The sources and accumulation rate of sedimentary organic matter in the Pearl River Estuary and adjacent coastal area, Southern China

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Abstract

In this study, the contents, sources and accumulation rate of sedimentary organic matter (OM) in the Pearl River Estuary (PRE) and adjacent coastal area were investigated.   The stable carbon isotopic composition ($\delta^{13}C$) is a reliable geochemical proxy and was used to indicate the OM origin here.   Nevertheless, the organic carbon and nitrogen molar ratios (TOC/TN) and the stable nitrogen isotopic composition ($\delta^{15}N$) were affected by diagenesis and could be the supplementary indicators.   The sources of OM were estimated based on the two end-member model.   The results showed that in the estuary, sedimentary OM originated from terrestrial and aquatic mixing origins, whereas, OM in coastal sediments was dominantly algae-derived.   The accumulation rate of sedimentary OM was analyzed based on ^{210}Pb dating.   Due to the sampling sites and the distinct hydraulic environments, the accumulation rates of TOC, aquatic and terrestrial OC were obviously higher in the estuary than in coastal area.   TOC accumulation rates were 18-27 mg·cm^{-2}·y^{-1} in the estuary, and 0.84-3.6 mg·cm^{-2}·y^{-1} in coastal area.   Aquatic OC accumulation rates were 7.9-11.3, 0.8-1.3, and 2.6-3.1 mg·cm^{-2}·y^{-1}, and terrestrial OC accumulation rates were 9.7-16.3, 0.02-0.14, 0.16-0.42 mg·cm^{-2}·y^{-1} in core 2, 5, 6, respectively. It could be seen from the high accumulation rate of organic matter in the estuary that, when nutrients increased in the river, phytoplankton biomass and productivity would also have increased.   As a result, phytoplankton sinking and organic matter sedimentation usually increased with primary productivity, resulting in the observed accumulation rate of aquatic OC in the estuary.   Further, terrestrial OC accumulation rates in the estuary and coastal area showed an increasing trend with the age.

Capsule: Estimated the sources and the accumulation rate of sedimentary organic mater in the Pearl River Estuary and adjacent coastal area.

Key words: sediment sources; organic carbon; carbon isotope ratio; accumulation rate of sediments; Southern China; the Pearl River Estuary

1. Introduction

The estuarine and coastal waters are dynamic regions receiving carbon inputs derived from both terrestrial and aquatic origins. Organic matter (OM) in estuarine and coastal sediments is of great significance to the biogeochemical cycling of C, N, P and S, primary productivity and ecosystems in the water column. The storage of organic carbon (OC) in coastal sediments is a major pathway for the transport of OC from the biosphere to geosphere and helps modulate the global carbon cycle (Walsh et al., 1981). Therefore, the origin of OM receives more attention. Various geochemical proxies have been developed and used to study the origin, the transport and transformation of OM, including stable carbon and nitrogen isotopic composition (δ^{13}C and δ^{15}N) and contents of OC, N (TOC/N ratio) (Nakatsuka et al., 1997; Graham et al., 2001; Goñi et al., 2003; Jia and Peng, 2003; Callahan et al., 2004; Ogrinc et al., 2005; Usui et al., 2006; Volkman et al., 2008), and biomarkers (Oldenburg et al., 2000; Ogier et al., 2001; Seki et al., 2006).

The Pearl River is the largest river in Southern China, and empties into the South China Sea through eight outlets named Humen, Jiaomen, Hongqimen, Hengmen, Modaomen, Jitimen, Hutiaomen and Yamen. The Pearl River Estuary (Lingding Bay) is created by the inflows of freshwater from the Pearl River to the South China Sea through four major discharge outlets namely Humen, Jiaomen, Hongqimen, Hengmen (Fig.1). The Pearl River Estuary (PRE) is a north-south bell-shaped area, with the distance from north to south averaging about 49 km, and from east to west varying from 4-58 km. With the rapid development of economy and urbanization in recent years, the Pearl River delta region has experienced increasing human influences and a growing pressure on the local environment. Increasing amounts of wastewater and other pollutants have discharged into the PRE without proper treatment, which has had a significant impact on the aquatic environment. Estuarine sediments are recognized as an important sink for a wide range of nutrients. The annual flows from the Pearl River to the South China Sea are approximately 300-325 billion m^3·y^{-1} (Ip et al., 2004), which maybe causes the increase of the export fluxes and the accumulation rate of sedimentary OM in the estuarine area. Superfluous terrestrial inputs from the Pearl River have resulted in deteriorating water quality and coastal eutrophication such as more than 100 red tide events since 1970s (Qian and Liang, 1999). In this study, our objectives were (1) to estimate the contents and sources of sedimentary OM, and (2) to investigate the accumulation rate of sedimentary OM in the Pearl River Estuary and

1   adjacent coastal area.

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3   **2. Materials and methods**

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5   *2.1. Sample collection*

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7   The sediment cores were collected in spring 2003 using a multiple corer with a volume of

8   overlying water.　Sediment cores 1, 2, 3, 4 were within the sub-tidal zone with strong freshwater

9   and marine water interactions (Wong et al., 1995), and the estuarine plume of the

10   freshwater-seawater mixture flows along the west part of the estuary due to the Coriolis effect

11   deflection.　Core 5 and 6 were located in the adjacent coastal area beyond the Pearl River

12   Estuary (Fig.1).　The sediment cores were sliced at 1cm intervals and stored in glass jars

13   (acid-washed and baked at 550 °C) filled with Ar gas and frozen at -20 °C until analysis.

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Fig.1

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17   *2.2. Elemental and isotopic analysis of sedimentary OM*

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19   The sliced samples were freeze-dried and used to analyze total organic carbon (TOC), total

20   nitrogen (TN) and isotopic composition after being acidified with 1.5 mol·L^{-1} HCl to remove

21   inorganic carbon.　TOC and TN contents of bulk samples were analyzed using a Vario EL-III

22   CHN analyzer, with the combustion temperature being set at 960°C.　The precisions of duplicate

23   analyses of samples were ±2% and ±3% of the mean for TOC and TN, respectively.　Stable

24   carbon and nitrogen isotopic compositions were determined with a DELTA^{tlus}XL isotope ratio

25   mass spectrometer, and expressed in the delta notation ($\delta^{13}C$ and $\delta^{15}N$) relative to Vienna PDB

26   and atmospheric nitrogen, respectively.　The precision of duplicate analyses was 0.2‰ for $\delta^{13}C$

27   and 0.3‰ for $\delta^{15}N$.

