Depth Profiles of δ^{13}C and Trace Element Concentrations in Mangrove Ecosystem of Tien Hai Natural Reserve, Vietnam

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Abstract—The objectives of present study are to examine the sources of sedimentary organic carbon (SOC) and depth profiles of 12 trace element concentrations (V, Cr, Mn, Co, Cu, Pb, Zn, Mo, Ag, Cd, Sn, and Sb) in a sediment core from mangrove forest of Tien Hai Natural Reserve, Vietnam. The profiles of δ^{13}C and C/N ratio demonstrated that the SOC originated from a mixture of mangrove litters and marine phytoplankton. The relative contribution of mangrove litters ranged from 35.3 to 75.1%, with an average of 49.6%, and gradually increased from the core bottom to surface sediment. The trace elements V, Cr, Mn, Co, Cu, Pb, Zn, Sn, and Sb concentrations increased from core bottom to 50 cm of depth, and then slightly varied to surface sediment. The trace elements Mo, Ag, and Cd concentrations slightly increased between core bottom and 11 cm of depth, and then decreased to surface sediment. The PCA results illustrated that the trace elements from industrial sources have probably impacted on the Tien Hai mangrove area in a long-term, and the high levels of TOC and fine sediment grain sizes were the major mechanisms of trace element absorptions in mangrove sediments.

Keywords: carbon stable isotope, C/N ratio, mangrove, trace elements, sediment core, Tien Hai Nature Reserve

INTRODUCTION

Mangrove ecosystems have high net primary production. As a result, they are considered to be an important sink of organic carbon. Mangrove organic carbon is stored in the above-belowground biomass and sediments. Sedimentary organic carbon (SOC) is composed of autochthonous mangrove plants and allochthonous sources (e.g., terrestrial organic matter and marine phytoplankton). The SOC has been recognized as one of important factor composing the carbon budget of mangrove ecosystems. However, the sources of SOC have rarely been described in detail.

Mangrove sediments are generally homogeneous in texture and rich in organic matter. They act as effective sinks of pollutants (i.e., trace elements) through tidal cycles and river outflows. From the sediment-water interface, trace elements can be transferred into mangrove plants (MacFarlane *et al.*, 2003) and benthic organisms (Saha *et al.*, 2006). Subsequently, they accumulated into higher trophic levels of animals in the local food webs (Jara-Marini *et al.*, 2009). Therefore, the mangrove sediments may shift from sink to source of trace elements in the coastal water systems (Harbison, 1986). The information of trace element concentrations in mangrove sediments is needed to assess the toxicological effects for benthic animals and to evaluate the functioning of mangrove ecosystems in the filtering and containment of terrestrial-derived pollutants.

In this study, carbon stable isotope (δ^{13}C), total organic carbon (TOC), atomic C/N ratios, and 12 trace element concentrations (V, Cr, Mn, Co, Cu, Pb, Zn, Mo, Ag, Cd, Sn, and Sb) were analyzed in a sediment core in order to (1) examine the sources of SOC, and (2) determine the trace element concentration profiles in a mangrove ecosystem from Vietnam.

MATERIALS AND METHODS

Study area

The present work was conducted in an estuarine mangrove ecosystem of Tien Hai Nature Reserve (THNR) in northern Vietnam (Fig. 1). Tien Hai Natural Reserve (THNR) is located in the northern part of the Ba Lat Estuary, Red River, which is the largest river in northern Vietnam. The THNR covers a total wetland area of 12,500 ha, of which about 3,000 ha is covered by mangrove forests. The mangrove species, including *Kandelia obovata*, *Sonneratia caseolaris*, and *Aegiceras corniculatum* are predominant. They provide great ecological and economical values, for example they are essential nursery grounds for many species of fishes, invertebrates, and waterfowl. However, there still remains a major deficiency of information on sources of SOC and trace element concentrations.

