clarify this ecosystem's carbon sink capacity. To this end, stratigraphic examination is adopted as it delineates the mangrove layer from the other layers and can be used in tandem with radioisotope methods to determine mangrove colonization time.

A considerable amount of data has been collected for OC stock as quantitative studies [14–17]. On the other hand, the source of OC has been studied as the qualitative determination of mangrove OC because OC source has a major impact on the overall carbon dynamics in intertidal mangrove ecosystems. C/N ratio is a useful parameter to predict the source of OC [18] reflecting levels of OC degradation, and X-ray fluorescence (XRF) analysis has been conducted to study the source of sediment deposited at different times [19]. Not only the source of OC, but also the quantity and the composition of the OC, may differ depending on the vegetation type [20]. Therefore, it is necessary to examine the spatial variation of OC in relation to vegetation type.

The nature of OC is another important qualitative feature because it may offer some insight into the stability of OC. Humic acid composition reflects the nature of OC as humic substances are chemically and biologically synthesized from litter and microorganism debris through microbial activity under the influence of the deposition environment. As humic acid composition is determined on the basis of the dynamic balance between OC input and decomposition [21], it is worth examining humic acid composition to predict the fate of OC.

This study has the following objectives: (1) to characterize OC of a mangrove ecosystem differentiating from non-mangrove OC; (2) to assess mangrove OC source in relation to vegetation type; and (3) to examine the nature of OC from the viewpoint of humic acid composition.

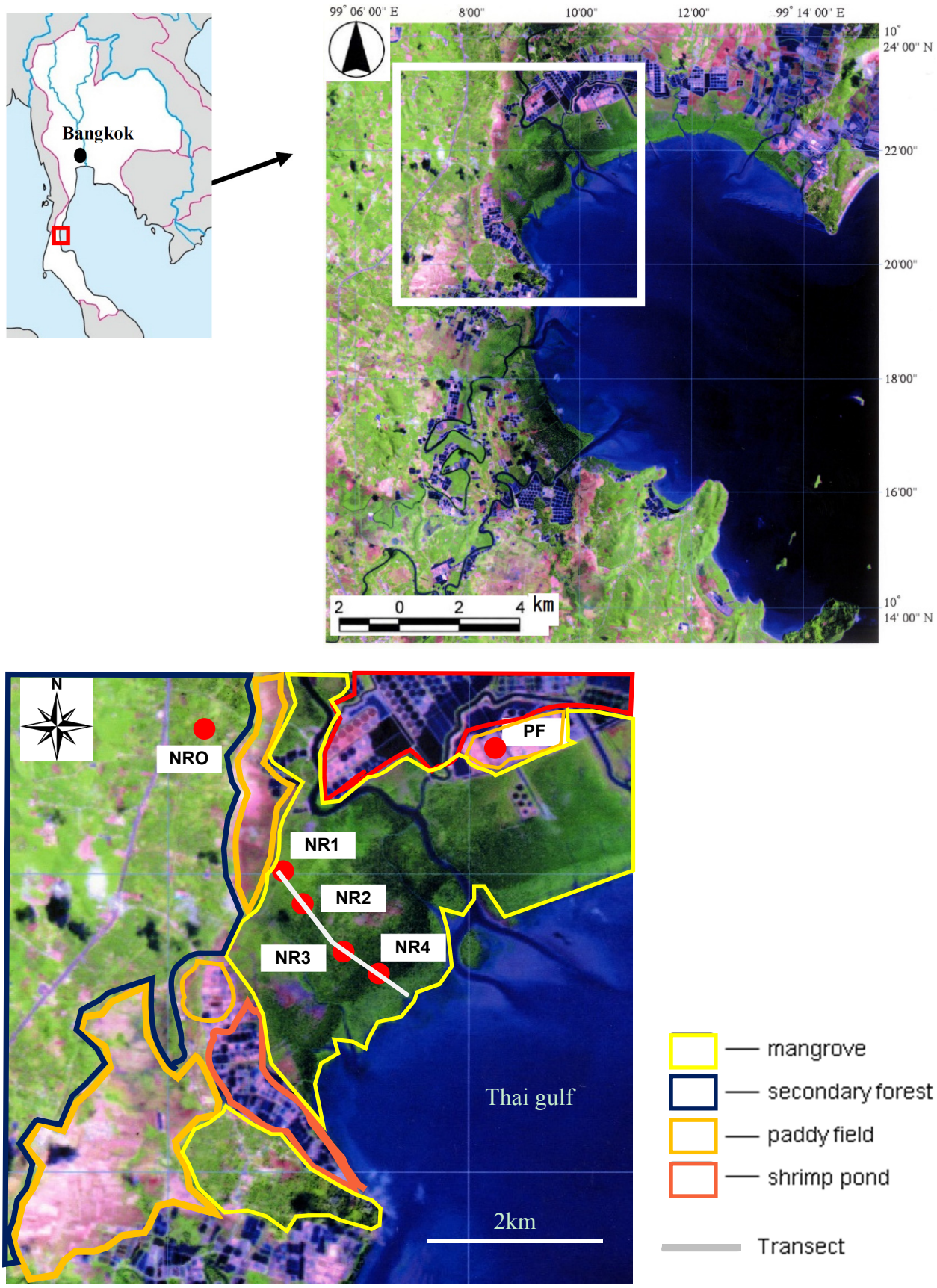

Figure 1. Location of study site is indicated by a white square in Landsat image. The transect was made by crossing different mangrove vegetation types. Boring survey was conducted in mangrove ecosystem (NR1–NR4), coconut plantation (NR0), and paddy field (PF).

2. Materials and Methods

2.1. Study Site

The study site was located in Tungka Bay, Chumphon, Thailand (Figure 1). The area has two monsoon seasons, which occur from December to April and from May to November, respectively. The mean monthly rainfall for the last 10 years (2005–2014) was 1883 mm. The rainy season was recorded during the months of October and November, whereas the low rainfall season was recorded from February to May, with February being the driest month. The average mean monthly temperature varied between 25.8 to 28.9 °C. The mean annual relative humidity was 81% (personal communication with Meteorological Office, Chumphon Province, Thailand, 2015). Mangrove forests at the study sites registered 19 species belonging to the families *Rhizophoraceae, Avicenniaceae, Sonneratiaceae, Meliaceae, Euphorbiaceae*, and *Combretaceae*.

Chumphon mangroves decreased from 8100 ha in 1961, to 3625 ha in 1986, and to 1818 ha in 1991 [22]. Considering that shrimp farm increased 2219 ha from 1987 to 1993 while mangrove area decreased by 1976 ha during the same period [23], loss of mangrove forest could be attributable to shrimp farming.

The study site was composed of coastal ecosystems (including mangroves) and terrestrial ecosystems, such as paddy field and secondary forest. Anthropogenic activities that were started in the 1960s, particularly shrimp aquaculture, had adversely affected mangroves in the study site. Those activities led to the continuous degradation and deforestation of mangroves, which resulted in significant soil carbon loss [24,25]. There were traces of human activity even in the midst of mangrove forests (Figure 1; NR3, NR4). In NR1 and NR2, which are located near Tungka village, human impact on the mangrove forests was enormous. Due to frequent exploitation, such as tree cutting since the 1980s, those areas were converted into *Acrostichum aureum* dominant fields.