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29   *2.3. ^{210}Pb dating*

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31   The ^{210}Pb activity in sediment core was determined by analysis of α- radioactivity of its

1   decay product ^{210}Po (Jia and Peng, 2003).   The Po was extracted, purified, and self-plated onto

2   silver discs at 75-80ºC in 0.5 mol·L^{-1} HCl, with ^{209}Po used as yield monitor and tracer in

3   quantification.   Counting was by computerized multi-channel α-spectrometry with gold-silicon

4   surface barrier detectors.   Supported ^{210}Pb was obtained by indirectly determining α-activity

5   concentration of the supporting parent ^{226}Ra, which was carried by coprecipitated $BaSO_4$.

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7   *2.4. Chronology and evaluation of the accumulation rate of sedimentary OM*

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9   In a Constant Initial Concentration Model (CIC) based on Kang (1986), the radioactivity of

10   excess ^{210}Pb (^{210}Pb$_{ex}$) could be expressed as:

11   $N_t = N_o e^{-\lambda t}$ (1)

12   N_t: radioactivity of ^{210}P$_{ex}$; N_o: initial radioactivity of ^{210}P$_{ex}$; t: age; λ: decay constant of ^{210}Pb

13   (0.031 y^{-1}).

14   If the sedimentation rate is S (cm·y^{-1}) at the depth of H (cm), the corresponding age should be

15   $t = H/S$.   (2)

16   N_H meant the radioactivity of ^{210}P$_{ex}$ at the depth of H.   Then we could get the equation (3)

17   combining (1) and (2):

18   $N_H = N_o e^{-\lambda H/S}$ (3)

19   ^{210}Pb$_{ex}$ data in each sediment core were exponentially fit, then the average sedimentation

20   rate could be gotten from equation (3).   The age at the depth of H (Y_H) could be calculated as:

21   $Y_H = Y_t - H/S$ (Y_t was the year doing this analysis).   The average accumulation rate (F_s) of the

22   sediment core could be calculated by the equation:

23   $F_s = S \cdot \Phi$ (4)

24   Φ was the drying density of sediment.

25   Further, the equation $F_x = C_x \cdot F_s$ was used to estimate the accumulation rate of OC.   The

26   subscripting x represented the OC (TOC, terrestrial or aquatic OC), F_x was the accumulation rate,

27   and C_x was the proportion of OC to the bulk sediment.

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29   **3. Results**

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3.1. Distribution of organic carbon, nitrogen and stable carbon and nitrogen isotopic composition

Vertical profiles of geochemical variables in sediment cores showed that TOC varied between 0.71% and 1.60%, 0.35% and 0.68% in the samples from the PRE and coastal area, respectively, and generally decreased seaward with the distance from river outlets (Fig.2). TOC contents in the upper layers of the cores were higher and more variable than in deeper layers in the estuary, whereas, in coastal sediments, TOC changed relatively slightly with depth (Fig. 2a). TOC/TN molar ratios were higher in the estuary (8.1~17.2) than in coastal area (4.1~7.1). It was noticeable that TOC/TN increased with the distance from the river outlets inside the estuary (Fig. 2b). $\delta^{13}C$ showed to be relatively negative ranging from -25.19‰ to -23.33‰ in the estuary, and prominently increased in coastal sediments (-21.75‰~-21.04‰, Fig. 2c). $\delta^{15}N$ changed from 3.73‰ to 6.57‰ in the estuarine and coastal samples, and seemed to decrease and become more variable with the depth in most cores (Fig. 2d).

Fig.2

3.2. Calculation of accumulation rate of the sedimentary OM

We selected core 2, 5 and 6 to be the representatives from different hydraulic environments in the estuary and coastal area. Core 2 located in the west shoal of the estuary and near the river mouths well represented the estuarine environment. The three short cores failed to go deep enough, and could not extend to the boundary layer of $^{210}Pb_{ex}$=0. The activity of $^{210}Pb_{ex}$ in core 2 and core 6 generally exponentially attenuated with depth. However, there was a lower value in the surficial sediment of core 5, which was excluded from the processing. The exponential fitting correlations were, $y = 3.6678e^{-0.0143x}$ (core 2), R^2= 0.6011; $y =5.6151e^{-0.1076x}$ (core5), R^2= 0.9491; and $y = 6.87e^{-0.0449x}$ (core 6), R^2= 0.8436, respectively. The average sedimentation rates were calculated as 2.21 (core 2), 0.29(core 5), and 0.69 cm·y^{-1}(core 6), respectively. The year of each sediment layer was calculated according to the average sedimentation rate. And the average accumulation rates of the sediment cores could be gotten as 1.68 (core 2), 0.24 (core 5), 0.53 (core 6) mg·cm^{-2}·y^{-1}, respectively. The activities of $^{210}Pb_{ex}$ were plotted versus age and shown in Fig.3.