Field sampling

The fieldwork was conducted from 2–10 February, 2008 during low tide in the mangrove forest of THNR, Vietnam (Fig. 1). Sediment core (75 cm in length) was taken by a hand corer with a PVC inner tube (1.5 m in length and 10 cm in diameter). The sediment core located at position (20°17′39″ N; 106°36′6″ E). It was assigned as core TH-01, and immediately capped, and maintained cool. It was processed within 12 hours of collection by first removing the outer layers (0.5 cm in thickness) and then slicing into 1 cm interval by a plastic knife. Sediment sections were packed in labeled polyethylene bags for further analysis. A part of sediment sample was also placed in a plastic cube (1 cm^3) for porosity analysis. Samples were immediately stored in iceboxes and transported to the laboratory where they were frozen at –20°C until further processing and analysis.
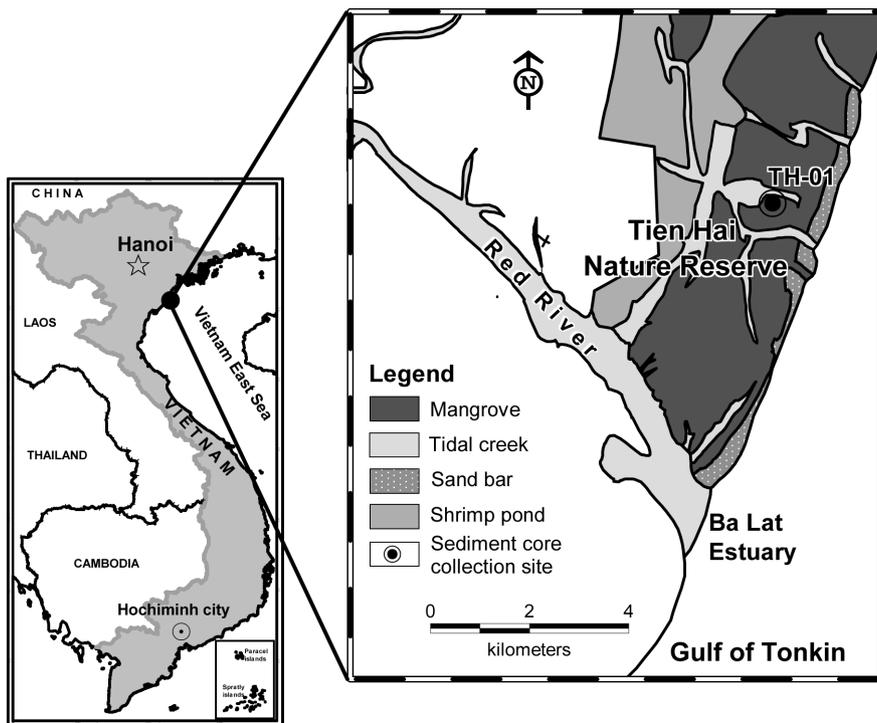
Fig. 1. Sampling sites showing location of sediment core TH-01 within mangrove forest from the Tien Hai Natural Reserve, Vietnam.

Sample analysis

Sediment samples were dried at 60°C for 48 hours in an electric oven and subsequently pulverized using a mortar and pestle. Sediment grain size (Mdφ) was measured by using a laser diffraction particle size analyzer (SALD-2100, Shimadzu Co.) according to the procedure described by Amano *et al*. (2006). The porosity measurement has been described elsewhere (Tue *et al*., 2011a).

For δ^{13}C, TOC, and C/N ratio analysis, sediment samples were processed following the methods of Tue *et al*. (2011a). δ^{13}C, TOC, and C/N ratios were analyzed by using a stable isotope mass spectrometer (ANCA-SL, PDZ Europa, Ltd.). The δ^{13}C was expressed in ‰ (per mil) deviations from the standard value by the following equation (1):

$$\delta^{13}C(‰) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \qquad (1)$$