2.2. Soil Sampling and Measurement

In order to characterize OC of a mangrove ecosystem, as well as to assess mangrove OC source and the nature of OC, soil samples were collected from surface and from belowground (Table 1). Sampling and analytical methods were decided *ad hoc* for surface soils along the transect (Figure 1) and for belowground samples via boring survey (Figure 2). A 2500 m long transect was made across different mangrove zones in August 2006 (Figure 1). Eighty-nine surface soil samples were collected from 0 to 5 cm soil depth with a 100 cc stainless steel cylinder (Daiki Rika Kogyo Co., Ltd., Akagidai, Japan) every 20 to 40 meters along the transect. Belowground samples were collected at four sampling points (NR1–NR4) in the mangrove areas along the transect, at a coconut plantation (NR0) and a paddy field (PF) in the terrestrial areas. Sampling was done with Soil Check Simplification Consortium (SCSC) in September 2007. SCSC is a boring machine equipped with an engine, and was developed for collecting undisturbed soil samples from large depths.

Table 1. Purpose of analysis, analytical items, places of soils/sediments sample collection and the methods of sample and analysis.

Purpose	Analytical items	Places of sample collection		Sample collection/ method
		Surface	Belowground	
Characterization of organic carbon (OC)	Three phase distribution	•	•	100 cc cylinder/Volumenometer
	Bulk density	•	•	100 cc cylinder/Cylindrical core method
	Redoxpotential (Eh)	•		Extract pore water *in situ*/Eh meter
	pH	•	•	Dilution/pH meter
	Electric conductivity (EC)	•	•	Extract pore water by centrifuge/Conductivity meter
	Particle size distribution	•	•	Bulk sample/Pipette method
	Leaf analysis	•		Leaf collection and digestion/ICP-MS
OC source	Total C and N	•	•	Bulk sample/NC analyzer
	Total chemical composition	•	•	2 mm sieved sample/X-ray fluorescence
	Radiocarbon dating		•	Shell, sediment/AMS, radiometric-standard method
OC nature	Humic acids	•	•	Soil, sediment/Fraction method

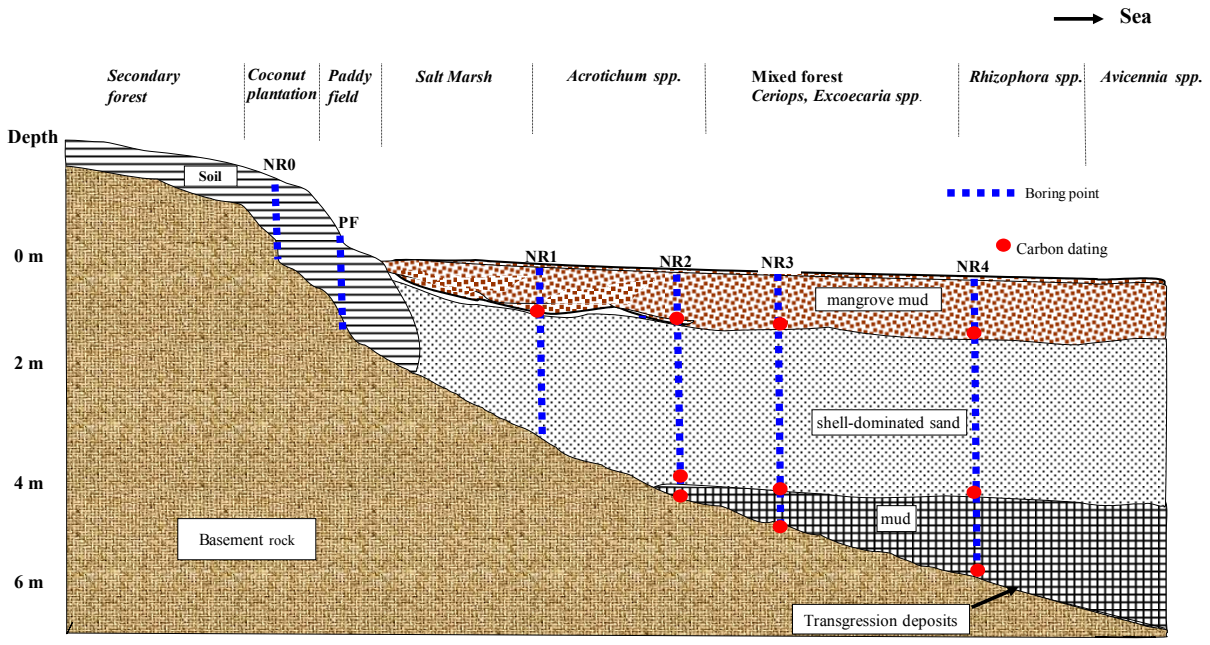

Figure 2. Geologic profile of study site. The mangrove area was composed of three layers: mangrove mud, shell-dominated sand, and mud layers.

Three-phase distribution and bulk density were determined from undisturbed soils removed with the same 100 cc stainless steel cylinder. For the three-phase distribution, solid and liquid phases of soil samples were measured with a volumenometer (DIK-1120, Daiki Rika Kogyo Co., Ltd., Saitama, Japan). After the wet weight was measured, the samples were dried at 105 °C for 3 days, and the weights of the soil samples were measured. Eh was measured *in situ* for extracted pore water, and pH of 1:5 dilutions

of the soil samples was measured in the laboratory with a Horiba D-54 Multi-Parameter Water Quality Meter (Horiba Co., Ltd., Kyoto, Japan).

EC of 0.5 mL of pore water diluted 20 times with distilled water was measured with a conductivity meter (TOA Electronics, Hamburg, Germany, TOA CM305). The direct centrifugation drainage technique was applied to obtain pore water to minimize the risk of contamination [26]. Centrifugation was used to extract soil water at precise time intervals at the matric suction of 1500 kPa. Total carbon and nitrogen were measured by the combustion method at 800 °C using a sumigraph NC-800-13N (Sumitomo-Kagaku Co., Ltd., Tokyo, Japan).

Composite samples were prepared from five samples, each of which were collected at NR0 and PF, and one sample was collected from each of the four layers at NR1–NR4 for the measurement of particle size distribution and X-ray fluorescence analysis. Particle size distribution was determined by the pipette method [27]. For analysis, samples were passed through a 2 mm sieve after drying in an oven at 100–105 °C. Total chemical composition analysis was conducted according to the method of Ochi and Okashita [28] with a XRF analyzer VF320-A (Shimadzu Co., Ltd., Kyoto, Japan) using prepared glass beads. The dried samples were pulverized and homogenized in an agate mortar and used for the XRF bead analysis (Shimadzu Co., Ltd., Kyoto, Japan). Approximately 600 mg of pulverized sample was mixed with 3600 mg of lithium tetraborate ($Li_2B_4O_7$), pre-oxidized at 500 °C with NH_4NO_3, and fused to glass beads [29].

Statistical analysis of measured elements was carried out using Tukey's test (JMP 4.0, SAS Institute Inc., Cary, NC, USA) and differences at the $p < 0.05$ level were considered to be significant.