Fig.3

4. Discussion

4.1. The sources of sedimentary OM

TOC% was obviously higher in the estuary than in coastal area, and showed a decreasing trend with the distance from the river mouths.   This suggested that the sampling location near the river outlets was more affected by the river terrestrial organic matter, and the influence became weak downstream, which could be indicated by the increase of $\delta^{13}C$ values.   The increasing TOC/TN values inside the estuary weren't consistent with the $\delta^{13}C$, which maybe was attributed to the influence of diagenesis (the preferential loss of OM-bearing N), on the other hand, the decrease of bound inorganic nitrogen. $\delta^{13}C$ values of coastal sediments (core 5 and 6, avg. −21.6‰) were slightly lower than that of the phytoplankton (−20.9‰, Chen et al., 2008) in this area. $\delta^{15}N$ ranged between 3.7‰ and 6.6‰ in the estuary and coastal area, with an average of 5.2‰, which was 3.1‰ below the value of the phytoplankton in this area (8.3‰, Chen et al., 2008).   So diagenesis maybe affected the chemical and isotopic compositions of OM, especially to the TOC/TN and $\delta^{15}N$ (Andrews et al., 1998; Yamamuro, 2000; Raymond and Bauer, 2001; Schubert and Calvert, 2001; Papadimitriou et al., 2005; Dai and Sun, 2007; Chen et al., 2008), whereas, such fractionation was much smaller than sources differences for $\delta^{13}C$ (Zhang et al., 2007).   If TOC/TN and $\delta^{15}N$ could indicate OM origin exactly, the negative correlations should be shown between $\delta^{13}C$ or $\delta^{15}N$ and TOC/TN (Graham et al., 2001; Wu et al., 2002).   Seen from Fig.4, the negative correlation maybe occurred between $\delta^{13}C$ and TOC/TN (R^2=0.505), whereas, it lacked between $\delta^{15}N$ and TOC/TN (R^2=0.015).   Adding the lack of correlation between $\delta^{13}C$ and $\delta^{15}N$ (R^2=0.212), it could be conjectured that $\delta^{15}N$ and OC/N couldn't be used as the reliable evidences indicating the origin and the fate of OM in this study.

Fig.4

OM produced from atmospheric CO_2 on land has average $\delta^{13}C$ value of ≈-27‰ and -14‰ for C_3 and C_4 plants, respectively.   OM produced from aquatic bicarbonate by algae has $\delta^{13}C$ values of between -22‰ and -20‰ (Meyers, 1997; Jia and Peng, 2003).   That makes $\delta^{13}C$ a perfect ruler to distinguish the terrestrial and aquatic origin.   The C_4 plants are minor in the Pearl

River drainage area, where the natural ecosystem is subtropical forest and the dominant cultivated plant is rice (a C_3 plant). Consequently, the C_4 plant contribution to the sedimentary OM could be neglected in this study (Jia and Peng, 2003). The sources of organic matter maybe were attributed to river input, atmospheric input, marine transport et al. In this area, river input and aquatic algae origin were taken into account generally (Jia and Peng, 2003; Hu et al., 2006). Previous study in this area showed that the $\delta^{13}C$ of the terrestrial organic matter imported by the Pearl River was −27‰ (Hu et al., 2006), and the $\delta^{13}C$ of the phytoplankton was −20.9‰ (Chen et al., 2008). $\delta^{13}C$ values of core 1, 2, 3, 4 (avg. -24.36‰) were almost between -27‰ and -21‰, suggesting that the OC originated from the mixing of terrestrial and aquatic origins. In comparison, $\delta^{13}C$ values of core 5 and 6 were slightly lower than that of phytoplankton and significantly higher than that of terrestrial OC, maybe indicating that the sedimentary OC mainly algae-derived. We attempted to assess the origin contribution of terrestrial organic matter and algae based on the two end-member mixing model (equation 5, Andrews et al., 1998), and the results were illustrated in Fig.5.

$$\delta^{13}C = F_T\delta^{13}C_T + F_A\delta^{13}C_A \qquad (5)$$

$\delta^{13}C$, $\delta^{13}C_T$ and $\delta^{13}C_A$ represented the carbon isotopic composition of the sample, terrestrial and aquatic end-member, respectively. The proportion of terrestrial OM was F_T and that of aquatic OM was $1- F_T$.

Fig.5

The contents of terrestrial OC in the estuary were much higher than that in coastal area (core 5 and 6, with similar values). Terrestrial organic matter deposited mainly in the west shore due to the Coriolis force, which contributed to the high terrestrial OC in estuarine cores. However, river influence became weak downstream with the distance from the outlets, as the contents of terrestrial OC in estuarine sediments were 0.70, 0.68, 0.58 mg·g^{-1} for core 1, 2, 3 downstream. The contents of aquatic OC were 0.48, 0.59, 0.58 mg·g^{-1} for core 1, 2, 3, respectively. The lowest aquatic OC in core 1 was consistent with the results from Hu et al (2006). Namely, the aquatic OC increased with the distance from the river mouths. It is known that spatial distribution in algal biomass and production in an estuary is regulated by river flow, light, and mixing induced by tidal cycles and winds (Cloern, 1996). The rapid river flow near the river mouth resulted to high current and turbidity, and didn't allow algal biomass to be accumulated, so it is expected that there will be a

limited primary production.   Therefore, there is often a downstream progression of phytoplankton biomass and production along the estuarine coastal plume, for example, in the Mississippi River-Northern Gulf of Mexico (Lohrenz et al., 1997) and the Yangtze River Estuary-East China Sea (Gong et al., 1996).   It was noticeable that in core 4, the contents of terrestrial and aquatic OC (0.64 and 0.39 mg·g^{-1}) weren't consistent with the trend of others, which maybe were attributed to the intense interaction of river water and seawater due to the geographical location.   The aquatic and terrestrial OC of the coastal sediments were 0.48 mg·g^{-1} (93%) and 0.05 mg·g^{-1} on average respectively, showing the dominance of aquatic OC.   By comparison, the average proportion of aquatic OC to bulk OC in the estuarine sediments was 45%.

4.2. The accumulation rate of sedimentary OM

     The particulate organic matter (POM) in the water column deposited to the water-sediment interface would be decomposed and resuspended.   Only a small proportion of POM was buried into the sediment as refractory OM.   The accumulation rate here meant the quantity of the OM buried into the sediment in unit time and area.   The accumulation rate of aquatic phytoplankton OM reflected the change of primary productivities, and that of terrestrial OM reflected the change of transport flux.   Based on the average accumulation rate of each sediment core and the proportions of OC to the bulk sediment, the accumulation rates of TOC, terrestrial and aquatic OC were calculated and shown in Fig.6.