where $R = {}^{13}C/{}^{12}C$, R_{sample} is the isotope ratio of the sample, and R_{standard} is the
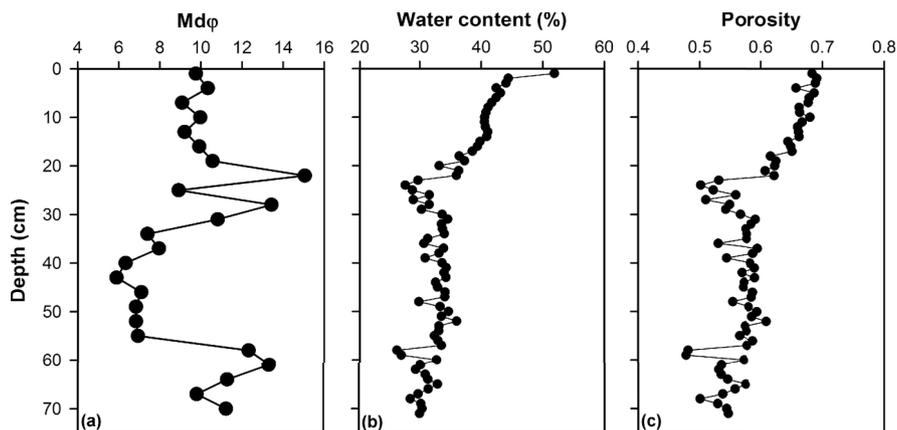
Fig. 2. Depth profiles of sedimentary parameters of sediment core TH-01. Mdφ is sediment grain sizes (μm).

isotope ratio of a standard referenced to Pee Dee Belemnite (PDB) limestone carbonate. The analytical error was ±0.1‰ for δ^{13}C.

The procedure used for measuring trace element concentrations has been previously described (Tue *et al.*, 2011b). Concentrations of 12 trace elements (V, Cr, Mn, Co, Cu, Pb, Zn, Mo, Ag, Cd, Sn, and Sb) were analyzed with an inductively coupled plasma-mass spectrometer (ICP-MS, HP-4500, Avondale, PA, USA) with rhodium as the internal standard. Accuracy and precision of the methods were assessed using the certified marine sediment reference material PACS-2 (National Research Council Canada), and recoveries of all the trace elements ranged from 89.3 to 111.6% of the certified values (Tue *et al.*, 2011b). In addition, triplicate analyses were applied for each sediment sample, and the concentrations of trace elements were displayed by the average values. One half of the value of the respective limits was substituted for those values below the limit of detection.

RESULTS AND DISCUSSION

Sediment characteristics

The sediments of core TH-01 were muddy, and colors were reddish brown, light olivine brown, and grayish brown. They were homogeneous and rich in organic matter. The Mdφ varied between 5.9 and 15 μm, with an average value of 9.9 μm. The Mdφ reached to maxima from 20 to 25 cm of depths, and then decreased to minima from 33 to 56 cm of depths (Fig. 2). The profile of water content was similar to that of porosity. It markedly decreased from surface sediments to 25 cm in depth, then slightly increased to 33 cm in depth, and then decreased gradually to the bottom of the core (Fig. 2). The grain sizes of
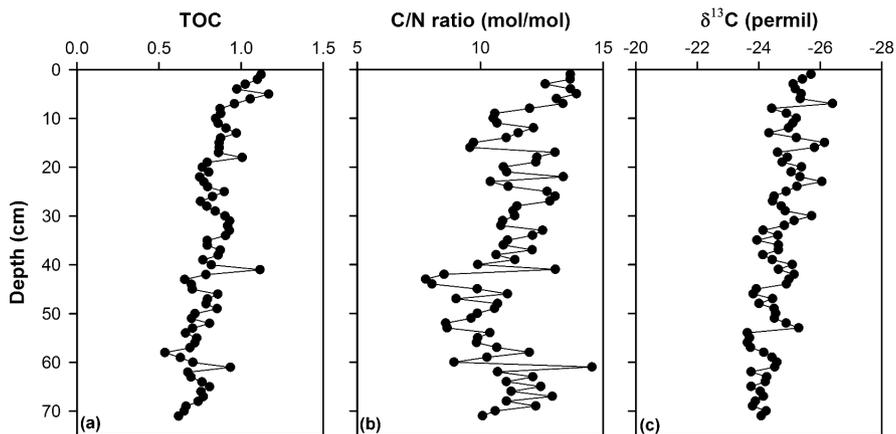
Fig. 3. Depth profiles of TOC (%), atomic C/N ratio (mol/mol), and δ^{13}C of sediment core TH-01.