2.3. Radiocarbon Dating

Radiocarbon dating was performed on two types of samples collected from the four layers at NR1–NR4. One was shell, which was pre-treated by acid etch and then measured by accelerator mass spectrometry (AMS). The shell is an ideal sample because it is an autochthonous fossil that shows accurately the sedimentation time in the area where it is buried [30]. Only a small number of shells could be collected in the sampling. Nevertheless, radiocarbon dating was possible, as AMS required only a few grams of the sample. The other sample was organic sediment, which was pre-treated by acid wash and then measured by the radiometric-standard method, which is widely used in radiocarbon dating. Mangrove colonization time was estimated from the results of radiocarbon dating of the mangrove mud layers previously identified by a stratigraphic survey [4]. Sampling was done at the boundary of each layer in order to know the starting time of formation for each layer (Figure 2).

2.4. Leaf Measurement

Leaves were collected in June 2013 from different vegetation zones in mangrove ecosystems and terrestrial zones. Sampled plant species were sedge (*Cyperus microiria*), *Acrostichum* (mangrove associate), *Excoecaria, Ceriops, Bruguiera, Rhizophora, Sonneratia*, *Avicennia* which were in wetland, and secondary forest (species names were not identified), coconut tree, rice which were in the terrestrial zone. Fifty young leaves were collected from each type of vegetation, as it was reported that fifty was a reliable number for use as bioindicators of heavy metal contamination [31]. The leaves were immediately washed with distilled water to remove adhered matter, and dried. The dried leaves were pulverized by a

mixer to make composite leaf samples. The composite leaf samples were digested by adding 5 mL of conc. HNO_3, and the mixture was left to stand overnight at room temperature for pre-digestion. Thereafter, another 5 mL of conc. HNO_3 was added, and the entire mixture was heated on a hot plate at 75 °C for 0.5 h, 130 °C for 0.5 h, and 200 °C for 2 h. The mixture was filtered through a membrane filter (pore size 0.45 μm), and the filtrate was used as the analysis solution for the determination of macro and micro elements, such as Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, and Fe, by an ICP-MS instrument (Model SPQ 8000A, Seiko Instruments, Chiba, Japan).

2.5. Humic Acid Determination

Humic acids were determined for the mangrove mud layer (NR1, NR2, NR3, NR4 0–5), the shell-dominated layer (NR4 305–310), and the mud layer (NR4 490–495). Six air-dried soil samples collected from each layer (four from the mangrove mud layer and one each from the shell-dominated layer and the mud layer) were used for the analysis. Humic acid components were separated following the fractionation method of Yonebayashi and Hattori [32]. Amberlite XAD-8 resin was pulverized and particles in the 50–200 μm size range were isolated. The sieved particles were washed with ethanol, acetonitrile, ethanol again, and packed into a column (20 cm × 1.8 cm i.d.). The column was conditioned with 0.1 M NaOH and then with the universal buffer adjusted to pH 3 with NaOH solution. Humic acid was dissolved in 0.1 M NaOH and treated with Amberlite IR-120 resin to transform it into the H^+-saturated form, made to 2% solution, and 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 the column at the flow rate of 1.5 $mL \cdot min^{-1}$. The pH of the column eluate was measured with a pH meter. 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 carried out at the flow rate of 1.5 $mL \cdot min^{-1}$. The elution profile was determined by measuring the optical density at 400 nm after the eluate was alkalified to above pH 12 by the addition of 10 M NaOH. Stepwise elution was carried out 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 that of pH-gradient chromatography. Each eluate was precipitated with sulfuric acid and dissolved in 0.1 M NaOH. As the humic acid fraction eluting at pH 7 was not precipitated by acidification, it was subjected to chromatography on a small XAD-8 column at pH 3 using NaOH solution as eluent. Each of the four eluates was dialyzed against distilled water and freeze-dried.

3. Results and Discussion

3.1. Soil/Sediment Properties

Mangrove soil had higher clay content (33.3%) than terrestrial soil (Table 2), and its clay content was almost twice that of PF soil (17.3%). Soil from PF that was converted from mangroves in the 1980s would have contained more clay but became sandy afterwards due to erosion. The shell-dominated layer had high sand content (83%), indicating that this layer was formed near the shore with the deposition of coarse materials. In contrast, the underlying mud layer (silt 23%, clay 35%) was formed offshore with the deposition of fine particles. The mangrove mud layer and the mud layer had almost the same clay

content. However, XRF analysis showed that Mg content in the mangrove mud layer was lower than that of the mud layer (Table 3). This difference indicated that the two layers were formed from different materials. The mud layer was formed mainly from marine deposits whereas the mangrove mud layer formation was influenced by mangrove forest [33,34].

Table 2. Particle size distribution of soils/sediments collected from terrestrial and mangrove ecosystems. In the mangrove ecosystem, sublayers were also examined.

		Sand (%)	Silt (%)	Clay (%)
Terrestrial ecosystem	Coconut plantation	91.4	6.0	2.6
	Paddy	76.6	6.1	17.3
Mangrove	Mangrove mud	48.7	18.0	33.3
	Shell-dominated	83.0	6.0	11.0
	Mud	42.1	23.0	35.0

Table 3. XRF analysis of soils/sediments in terrestrial and mangrove ecosystems.

		Al (%)	Mg (%)	Si (%)	P (%)	K (%)	Ca (%)	Ti (%)	Mn (%)	Fe (%)
Terrestrial areas	Coconut	1.04	2.28	95.54	0.00	0.00	0.20	0.29	0.01	0.62
	Paddy field	6.32	0.20	90.75	0.01	0.80	0.06	0.34	0.01	1.52
Mangrove	Mangrove mud	10.23	0.89	79.41	0.03	1.94	1.28	0.70	0.04	5.49
	Shell-dominated	4.85	1.22	84.29	0.03	1.19	4.53	0.33	0.09	3.47
	Mud	13.64	1.85	73.07	0.06	2.17	2.46	0.81	0.08	5.88

As clay had high carbon capturing capacity [17,35], the high clay content in the mangrove mud layer was responsible for the high carbon sink capacity of the mangrove (Table 4). The mud layer had comparable clay content to the mangrove mud layer, but its carbon content was not high. It was likely that the mud layer received no fresh organic matter (OM) supply and maintained the same OM level that it had in the past.

Table 4. Physical and chemical characteristics of soils/sediments collected from terrestrial and mangrove ecosystems.

Land type and depth (cm)	Air	Liquid (%)	Solid	Porosity	Bulk density (g/mL)	pH	EC (dS/m)	Total-C (%)	Total-N (%)	CN
Secondary forest	24.31	31.87	43.82	56.18	1.12	6.61	2.61	1.244	0.079	16
Coconut plantation										
NR0 0–5	44.43	14.57	41.00	59.00	1.12		3.49	0.382	0.023	17
NR0 50–55	23.71	15.23	61.06	38.94	1.61		0.11	0.104	0.005	21
NR0 85–90	24.38	17.56	58.06	41.94	1.54		0.34	0.030	0.001	30
Paddy field										
PF 0803 0–5	8.36	36.44	55.20	44.80	1.44	4.91	0.48	0.515	0.035	15
PF 0803 10–15	5.59	33.65	60.76	39.24	1.57	4.78	0.23	0.636	0.041	16
PF 0803 20–25	5.30	29.76	64.94	35.06	1.68			0.647	0.026	25
PF 0803 30–35	6.44	29.29	64.27	35.73	1.68			0.270	0.009	30