Fig.6

     TOC accumulation rates were 18-27 mg·cm^{-2}·y^{-1} in the estuary, and 0.84-3.6 mg·cm^{-2}·y^{-1} in coastal area.   Terrestrial OC accumulation rates were 9.7-16.3, 0.02-0.14, 0.16-0.42 mg·cm^{-2}·y^{-1} in core 2, 5, 6, respectively.   The accumulation rates of TOC and terrestrial OC were obviously higher in the estuary than in coastal area due to the sampling sites and the distinct hydraulic environments.   In addition, core 2 with more available values showed an abrupt high datum in the surficial sediment with a high content of TOC, maybe indicating the environment change, that is to say, an abrupt increase of terrestrial nutrient recently.   Aquatic OC accumulation rates were 7.9-11.3, 0.8-1.3, and 2.6-3.1 mg·cm^{-2}·y^{-1} in core 2, 5, 6, respectively.   The aquatic OC accumulation rate in the estuary was also higher than that in coastal area, suggesting that when

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nutrients increased in the river, phytoplankton biomass and productivity would also have

increased.　As a result, phytoplankton sinking and organic matter sedimentation usually

increased (Parsons et al., 1984).　TOC accumulation rate of core 6 showed a slight increasing

trend with the age, and terrestrial OC accumulation rates in core 5 and 6 also increased with age,

suggesting an influence of terrestrial nutrient imported by river in recent years.　Homoplastically,

In the work of Jia and Peng (2003), the sediment core in the estuary (near Honqimen river mouth)

under a high energy environment had the TOC accumulation rate changing from 4.5 to 31.5

mg·cm^{-2}·y^{-1} upcore from 1877 to 1997.　That showed the increase of TOC accumulation rate

with the age, especially a rapid increase in the last decades of the 20th.　In our study, estuarine

sediment core 2 showed the apparent high TOC accumulation rate, which was consistent with the

high values in the work of Jia and Peng, even if core 2 was sampled for only more than a decade

(about 1991-2003).　That might indicate the increasing nutrient imported by river during the

period of the end of 20th and the beginning of 21st in this study.

　　　In addition, an examination of the geographical locations of cores 5 and 6 suggested that

more terrestrial OM would be deposited at core 5.　However, the TOC, terrestrial and aquatic OC

accumulation rates were higher in core 6 than in core 5.　Previous work (Hu et al., 2006)

demonstrated that the fine-grain sediment in core 6 accounted for 91.9%, whereas 86.6% in core 5,

indicating that more coarse-grain material containing less OC deposited in core 5.　Consequently,

the OC concentration in core 5 was diluted.　Further, core 5 recorded about 100 years, and OC

accumulation rate kept lower and stable (TOC accumulation rate of 1.02 mg·cm^{-2}·y^{-1}), suggesting

a stable deposition environment.

5. Conclusions

　　　δ^{13}C is a reliable geochemical proxy indicator of organic matter origin in the study area,

based on which, the sources of sedimentary OM was estimated using the two end-member model.

Results showed that in the estuary sedimentary OM derived from terrestrial and marine mixed

origins, whereas, OM in coastal sediment was dominantly algae-derived.　Accumulation rate of

TOC, aquatic and terrestrial OC were obviously higher in the estuary than in coastal area due to

the sampling sites and the distinct hydraulic environments.　The high accumulation rate of

terrestrial OC in the estuary indicated the increasing of nutrients in the river, then phytoplankton

biomass and productivity would also have increased.   As a result, phytoplankton sinking and
organic matter sedimentation usually increased with primary productivity, resulting in the
observed accumulation rate of aquatic OC in the estuary.   TOC and terrestrial OC accumulation
rates in the estuary and coastal area showed an increasing trend with the age, indicating the
influence of nutrient imported by Pearl River in recent years.

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11   **Lists of Figures**

22

23

24

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1

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39   Fig.1. Map showing the location of the Pearl River Estuary and the sampling sites of sediment cores