suspended sediments in Red River varied between 4 and 8 μm in both dry and wet seasons (van Maren, 2007). Thus, the dominant of fine grain size sediments in the entire core indicate that the discharge of Red River and tidal suspended matters were important sources for the long-term sediment accretion in mangrove forest of THNR.

The depth profiles of TOC, C/N ratios, and δ^{13}C and sources of SOC

TOC content varied considerably from 0.54 to 1.17%, with an average of 0.81%. The TOC profile showed a gradual increase from core bottom to surface sediment, and formed three peaks at 5, 41 and 61 cm of depths. The atomic C/N ratios ranged between 7.8 and 14.6, with an average of 11.3. The C/N ratios decreased gradually from 12.2 to 7.8 between core bottom and 43 cm of depth, and then rapidly increased to 13.7 at the surface sediment (Fig. 3). δ^{13}C values ranged from –26.4 to –23.6‰, with an average of –24.6‰. δ^{13}C values gradually increased from the core bottom to surface sediment, and showed the same pattern with the TOC profile (Fig. 3).

The sources of SOC in the core TH-01 were determined by using the atomic C/N ratio and δ^{13}C variations (Tue *et al.*, 2011a). The result showed that the organic carbon in sediment core originated from the mixture of mangrove litter (δ^{13}C: –28.06 ± 1.41‰, C/N: 27.1 ± 10.4, unpublished data) and marine POM (δ^{13}C: –21.18 ± 0.45‰, C/N: 9.8 ± 1.2, unpublished data). A simple mixing model has been applied to calculate the relative contribution of mangrove litters to the sediment cores (Tue *et al.*, 2011a). In present study, the application of the simple mixing model showed that the relative contribution of mangrove litters ranged from 35.3 to 75.1%, with an average of 49.6%. The mangrove contribution gradually increased from core bottom to surface sediment.
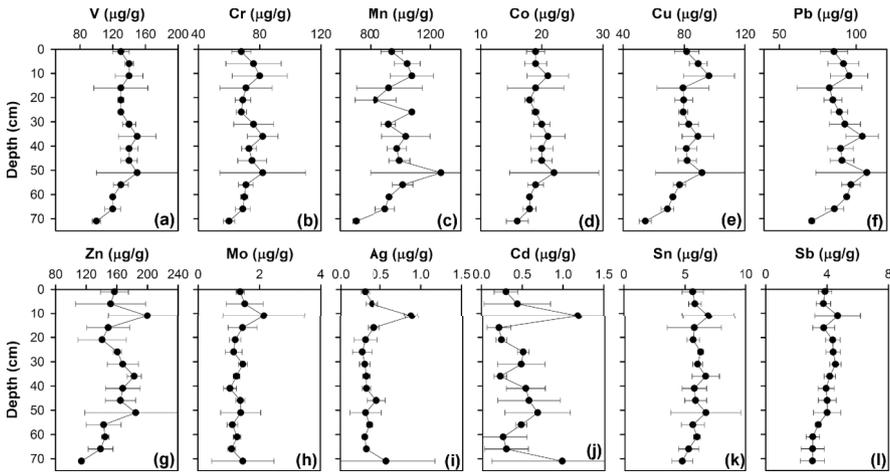
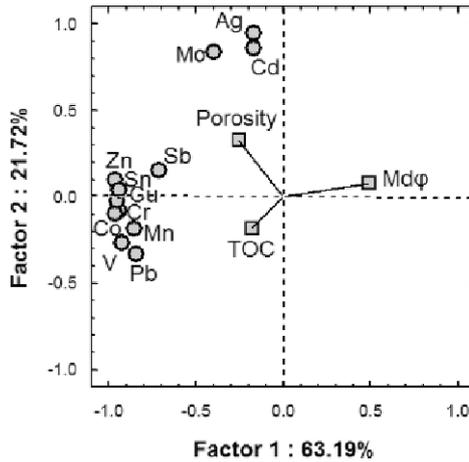Fig. 4. Depth profiles of trace element concentrations (µg/g dry wt.) in sediment core TH-01.