Table 4. *Cont.*

PF 0803 40–45	8.16	31.23	60.61	39.39	1.59		0.25	0.233	0.006	39
PF 0803 50–55	9.98	30.95	59.07	40.93	1.57		0.41	0.177	0.005	35
Mangrove										
NR1 0–5	18.80	58.17	23.03	76.97	0.56		37.5	9.643	0.620	16
NR1 35–40	7.19	58.58	34.23	65.77	0.89		32.0	2.338	0.091	26
NR1 100–105	6.85	52.58	40.57	59.43	1.10	8.13	31.9	0.485	0.028	17
NR1 145–150	8.29	49.61	42.10	57.90	1.18	8.25	42.0	0.546	0.026	21
NR1 190–195	9.47	41.76	48.77	51.23	1.32	8.31	44.0	0.369	0.011	34
NR1 245–250	3.57	41.01	55.42	44.58	1.51	7.86	56.2	0.440	0.009	49
NR2 0–5	16.88	69.71	13.41	86.59	0.29		40.0	14.234	0.873	16
NR2 40–45	6.62	65.49	27.89	72.11	0.68	4.92	39.8	4.904	0.208	24
NR2 75–80	5.33	67.83	26.84	73.16	0.70	2.99	46.6	3.071	0.116	26
NR2 130–135	4.36	47.37	48.27	51.73	1.28		52.2	0.505	0.021	24
NR2 200–205	6.26	44.89	48.85	51.15	1.32		53.8	0.398	0.017	23
NR2 235–240	5.25	45.56	49.19	50.81	1.33		62.4	0.491	0.016	31
NR2 270–275	2.78	41.86	55.36	44.64	1.47	5.83	61.6	0.303	0.006	51
NR2 330–335	1.14	46.31	52.55	47.45	1.41	5.22	63.2	0.502	0.010	50
NR2 385–390	1.93	60.05	38.02	61.98	1.07	7.81	67.4	1.514	0.044	34
NR2 440–445	0.00	63.55	36.45	63.55	0.98	7.57	67.8	1.648	0.053	31
NR2 500–505	2.30	57.26	40.44	59.56	1.09	8.15	67.4	1.228	0.040	31
NR3 0–5	11.06	65.21	23.73	76.27	0.58		45.0	3.412	0.181	19
NR3 35–40	6.53	64.77	28.70	71.30	0.71	5.39	45.4	4.693	0.160	29
NR3 100–105	4.39	67.35	28.26	71.74	1.00		71.6	1.050	0.048	22
NR3 135–140	6.07	51.24	42.69	57.31	1.14			0.660	0.030	22
NR3 205–210	2.75	50.96	46.29	53.71	1.26		67.2	0.707	0.031	23
NR3 270–275	5.13	42.82	52.05	47.95	1.40	8.23	70.2	0.499	0.014	36
NR3 305–310	6.37	44.69	48.94	51.06	1.33		69.8	0.446	0.014	32
NR3 345–350	2.26	43.40	54.34	45.66	1.45	8.38	69.6	0.358	0.008	45
NR3 380–385	6.13	58.34	35.53	64.47	0.96	8.19	72.6	1.537	0.049	31
NR3 465–470	1.23	58.67	40.10	59.90	1.09		72.2	1.490	0.059	25
NR3 530–535	10.14	36.99	52.87	47.13	1.51	7.63	83.0	0.448	0.019	24
NR4 0–5	15.43	64.60	19.97	80.03	0.48	8.29	39.4	4.842	0.219	22
NR4 45–50	10.95	62.57	26.48	73.52	0.66	5.28	38.3	3.484	0.132	26
NR4 150–155	11.23	53.53	35.24	64.76	0.94	7.71	45.0	0.829	0.032	26
NR4 185–190	7.83	51.20	40.97	59.03	1.07		46.6	1.438	0.060	24
NR4 225–230	10.52	51.12	38.36	61.64	1.04		46.2	1.238	0.059	21
NR4 305–310	8.95	46.17	44.88	55.12	1.21		48.4	0.791	0.024	33
NR4 365–370	4.15	41.72	54.13	45.87	1.43		53.0	0.930	0.018	52
NR4 490–495	4.41	48.36	47.23	52.77	1.25		52.6	1.127	0.022	51
NR4 570–575	4.45	53.06	42.49	57.51	1.16		53.2	0.925	0.023	40
NR4 610–615	0.56	64.05	35.39	64.61	0.97	7.94	52.8	1.272	0.044	29

The low content of alkaline-earth metals such as K, Ca, and Mg meant that terrestrial soil was highly weathered (Table 3). In contrast, K, Ca, and Mg content was high in mangrove soil. This was because of not only the slow weathering due to water inundation, but also the continuous supply of those chemical

elements from mangrove vegetation. PF soil had lower sand content and higher clay content than the coconut plantation soil. This would be related to land management, as PFs were artificially waterlogged for a certain period, and the waterlogged condition suppressed intensive weathering.

The mangrove soil was characterized by a high liquid content and a low solid content (Figure 3). The large proportion of pores that were filled with either water, gas, or air played a major role in the biogeochemical process in the mangrove ecosystem.

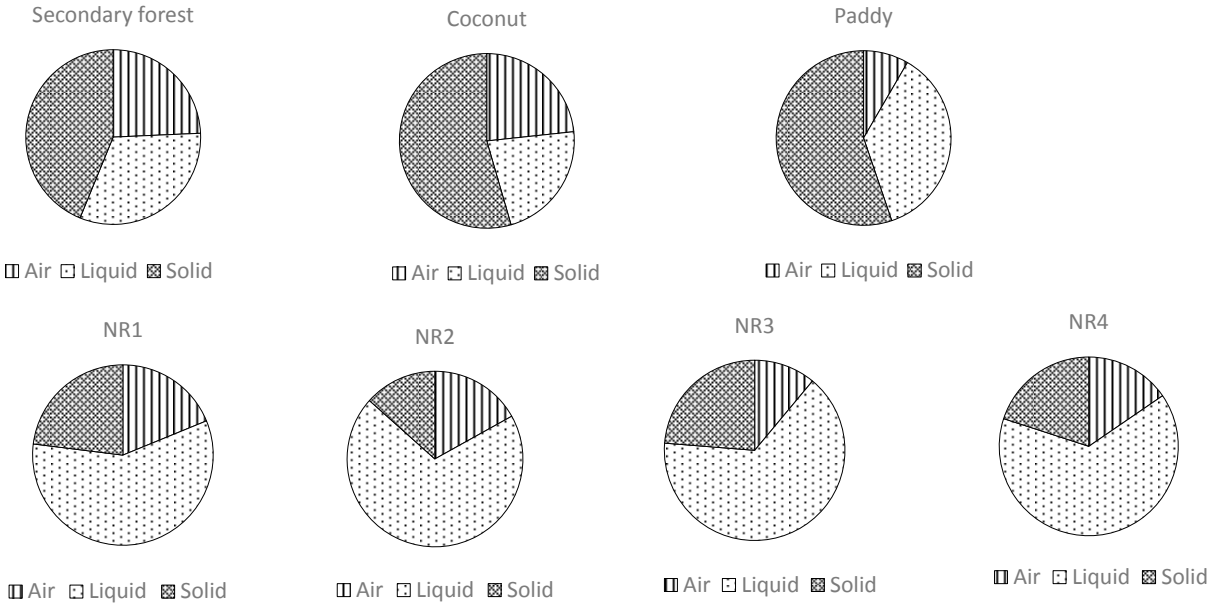

Figure 3. Three-phase distributions of soils collected at 5 cm soil depth from seven places. Top pie charts are for the terrestrial ecosystem (secondary forest, coconut plantation, and PF), and bottom ones are for the mangrove ecosystem.

