



## A multi-proxy study of sedimentary humic substances in the salt marsh of the Changjiang Estuary, China

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### ABSTRACT

To better understand the origin, composition, and reactivity of sedimentary humic substances (HSs) in salt marshes in the Changjiang Estuary, HS samples were isolated from a sediment core that was collected from the Eastern Chongming salt marsh. Chemical and spectroscopic methods were used to analyze the features of these HSs. The results indicate that the studied HSs in the salt marsh sediments are mainly terrestrial-derived and that the sedimentary organic matter (SOM) in the top layer may contain more organic matter from marine sources and/or autochthonous materials due to the dramatic decreasing of the sediment supply as a result of damming. The degradation of labile carbohydrates and proteins and the preservation of refractory lignin components dominate the early diagenetic reactions of SOM in the salt marsh area. The average contents of the carboxylic groups in FAs and HAs are  $11.64 \pm 1.08$  and  $7.13 \pm 0.16$  meq/gC, and those of phenolic groups are  $1.95 \pm 0.13$  and  $2.40 \pm 0.44$  meq/gC, respectively. The content of carboxylic groups increased with increasing depth, while there were no obvious changes in the content of phenolic groups. The average concentration of total proton-binding sites is approximately  $12.5 \mu\text{mol/g}$  sediment for the studied HSs. These values may provide insight into the migration and fate of HS-bound contaminants in sediments and the overlying sea water in the salt marsh areas of the Changjiang Estuary.

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### 1. Introduction

Salt marshes are commonly found in intertidal zones along temperate coastlines throughout the world. They are dynamic regions of coastal environments that are of vast environmental and economic importance. Salt marshes not only have a high net primary production and accordingly are key to carbon and nutrient cycling in estuarine and offshore areas but are also important sources and sinks for a variety of natural and anthropogenic materials (Filip and Alberts, 1994; Williams et al., 1994; Mendonça et al., 2004).

Humic substances (HSs) in salt marsh sediments are considered to be important components in determining the cycling and stabilization of carbon and nutrients as well as the binding ability of inorganic and organic contaminants (Filip and Demnerova, 2007; Clark et al., 2008; Santín et al., 2008). However, compared to

terrestrial and marine environments, relatively little work has been directed toward HSs in salt marshes and estuarine environments. Among the reported studies regarding salt marsh sedimentary organic matter (SOM) or HSs, most of them were carried out in North America (Alberts et al., 1988, 1989; Filip and Alberts, 1994; Wang et al., 2011; Dodla et al., 2012) and Europe (Mendonça et al., 2004; Santín et al., 2008; Ferreira et al., 2013), and only a few studies focus on the salt marshes along the coastlines of China (Zhou et al., 2006, 2007). This limits our understanding of the SOM dynamics in Chinese coastal regions.

The present work is an extension of our previous studies of the HSs in a mangrove-fringed estuarine system in Hainan, China (Zhang et al., 2011, 2013a). In this study, a combination of techniques including elemental analysis, cross polarization magic angle spinning (CPMAS)-<sup>13</sup>C nuclear magnetic resonance (NMR), and potentiometric titrations were used to analyze the features of the sedimentary HSs isolated from a salt marsh site in the Changjiang Estuary to better understand the origin, composition, and reactivity of sedimentary HSs in the salt marshes of the Changjiang Estuary.

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## 2. Materials and methods

### 2.1. Sampling site descriptions

The salt marsh sediments were collected from the Eastern Chongming (CM) exposed tidal wetland, which is the largest island in the Changjiang Estuary, in October 2008 (Fig. 1). The native vegetation communities of the Eastern CM are dominated by *Scirpus mariqueter* in the lower marsh and *Phragmites communis* in the higher marsh (Yang et al., 2008). The sediment core was taken from one lower marsh site, which is inundated during the semi-diurnal tides. The samples were sliced into 4 different depth ranges (0–20, 20–40, 40–60, and 60–80 cm). The average sedimentation rate and the corresponding ages of each layer were measured and calculated as described in our previous work (Jiang et al., 2012). The sediment grain size of the collected samples was analyzed with a laser particle analyzer (LS100Q, Berman, USA).

### 2.2. Extraction and purification of fulvic acids and humic acids

Following sampling, the sediments were kept frozen during transportation and air-dried in the dark prior to extraction. Fulvic acids (FAs) and humic acids (HAs) were extracted according to the procedures established by the International Humic Substances Society (IHSS). Briefly, HSS were extracted with 0.1 M NaOH under a N<sub>2</sub> atmosphere at an extract to sediment ratio of 10:1. The extracted HSS were then separated into FAs and HAs by acidifying the extract to a pH of 1. The HA precipitates were treated with 0.1 M HCl/0.3 M HF several times, and then dialyzed against distilled water. The FAs were purified using an XAD-8 adsorption resin, and the alkaline eluate was passed through an H<sup>+</sup>-saturated cation exchange resin. Subsamples of both the FAs and HAs were freeze-dried for further analysis (Swift, 1996).