Fig. 5. PCA loading plot of trace elements and environmental parameters (TOC, Mdφ, and porosity) in sediment core TH-01.

Trace element concentration profiles in the sediment core

Trace element concentrations (mean (range) in µg/g dry wt.) were 132.7 (100–150), 72.7 (60–82), 979.8 (705–1270), 19.3 (16–22), 80.3 (54.6–96.1), 90.8 (71.1–107), 158 (114–200), 1.36 (1.05–2.15), 0.39 (0.27–0.88), 0.5 (0.2–1.12), 5.8 (4.7–6.9) and 3.9 (3.1–4.7) for V, Cr, Mn, Co, Cu, Pb, Zn, Mo, Ag, Cd, Sn, and Sb, respectively. The depth profiles of trace element concentrations are

presented in the Fig. 4. The concentrations of trace elements V, Cr, Mn, Co, Cu, Pb, Zn, Sn, and Sb increased from core bottom to 50 cm of depth, and then slightly varied to surface sediment. The concentrations of these elements formed three peaks at 11, 36, and 50 cm of depths. The concentrations of trace elements Mo, Ag, and Cd slightly increased between core bottom and 11 cm of depth, and then decreased to surface sediments.

Principal component analysis (PCA) was applied to interpret relationship between trace element concentrations and environmental parameters (TOC, Mdφ, porosity). As shown in Fig. 5, the core TH-01 was loaded by two principal factors. The first factor accounted for 63.19% of total variance. The loadings of trace elements Co, Cr, Cu, Mn, Sb, Sn, V, Pb, Zn, and Mdφ on the first factor were –0.96, –0.93, –0.96, –0.86, –0.71, –0.92, –0.93, –0.82, –0.97, and 0.49, respectively. The high loading of these trace elements suggested that they likely originated from similar sources (Callaway *et al*., 1998). In addition, the loading of these trace elements is related to TOC, reflecting that these trace elements were correlated and closely bound with TOC. The correlations of trace elements with TOC were consistent with the classical sediment geochemical and environmental studies that TOC generally acts as a trace element carrier. The second factor accounted for 21.72% of total variance. The loadings of trace elements Ag, Cd, Mo, and porosity were 0.94, 0.8, 0.86, and 0.33, respectively. The high loading of Ag, Cd, and Mo on the second factor showed that the local untreated effluents of the urban and industrial sources have probably impacted on the Tien Hai mangrove area in a long-term (Tue *et al*., 2011b). The loadings of these trace elements were related with porosity (Fig. 5). In general, the porosity depends on the grain sizes, the shapes of the grains, the degree of sorting, and the degree of cementation in sediments. In this study, the positive correlation between porosity and trace elements is likely related to change in sediment compositions. As shown in Fig. 5, the Mdφ is negative correlated with trace elements and TOC. This pattern suggested that the finer sediment grain sizes can easier adsorb the trace elements. The very fine sediment grain sizes (i.e., clays) provide larger reactive surface area that can gather the trace elements, and as well as organic matter and hydrous oxides (i.e., iron hydroxides), which in turn may also make the trace element complexes. Moreover, very fine sediment grain sizes like clays which also have a negative surface charge and cation exchange capacities that readily attract trace elements and trace element-carrying substrates (Tam and Wong, 2000). Overall, the combination of effluence-rich trace elements and the high levels of TOC and fine grain sizes were the major mechanisms of high trace element concentrations in mangrove sediments of THNR.

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