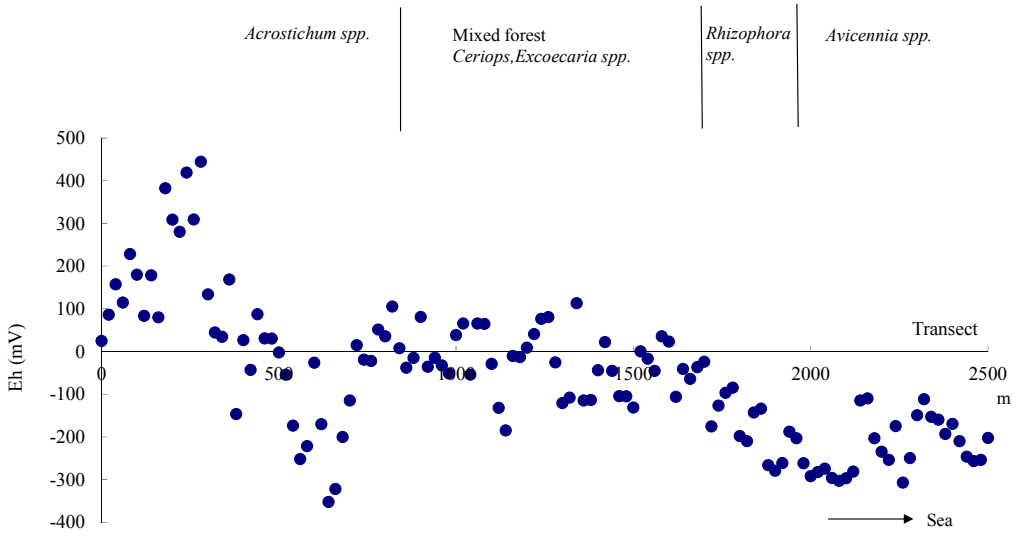

Figure 4. Redox potential (Eh) changes along the transect. Eh decreased towards the sea.

Eh varied markedly in the *Acrostichum* spp. zone (Figure 4). The degradation of OM, which was present at high concentrations in most wetland sediments, was partly responsible for the variation of sediment Eh [36]. The high variability of Eh was attributable to the variable redox state brought about by undulating microtopography, which created different conditions for the degradation of OM by location.

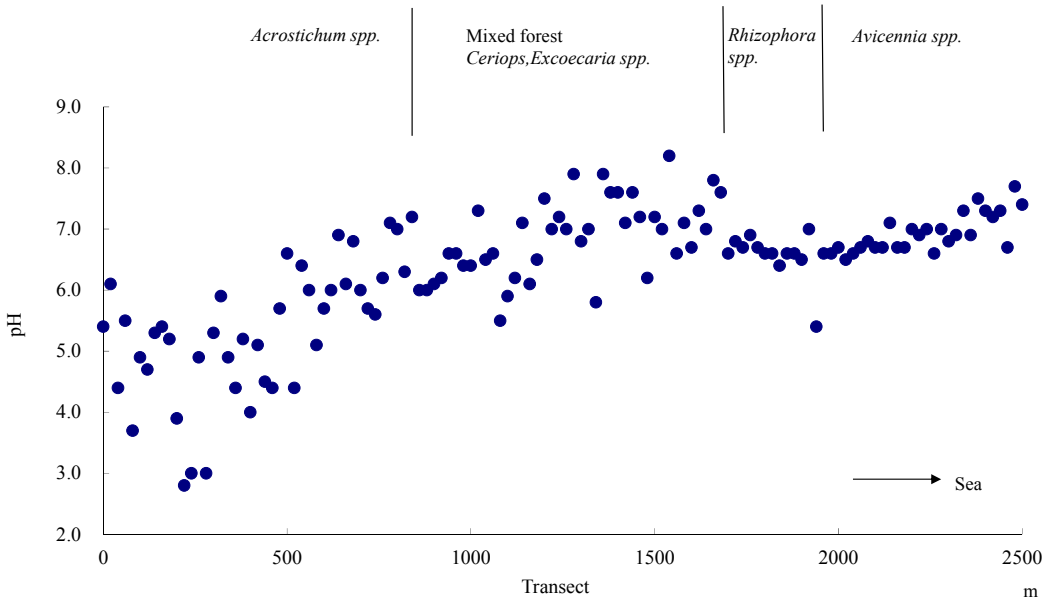

Figure 5. pH changes along the transect. The low pH in *Acrostichum* spp. zone is due to rapid OM decomposition.

Eh was rather low in the area around 600 m from the start of the transect. The rapid oxygen consumption by aerobic microorganisms, which was driven by the high OM content, generated a strong anaerobic condition. pH in the *Acrostichum* spp. zone was significantly different from that of the mangrove zone ($p < 0.01$); the mean pH in the *Acrostichum* spp. zone was 4.67 ($n = 19$) and that of the mangrove zone was 6.08 ($n = 42$). The pH values in the area at 200 m were lower than 3 as a result of the strong acidification (Figure 5). Human disturbance in the form of excavation, which led to soil oxidation, might have caused the generation of extremely acidic soil.

Eh increased slightly in the area around 2300 m in the *Avicennia* spp. zone. Nevertheless, no significant difference was found by statistical analysis. It was reported that Eh was significantly different between the *Avicennia* spp. zone and the *Rhizophora* spp. zone because of the difference in litter composition [37] and in OM decomposability [16]. As the major organic materials entering the coastal ecosystem were plant litter and root exudates, the significant differences in Eh among the areas are related to the differences in mangrove species.

3.2. OC in Surface Soils

Surface soil OC contents were higher in the mangrove areas than in the terrestrial areas (Table 4), implying that the mangrove ecosystem had higher capacity for OM production and storage. At NR2, a sampling point in the *Acrostichum* spp. zone, total carbon content was the highest at 14.2%. NR1, another sampling point in the *Acrostichum* spp. zone, also had high total carbon content, as shown by the mean OC values of 17.6% in the *Acrostichum* spp. zone ($n = 19$) and 5.1% in the mangrove area ($n = 42$) with

a significance level of $p < 0.05$. It was speculated that *Acrostichum* spp. would have the capacity to produce a large amount of OM. Meanwhile, OC content in PF was low. As PF was originally a mangrove before the 1980s, carbon was lost by land use change. A significant amount of carbon might have been lost from the coastal ecosystem, considering that a large mangrove area was converted into shrimp ponds in the study area.

