

Catchment environmental change over the 20th Century recorded by sedimentary leaf wax n -alkane $\delta^{13}\text{C}$ off the Pearl River estuary

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The compound-specific stable carbon isotope compositions ($\delta^{13}\text{C}$) of leaf wax n -alkanes from two short sediment cores recovered off the Pearl River estuary (PRE) were analyzed to check for their capability of indicating decadal scale catchment environmental change. Sedimentary long-chain n -alkanes exhibited an odd-over-even predominance, with a maximum at n -C₂₉ or n -C₃₁, indicating their leaf wax origin was from vascular plants. The $\delta^{13}\text{C}$ values of C₂₉ and C₃₁ n -alkane in all the sediment samples were in the range of -28.8‰ to -31.2‰ , consistent with the C₃ plant-dominated vegetation in the Pearl River catchments. The time series of $\delta^{13}\text{C}$ records from the two cores were comparable and displayed a decreasing trend from the early 20th century to the end of the 1970s, followed by a reversal in that change leading to continued increase for ca. 15 years. After being corrected for the effect of atmospheric CO₂ rise and $\delta^{13}\text{C}_{\text{atm}}$ decline, the $\delta^{13}\text{C}_{29}$ records largely retained their raw changing pattern; the post-1980 increase being more conspicuous. The slightly decreasing trend in corrected $\delta^{13}\text{C}$ records before around 1980 may have been caused by an increase in precipitation, whereas the subsequent increase of $\delta^{13}\text{C}$ is likely associated with the observed dry climate and/or intensive anthropogenic deforestation. Our results thus demonstrate that leaf wax n -alkanes buried in the sediments off the PRE may well reflect change in the regional climate and/or human activity in the river catchments over the past century.

Leaf wax n -alkanes, compound-specific $\delta^{13}\text{C}$ values, environmental change, Pearl River estuary

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Terrestrial fresh water and particulate materials continuously enter the ocean through rivers, making coastal areas near river mouths active interfaces between land and ocean. Terrestrial sediments accumulate more quickly in coastal regions than they can disperse in open marine environments (Wright, 1977), favoring the preservation of high-resolution sedimentary archives of weathering and climate products in river catchments. Moreover, archives from large rivers potentially document continental-scale climate change, which

is rarely available from localized inland deposits, e.g., peats and lakes (Bianchi and Allison, 2009). However, recently deposited riverine muds on a shallow inner shelf are subjected to erratic erosion and transport induced by coastal current variability, especially that caused by storm- and surge-induced waves (Bianchi and Allison, 2009). As to the terrestrial organic matter that is useful for tracing changes in terrestrial ecosystems, reworking by marine processes such as successive resuspension and deposition may act to enhance its degradation. Moreover, terrestrial organic matter might reside a long time—up to thousands of years—in soils and during transit before finally being buried in marine

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sediments (Eglinton et al., 1997; Drenzek et al., 2007). Thus, although it is acknowledged that river-dominated coastal sediments are important in constructing continental ecosystem and climate change records, further work is needed to check the accuracy and time resolution of the change documented in such sediments.

The Pearl River flowing into the South China Sea (SCS) is one of the world's 25 largest rivers in terms of annual water discharge and sediment load (Wu et al., 2012). It has a catchment area of over 0.45 million km² and a trumpet-like estuary located on the south coast of China (Figure 1). The majority of Pearl River sediments are trapped inside the estuary and nearby alongshore area (Liu et al., 2009). In this study, the carbon isotope compositions ($\delta^{13}\text{C}$) of terrigenous leaf wax *n*-alkanes in two short sediment cores outside the Pearl River estuary (PRE) are reported. Leaf wax *n*-alkanes are produced by vascular plants and characterized by odd-over-even predominance of carbon numbers in long-chain (C₂₃–C₃₃) homologs (Eglinton and Hamilton, 1967; Rieley et al., 1991). $\delta^{13}\text{C}$ values of leaf wax *n*-alkanes in sediments have been extensively used to infer past terrestrial vegetation dynamics and associated climate change over long-term time scales ranging from thousands to millions of years (e.g., Hu et al., 2003; Zhang et al., 2010; Jia et al., 2012). However, their accuracy for reflecting climate change over shorter time scales, e.g., the past hundred years, needs to be clarified considering their possibly significant residence times before being buried. By interpreting downcore *n*-alkane $\delta^{13}\text{C}$ values, we show that this information readily reflects the climate change in the Pearl River catchments during the past century. Thus, the residence time between production and burial in coastal sediments is unlikely to be significant for leaf wax *n*-alkanes in this near estuarine environment.