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TOC/ %

0.2　　　0.6　　　1　　　1.4　　　1.8

0

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Depth/cm

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30

40

50

a

1 ····◆···· 2 —◇— 3 – – 4 —■— 5 —△— 6

TOC/TN

0　　　5　　　10　　　15　　　20

0

10

Depth/cm

20

30

40

50

b

1 ····◆···· 2 —◇— 3 – – 4 —■— 5 —△— 6
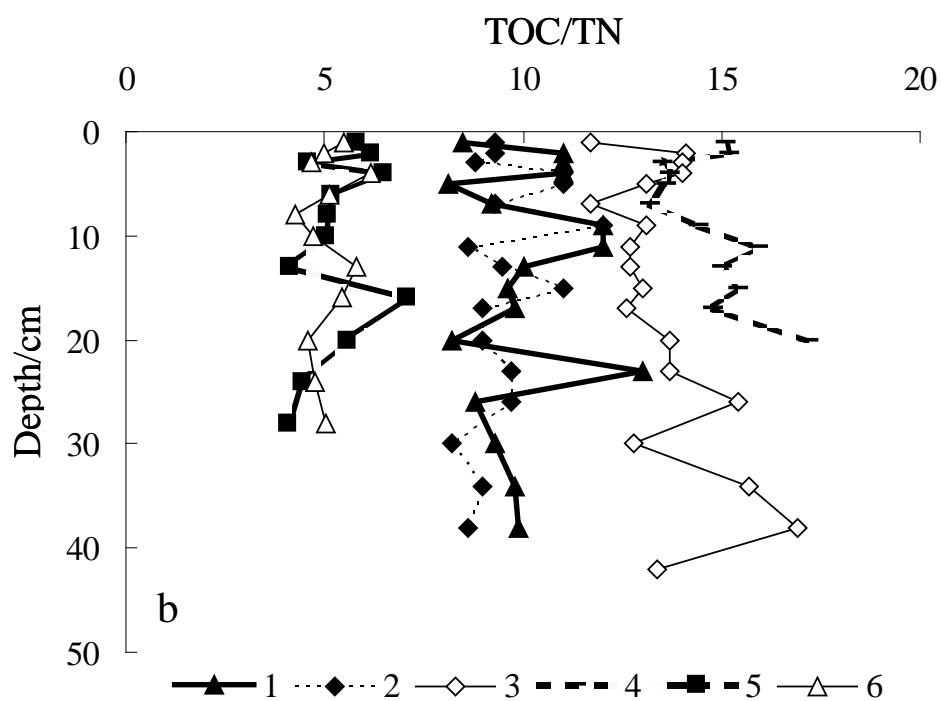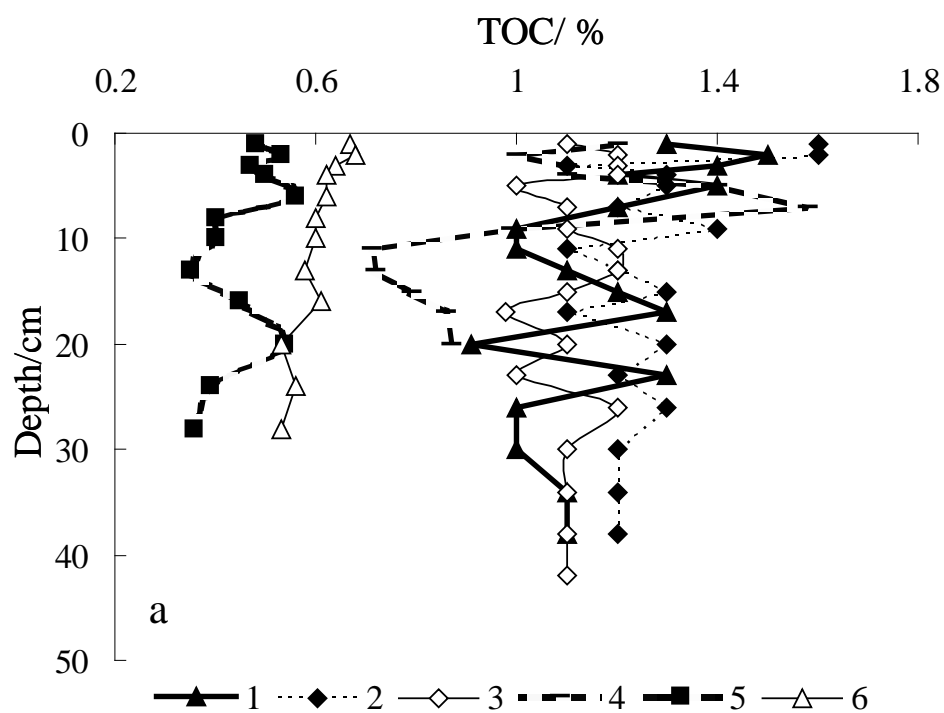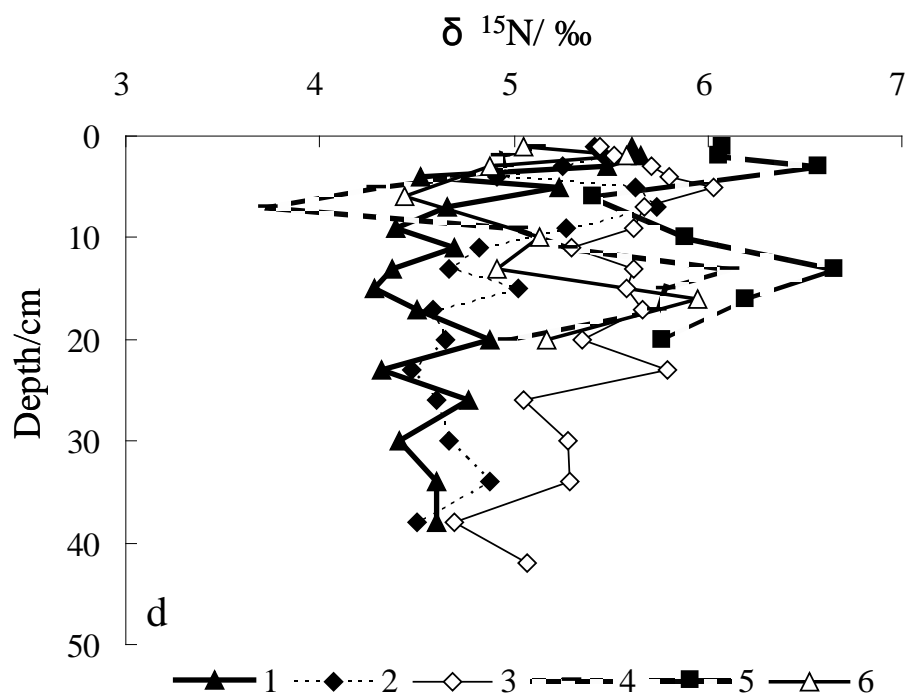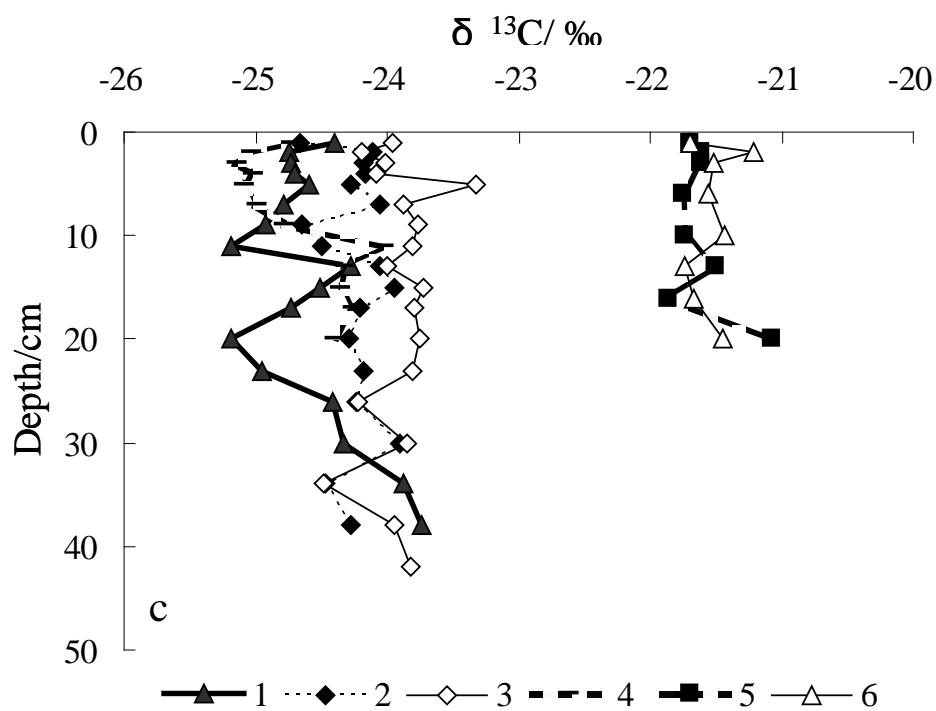
Fig.2. Geochemical variables plotted versus depth in the sediment cores.