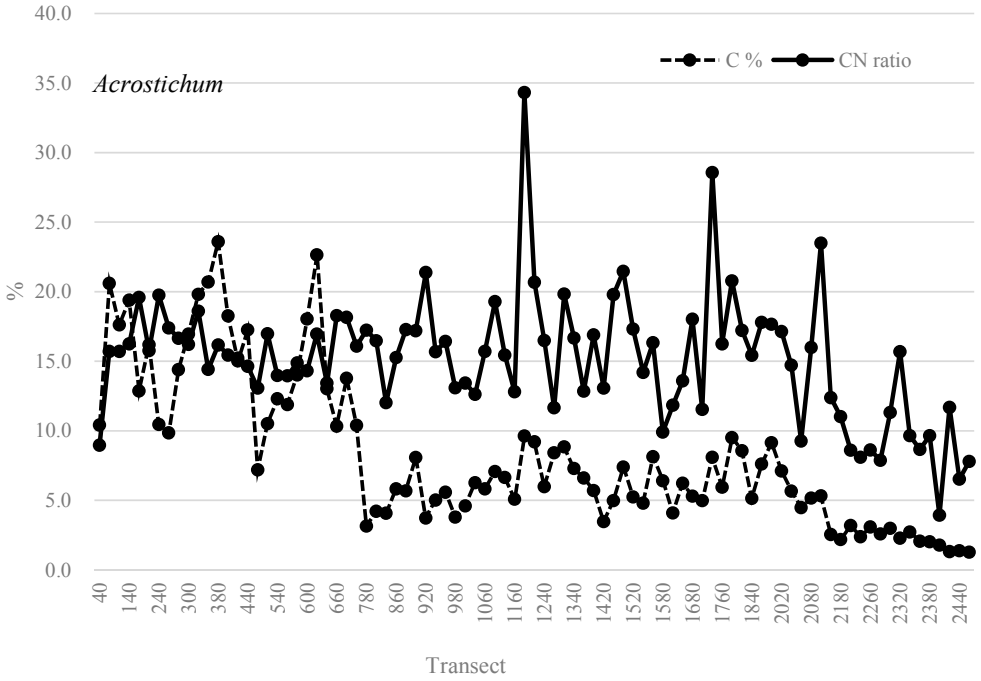

Figure 6. OC contents and C/N ratios in surface soils collected at 5 cm soil depth along the transect. Note that soil from *Acrostichum* spp. zone had high OC content and C/N ratio was low near the shoreline.

The C/N ratio of topsoil decreased seaward (Figure 6), but increased from the upper layer to the lower layer (Table 4). The C/N ratio was often used as an indicator of the source of OM in aquatic sediments. The C/N ratio in aquatic systems was governed by the mixing of terrestrial and autochthonous OM [38,39]. OM derived mainly from plankton had a C/N ratio of 6 to 9 [40,41], whereas OM derived from terrestrial vascular plants and their derivatives in sediments had a C/N ratio of 15 or higher [42,43]. Therefore, the low C/N ratio in *Avicennia* spp. zone could be influenced by carbon originating from biological sources, such as plankton or algae.

Correlation analysis of soil properties was conducted in 74 surface soil samples collected along the transect (Table 5). In the surface soil samples, pH was correlated to C% ($r = -0.66$, $p < 0.01$). Organic acids released by OM decomposition increased acidity. pH was also influenced by the reductive condition (Eh) ($r = -0.58$, $p < 0.01$). The strong correlation between carbon and nitrogen indicated that carbon was the major source of nitrogen. The majority of nitrogen in the soil samples existed in the organic form. After decomposition by microorganisms (mineralization), organic nitrogen was transformed into inorganic nitrogen in the form of NH_4 or NO_3, which are the available forms of nitrogen for utilization by plants. Mineralization provided much of the nitrogen needed to maintain high primary production in mangrove forests [44,45] and salt marshes [46].

Table 5. Correlation matrix of surface soil properties along the transect (n = 74).

	C%	N%	CN ratio	pH	Eh
N%	0.83 *				
CN ratio	0.34 **	−0.09			
pH	−0.66 *	−0.58 *	−0.13		
Eh	0.33 **	0.30 **	0.17	−0.58 *	
EC (ms/cm)	−0.37 **	−0.29 **	−0.20	0.35 **	−0.17

* and ** indicate 1% and 5% levels of significance, respectively.

The relatively weak correlation between carbon and C/N ratio meant that there were a number of carbon sources and different degrees of biological activity. Carbon source would primarily originate from vegetation or plankton, and its decomposability would be affected by both the chemical constituents in OM and the condition of the soil, *i.e.*, its pH and Eh.

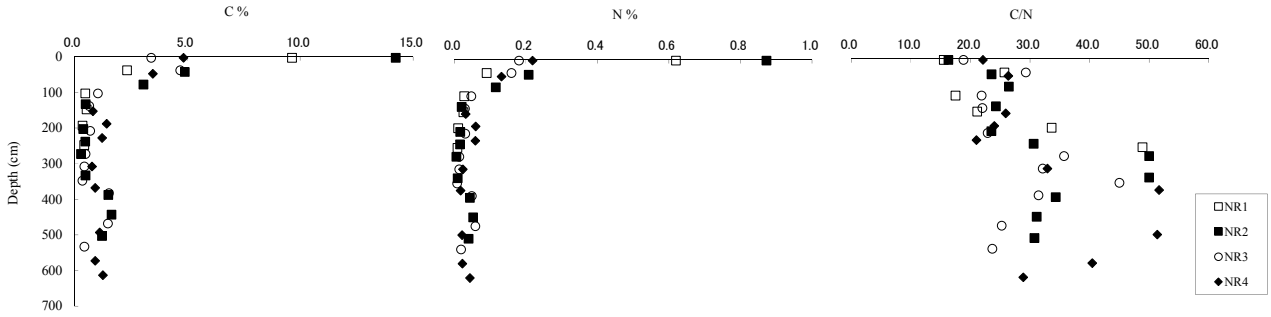

Figure 7. Belowground OC and N contents, and C/N ratios at different depths along the transect. Note that the mangrove mud layer had higher OC content and lower C/N ratio than the other layers.

3.3. Belowground OC and N

Belowground OC contents were higher in the mangrove mud layer than in the other layers (Figure 7), indicating that the mangrove mud layer had accumulated much OM provided by the mangrove forest. OC contents at NR1–NR4 in the shell-dominated layer and the mud layer were identical.

The belowground C/N ratios showed large variations (Figure 7), which were likely due to the difference in sources. The large variation in the shell-dominated layer was due to deposition that occurred nearshore, thereby accumulating different sources, either terrestrial or marine source.

3.4. Leaf Analysis

Chemical element uptake was significantly greater in plants grown under wetland conditions than in those grown under dryland conditions [47]. Compared with the terrestrial ecosystem, Na, P, Mg, and Cl showed greater accumulation in the flooded zone, including the mangrove area (Table 6, Figure 7). An increase of Na content in leaf was noted along the transect (Figure 8). This tendency corresponded to the salt tolerance of mangrove species. Na content in major mangrove species was higher than 15 g/kg, markedly contrasting that of terrestrial plants, which was less than 5 g/kg (Figure 7). The significantly high

Na content in sedge, the dominant plant species in salt marsh, could be due to its selective absorption capacity. Eh and pH gradients played an important role in the mobility and uptake of P and Mg. P became available when pH became alkaline. Therefore, mangrove plants absorbed more P than terrestrial plants.

Table 6. Macro and micro element concentrations (g/kg) determined by leaf analysis.