### 2.3. The elemental analysis of the whole sediments and the isolated FAs and HAs

The contents of TOC and TN in the whole sediments as well as the elemental compositions (C, H, N and S) of the isolated FAs and

HAs were determined in duplicate using a Vario EL 3 Elemental Analyzer (Elementar, Germany). The elemental oxygen content for the isolated FAs and HAs was calculated by subtracting the percentage of C, H, N, and S from 100% of the base of moisture and ash free. The  $\delta^{13}\text{C}$  (the PDB standard) values were measured in duplicate on a Delta plus XP isotope ratio mass spectrometer (Thermo Finnigan, USA).

### 2.4. Solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) of FAs and HAs

The <sup>13</sup>C NMR spectra were acquired using a Bruker Advance DSX 300 MHz spectrometer equipped with a 4-mm magic angle spinning probe. Each FA or HA sample was packed into a zirconia rotor and spun at 8 kHz during data acquisition (Cook and Langford, 1998). The spectra were acquired using a ramp-cross-polarization pulse sequence with composite pulse TPPM15 proton decoupling and magic angle spinning. The contact time and delay time were 1 ms and 1 s, respectively. The <sup>13</sup>C chemical shifts were externally referenced to the glycine resonance at 176.03 ppm.

### 2.5. Potentiometric titrations of FAs and HAs

The content of the carboxylic and phenolic functional groups in the FAs and HAs was measured by potentiometric acid-base titrations. All titrations were conducted using a computer-controlled PC-titration system (DL50 Automatic Titrator, Mettler Toledo) with a pH electrode (Delta 320). Solutions containing 500 mg/L (1.0 M NaNO<sub>3</sub>) of either FAs or HAs were titrated with 0.1972 M CO<sub>2</sub>-free NaOH solution at 25.0 ± 0.1 °C under a water-saturated atmosphere of argon. More than 100 points were included in each titration from a pH of 3–11, and each sample was titrated in triplicate.

The total organic charge density (Q<sub>TOT</sub>, meq/gC) of each titration point can be calculated by using the electroneutrality equation as described by previous works (Ritchie and Perdue, 2003; Zhang et al., 2013b). The Q<sub>TOT</sub> was plotted against the pH, and the charge curves were fitted with a modified Henderson–Hasselbalch equation (Ritchie and Perdue, 2003):

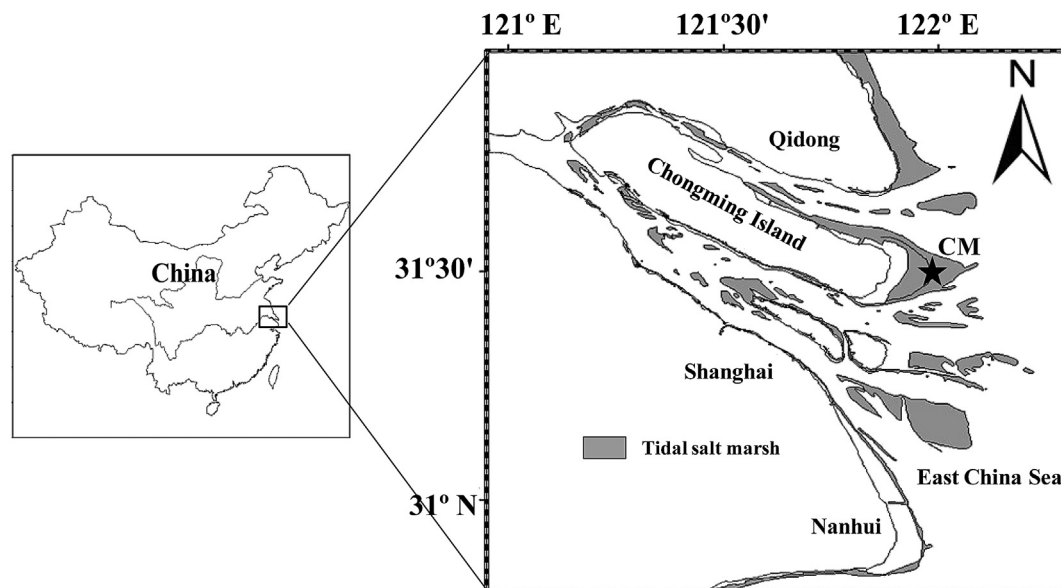


Fig. 1. The sampling location of the sedimentary samples at the Eastern Chongming Island.

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