Core 2

Core 5

Core 6
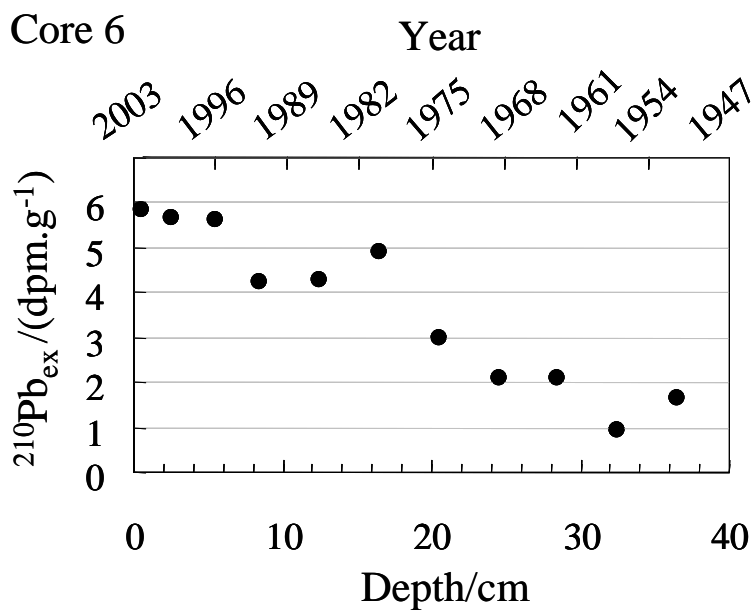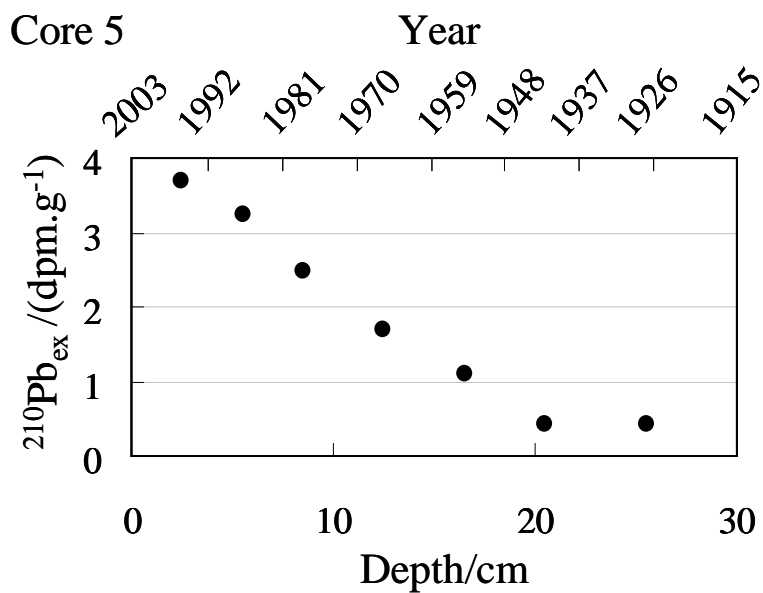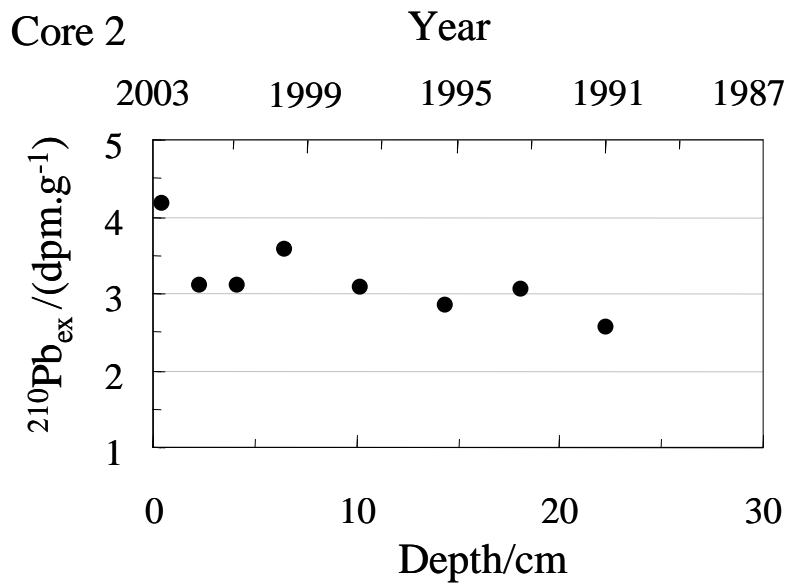
Fig.3. $^{210}Pb_{ex}$ activities plotted versus depth and age in the sediment cores (core 2, 5 and 6).