Vegetation	Na	Mg	Al	Si	P	S	Cl	K	Ca	Mn	Fe
SF 1	1.20	1.29	0.08	0.82	0.16	4.63	12.9	2.54	9.02	1.01	0.23
SF 2	0.15	8.03	0.05	0.77	0.23	7.03	5.4	3.97	10.53	1.70	0.22
Coconut	2.27	2.20	0.05	2.63	0.22	7.92	8.4	3.13	5.30	0.21	0.18
Rice	1.58	0.94	0.02	0.74	0.51	9.52	56.8	14.40	1.79	0.06	0.47
Sedge	29.09	1.18	0.01	0.22	0.23	16.44	125.0	17.21	2.02	0.03	0.14
Acrostichum	8.67	5.02	0.02	0.18	0.25	11.54	39.5	18.56	12.38	0.10	0.11
Excoecaria	2.60	3.02	0.04	0.41	0.32	11.43	45.7	9.85	1.70	0.19	0.25
Ceriops	8.54	9.79	0.06	0.06	0.23	29.14	54.0	6.29	14.08	0.23	0.17
Bruguiera	21.25	8.05	0.07	0.08	0.23	10.84	144.9	5.97	19.48	0.27	0.12
Rhizophora	16.38	7.37	0.34	0.21	0.38	4.61	0.0	8.87	9.54	0.46	0.36
Sonneratia	25.31	6.17	0.07	0.14	0.45	14.18	123.9	7.79	7.73	1.07	0.17
Avicennia	26.59	4.57	0.02	0.10	0.44	7.07	49.0	13.99	5.23	0.27	0.07

SF: Secondary forest.

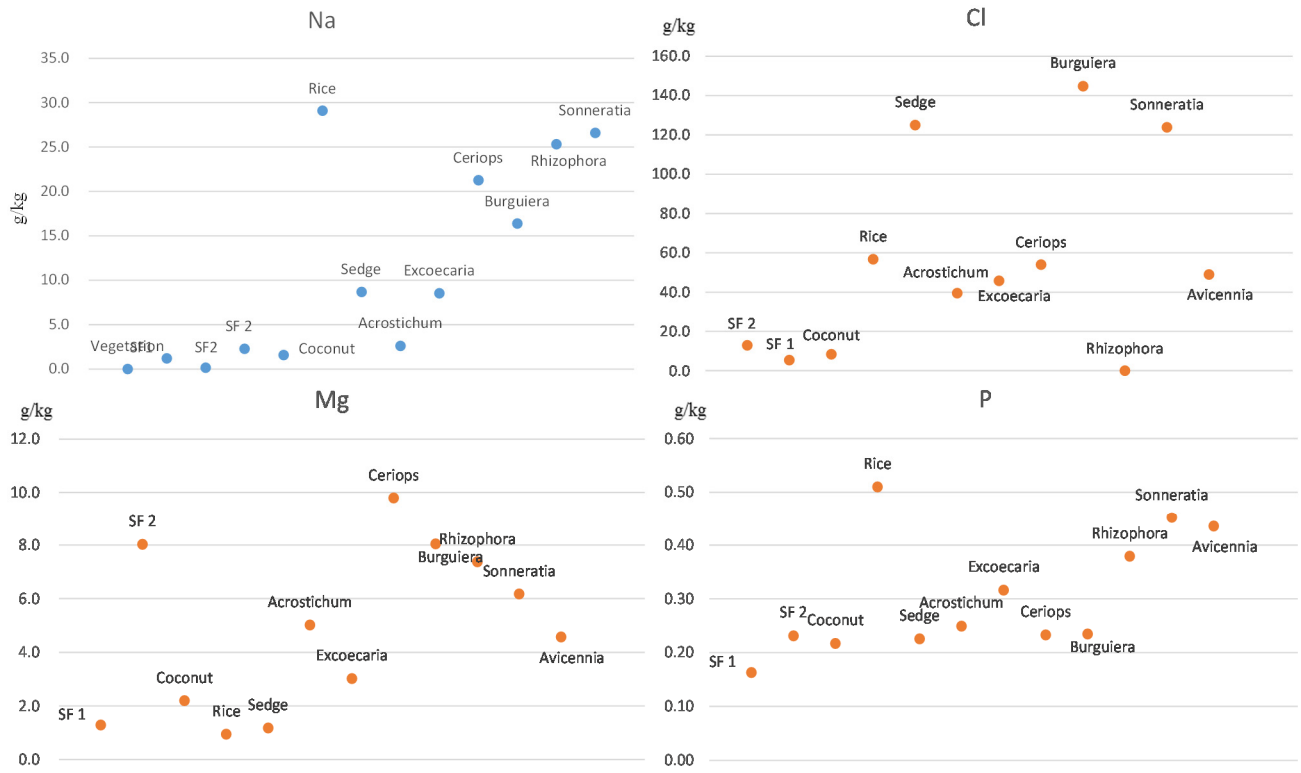

Figure 8. Leaf Na, P, Mg, and Cl contents in different types of vegetation along the transect. SF denotes secondary forest.

Significant differences were noted for particular elements among the three mangrove species. Fe content was high in *Rhizophora* leaf tissues, whereas Al, Mn, and S contents were high in *Avicennia*, *Sonneratia*, and *Ceriops*, respectively. Thus, mangrove species appeared to have uptake preference for elements, and

this might indicate their possible use as ecological indicators for inorganic compound monitoring in mangrove ecosystems.

3.5. Radio Carbon Dating Analysis

The formation of the mud layer started around 6460–7030 ^{14}C years BP, as shown in the radiocarbon dating of mud layer bottom (NR2, 6462; NR3, 7540; NR4, 7030 ^{14}C years BP) (Table 7). As Fujimoto *et al.* [48] reported, the first regression occurred before 7200 ^{14}C years BP in the southwestern coast of Thailand; the mud layer could have been formed during the transgression period.

Table 7. Results of radiocarbon dating analysis.

Site	Layer	Depth *	Type of sample	Measured ^{14}C age (year BP)	δ^{13}C (‰)	Conventional ^{14}C age (year BP)
NR1	Mangrove mud	105–115	organic sediment	1820 ± 110	−25.00	1820 ± 110
NR2	Mangrove mud	100–104	organic sediment	1610 ± 70	−25.70	1600 ± 70
	Shell-dominated	400–404	organic sediment	6020 ± 80	−25.90	6000 ± 80
	Mud	530–540	shell	6070 ± 40	−1.40	6460 ± 40
NR3	Mangrove mud	105–112	organic sediment	1730 ± 100	−24.40	1730 ± 100
	Shell-dominated	385–393	organic sediment	6080 ± 80	−25.90	6070 ± 80
	Mud	535–542	organic sediment	7530 ± 40	−24.20	7540 ± 40
NR4	Mangrove mud	174–176	shell	1020 ± 40	−5.80	1330 ± 40
	Shell-dominated	387	shell	3400 ± 40	1.80	3840 ± 40
	Mud	700–710	organic sediment	7050 ± 40	−26.20	7030 ± 40

* Depth where sample was collected.