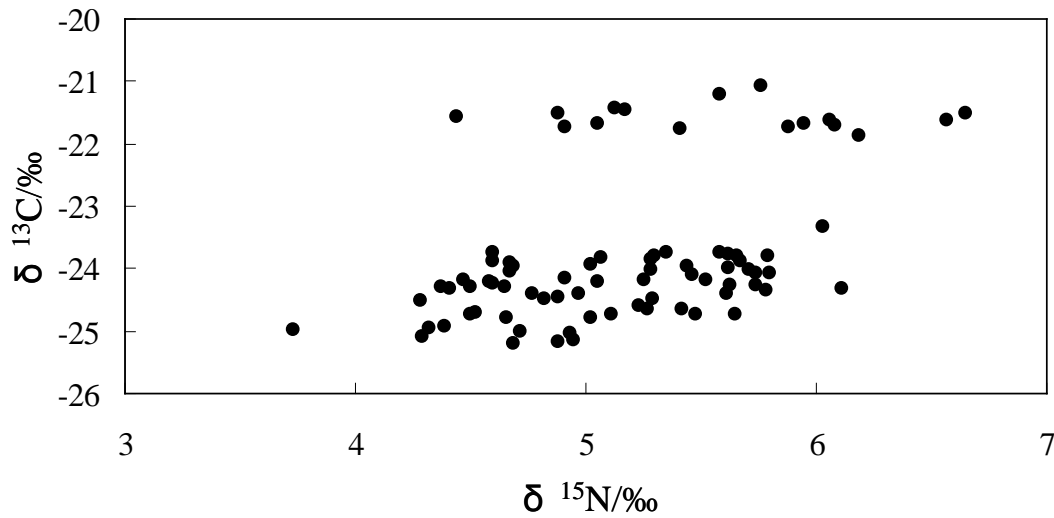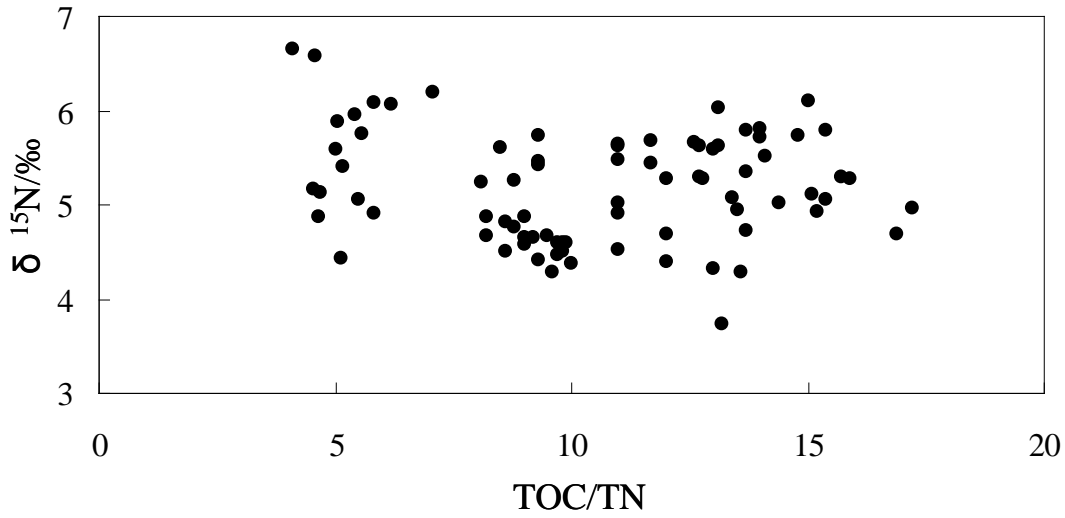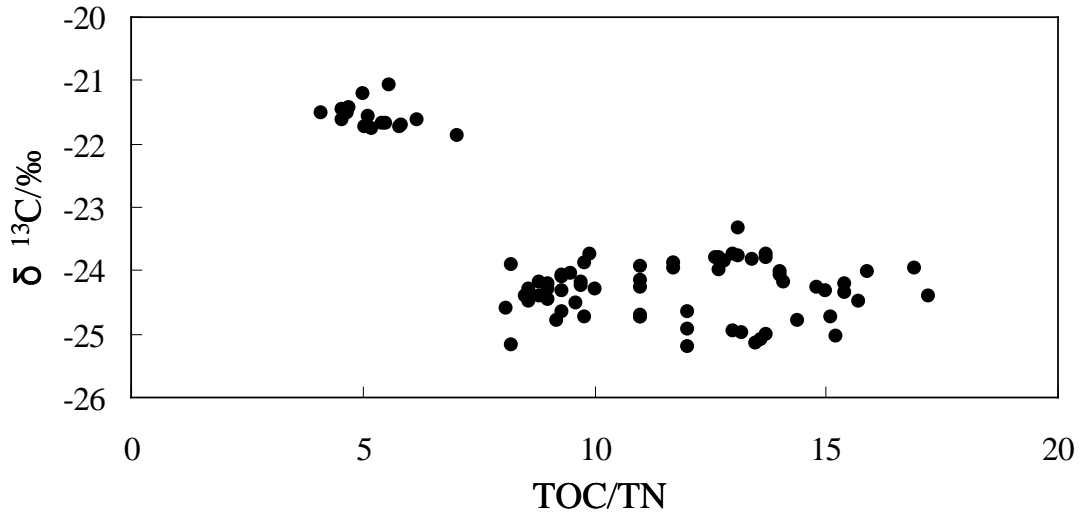
30   Fig.4. Relationships of $\delta^{13}C$ or $\delta^{15}N$ and TOC/TN, as well as $\delta^{13}C$ and $\delta^{15}N$ in the sediment cores.
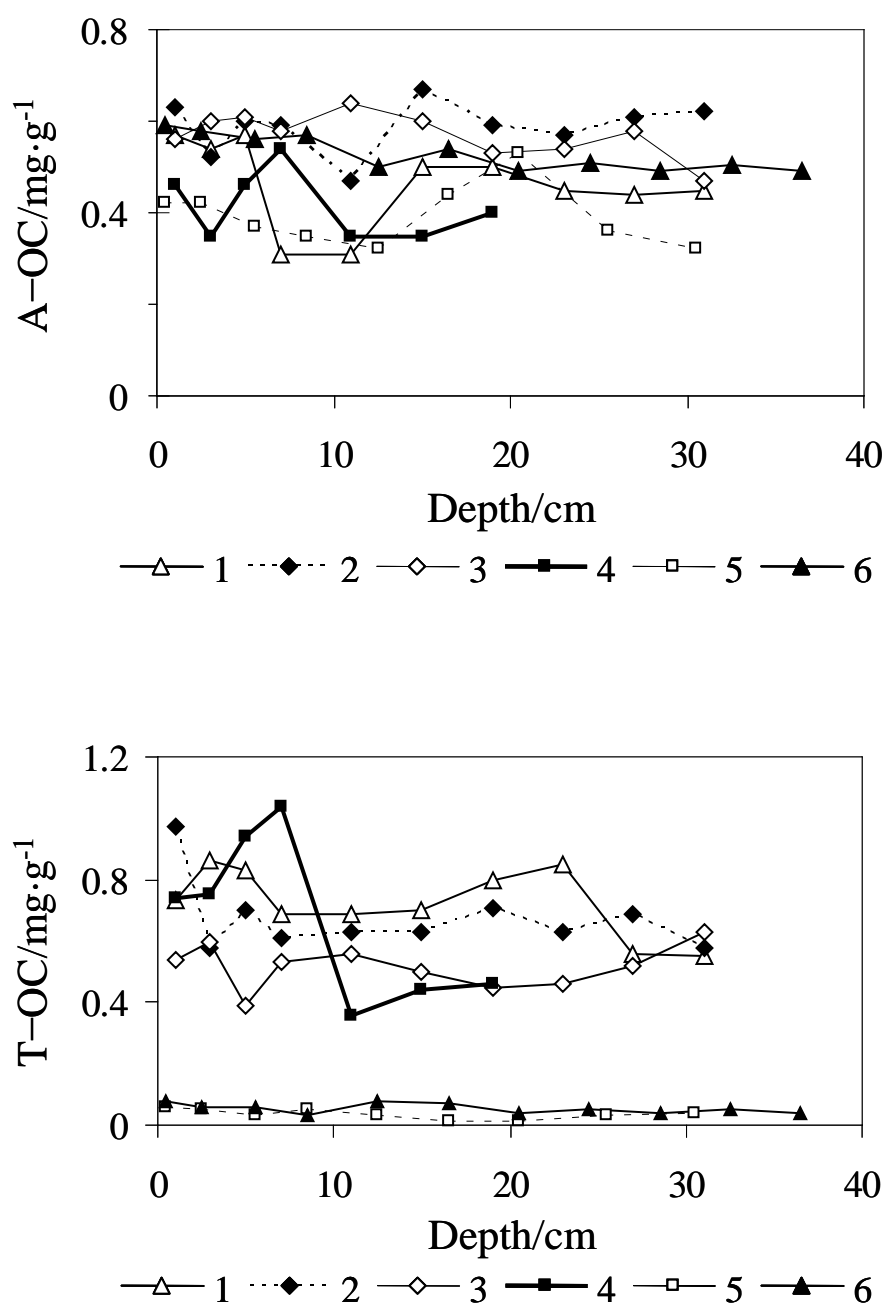