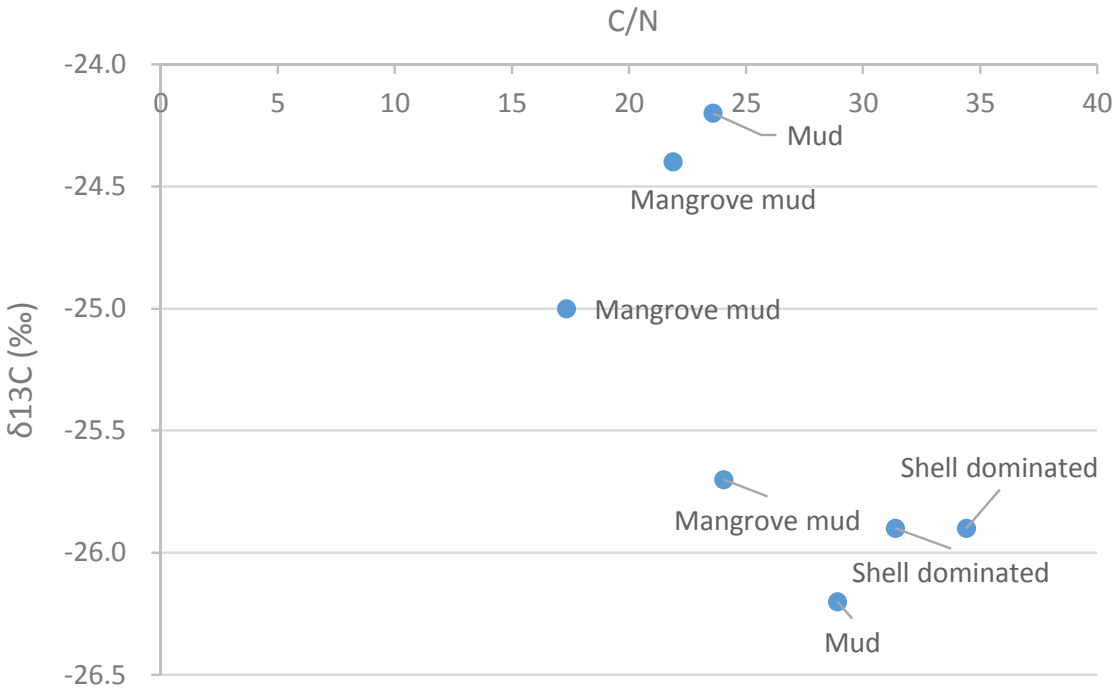

Figure 9. δ13C values and C/N values of soils and sediments in the layers.

The deposition of the organic-rich mangrove mud layer started around 1330–1820 ^{14}C years BP. The sea level started to change around 2200 ^{14}C years BP in the southwestern coast of Thailand [48]. The mangrove mud layer at the study site started to form after those periods.

A comparison of the carbon dating results obtained from different locations in the mangrove mud layer revealed that sedimentation was likely to start earlier inland than offshore. This was in agreement with the idea that the mangrove ecosystem was developing in the offshore direction. The distance between NR1 and NR4 was 2000 m, and their sedimentation times differed by 500 years. By computing those values, it was found that the mangrove would have moved 4 m seaward per year.

Bulk sediment δ13C and C/N values were the result of autochthonous inputs from wetland vegetation and allochthonous sources, such as algae and particulate organic matter [49–51]. δ13C (‰) in organic sediment was between −26‰ and −24‰ (Table 7), which resembled that of terrestrial carbon sources, whose range was between −33‰ and −25‰ [52], and of fresh water phytoplankton δ13C, whose range was between −30‰ and −25‰ [53]. However, δ13C (‰) in the mangrove mud layer varied greatly (Figure 9), which might indicate diverse source, *i.e.*, not only terrestrial but also marine source.

3.6. Humic Acid Determination

The type of humic acid is representative of the deposition environment. Carboxylic humic acid is composed of aromatic compounds that are most likely derived from lignin of vascular plants [54]. It is thought that, during humification, carboxylic acid content in OM increases [55]. Thus, carboxylic acid content can be used as an indicator of the degree of humification.

Carboxylic acid content in the mangrove mud layer ranged from 24% to 52%, and aliphatic content, from 34% to 66% (Table 8). Considering that carboxylic acid content and aliphatic content were generally 76%–95% and 5%–27%, respectively, in terrestrial ecosystems [56], the mangrove OM had not yet progressively humified. Mangrove soils were mostly reductive due to waterlogging, which retarded humification.

Table 8. Compositions (%) of humic acids at different sites and depths.

Site	Depth	Layer	Aliphatic	Phenolic	Carboxylic
NR1		Mangrove mud	38	10	52
NR2		Mangrove mud	66	10	24
NR3		Mangrove mud	36	12	52
NR4					
	0–5 cm	Mangrove mud	34	15	51
	305–310 cm	Shell-dominated	22	11	67
	490–495 cm	Mud	19	12	69

Humic acids at NR2 were characterized by a high aliphatic content, resembling the chemical characteristics of humic acids in sea-bottom or lake-bottom sediments. The high OC production of *A. aureum* (Figure 6) and the reductive condition (Figure 5) might have influenced the buildup of this aliphatic-rich humic composition.

Aliphatic-rich mangrove soils are susceptible to decomposition because they are prone to oxidation [57]. Under the aerobic condition, aliphatic compounds are easily degraded by microbial activity because the

compounds possess a long aliphatic chain in their chemical structures [56]. Land use change, such as the conversion of mangrove into shrimp pond, may cause structural changes in mangrove humic substances. Carbon decomposition will be accelerated by the decrease of moisture regime and the increase of soil temperature. Therefore, it is necessary to study the fate of mangrove OCs in relation to land use change, with water/soil condition monitoring from the viewpoint of humic substances.

Carboxylic acid content was high, and aliphatic content was low in humic acids from the shell-dominated and mud layers at NR4. The increase of the carboxylic acid content and the decrease of the aliphatic content are related to structural changes caused by the humification process. In the event of dehydration, demethylation of the aliphatic components would proceed, increasing carboxylic acid components, which are weathering-resistant components, and hence advancing humification. Sediments in the sublayers, which partly included marine-originating deposits, were mostly transported from the land. Humification of terrestrial OM took place more rapidly because the terrestrial condition was normally drier and aerobic. OM with a high degree of humification was transported from the land and deposited as sublayers; therefore, humic acids in the sublayers had high carboxylic acid content but not aliphatic content. In PF, where water was stagnant in a pond, humification did not occur progressively due to the prolonged wet condition.

4. Conclusions

Surface soil OC content in mangrove stands varied greatly depending on the vegetation type along the 2500 m long transect. The large variations in δ13C and the C/N ratio in surface soil indicated different sources, namely, autochthonous and allochthonous. The pH and Eh gradients were important factors affecting OC stock and the mobility/uptake of chemical elements. P and Mg content in the leaf increased with increasing pH. Mangrove species showed preference for uptake of particular elements. Eh was positively correlated with OC content, and OC content became high when Eh was positive in the *Acrostichum* spp. zone. The significant fluctuation of Eh in the *Acrostichum* spp. zone could be caused by human disturbance in the form of excavation. OC in the mangrove mud layer was characterized by high aliphatic content, indicating that the soils were not yet humified and were susceptible to decomposition.

Acknowledgments

This research was undertaken mostly as part of a Joint Research Project participated by the Department of Marine and Coastal Resources (DMCR), Thailand, Kansai Electric Power Co., Inc., Osaka, Japan, and The General Environmental Technos Co., Ltd. (KANSO), Osaka, Japan, from 1998 to 2007, and partly as an additional study conducted solely by KANSO from 2009 to 2013. The authors are deeply indebted to Emeritus Koyo Yonebayashi, Ishikawa Prefectural University, and Munehiro Ebato, National Institute of Livestock and Grassland Science, for their valuable guidance and advice both in laboratory work and in interpreting analyzed data from humic acid measurement. They also thank the members of Soil Science Laboratory, Kyoto University, for their valuable work in soil physicochemical and leaf analyses.

Author Contributions

Conceived and designed the study: N. Matsui. Perfomed the study: N. Matsui, W. Meepol, J. Chukwamdee. Collection of field data: W. Meepol, J. Chukwamdee. Analyzed the data and wrote the paper: N. Matsui.

Conflicts of Interest

The authors declare no conflict of interest.

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