Fig.5. Plot of aquatic (A-OC) and terrestrial (T-OC) organic matter versus depth in the sediment cores.
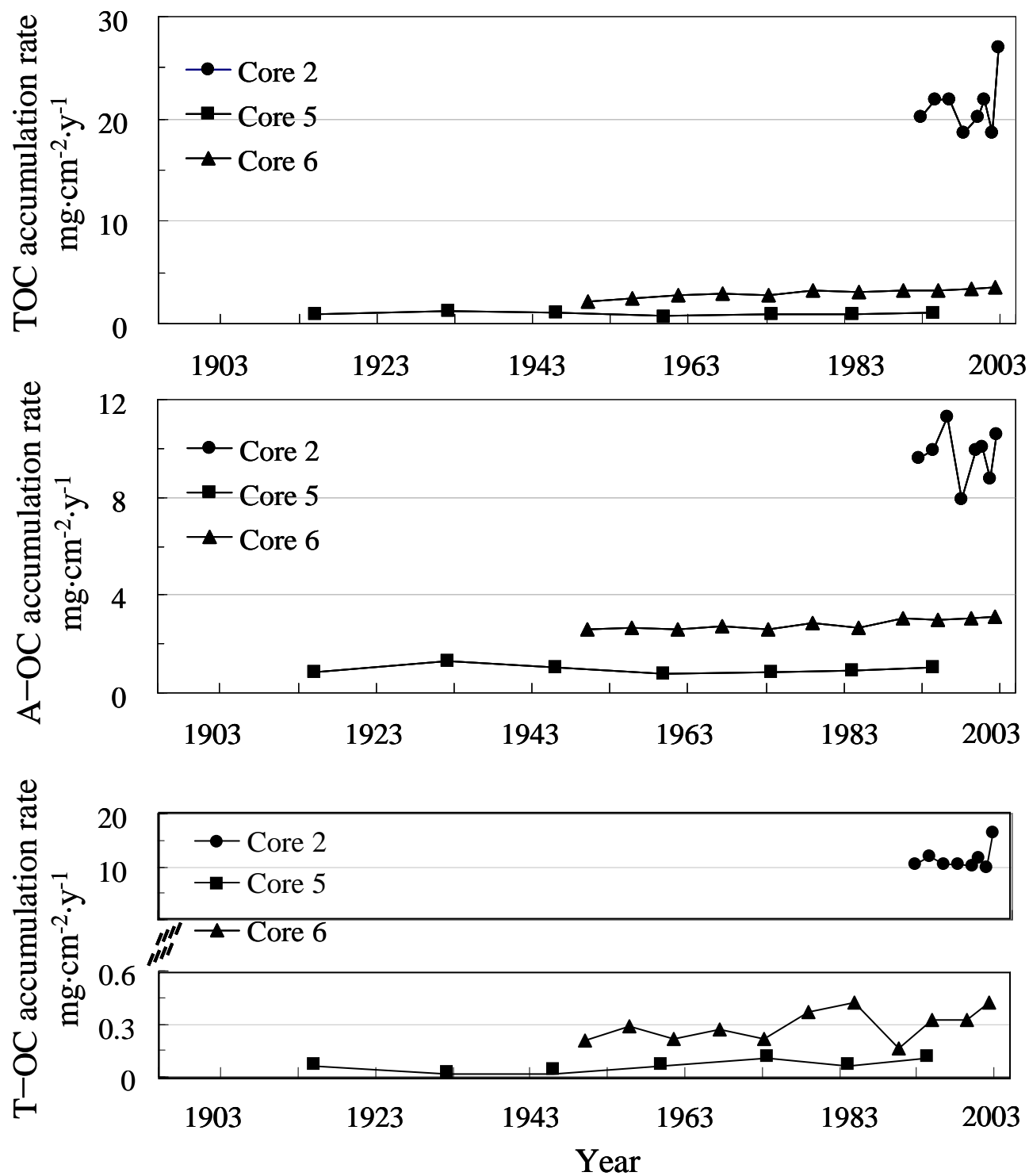
Fig.6. Plot of the accumulation rate versus age in the sediment cores (TOC: total OC; A-OC: aquatic OC; T-OC: terrestrial OC).