1. Materials and methods

1.1 Study area

Almost all of the Pearl River catchment lies in the subtropical monsoon climate zone. The cool and dry season extends from October to March, followed by a hot and rainy season from April to September. The multi-year mean annual temperature within the catchment is 14–22°C and the catchment-wide average precipitation is 1470 mm yr⁻¹ (Dai et al., 2008). The main vegetation in the river catchment consists of agricultural plants (e.g., rice, sugar cane, corn) and subtropical evergreen broad-leaved and coniferous forests, with minor grasses in the lower-reach flood plain and upper drainage basin (Sun et al., 1999; Yu et al., 2010). The river is a compound river system comprising three major tributaries, i.e., the West River, the North River, and the East River. These tributaries converge at the river delta and finally empty freshwater into the northern SCS via the PRE (Figure 1).

We studied two short marine sediment cores, A9 and A6 (Figure 1), located just outside the PRE. They were collected in August 2009 during a cruise along a NW-SE transect away from the coastline. Details of sample collection and ²¹⁰Pb dating results for the cores have been reported by Jia et al. (2013) and are summarized in Table 1.

1.2 Experiments

Sediment samples were freeze-dried and ultrasonically extracted six times, twice each with MeOH, dichloromethane (DCM)/MeOH (1:1, v/v), and DCM, and then the solvent in the combined extracts was removed by rotary evaporation. The hydrocarbon fraction was isolated from the total extract using silica gel column chromatography by eluting with hexane, and was further purified for *n*-alkanes using a urea adduction method prior to subsequent compound-specific $\delta^{13}\text{C}$ analysis. *N*-alkanes were identified by comparing the retention times of mixed *n*-alkane standards as defined by gas chromatography (GC) analysis.

Compound-specific $\delta^{13}\text{C}$ values of *n*-alkanes were analyzed by GC-isotope ratio mass spectrometry (IRMS), with an HP 6890 GC connected to a Delta Plus XL mass spectrometer via a GC-C III interface. The $\delta^{13}\text{C}$ values of individual *n*-alkanes were calculated using CO₂ as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis. All the data were calibrated relative to Vienna Pee Dee Belemnite (VPDB). Throughout the entire test, a standard mixture of *n*-alkanes

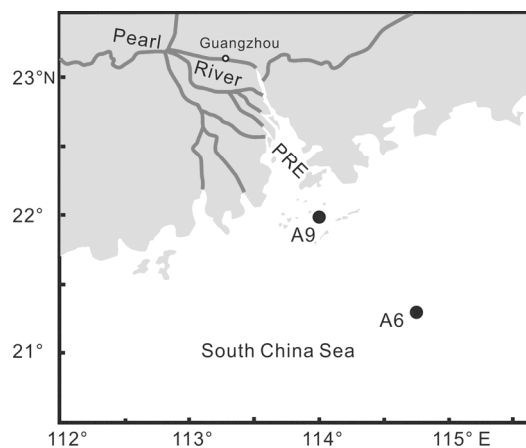


Figure 1 Location of sediment core A9 and A6 in this study (PRE, Pearl River Estuary).

Table 1 Information on sediment cores and ²¹⁰Pb dating results ^{a)}

Site Title	A6	A9
Latitude	21°16'N	22°00'N
Longitude	114°44'E	114°00'E
Water depth (m)	89	33
Cores length (cm)	30	50
MAR (g cm ⁻² yr ⁻¹)	0.33	0.48

a) MAR: Mass accumulation rate.

(C₁₄ to C₃₂) with known isotopic compositions provided by Indiana University was routinely used to check the instrumental performance and monitor the accuracy of measurements of the GC-IRMS system. In our study, each sample was analyzed at least twice with the accuracy within 0.3‰.

2. Results

In sediment samples, C₂₉ and C₃₁ *n*-alkanes were the most abundant homologs in the long-chain *n*-alkanes. A predominance of odd-carbon-numbered compounds was clearly shown, as indicated by the average carbon preference indices (CPI_{26–32}) of 2.19 (1.31–2.96) and 1.89 (1.53–2.69) in the A9 and A6 cores, respectively. The mean δ¹³C values of C₂₉ *n*-alkane (δ¹³C₂₉) were –30.4‰ in both of the core samples, and the mean δ¹³C₃₁ values were –29.6‰ in A9 and –29.7‰ in A6. Down the two cores, both δ¹³C₂₉ and δ¹³C₃₁ exhibit a decreasing trend from the early 20th century to the end of the 1970s (Figure 2a, b). The decreasing rate of

δ¹³C₂₉ ranged from –0.007‰ yr^{–1} to –0.009‰ yr^{–1} from 1920 to 1970, and then became greater between –0.038‰ yr^{–1} and –0.099‰ yr^{–1} during the 1970s. Following the decreasing trend, a reversal occurred, with δ¹³C₂₉ and δ¹³C₃₁ continuing to increase for ca. 15 years, after which the increasing trend either stopped or began to reverse again in the last decade. It is clear that δ¹³C₂₉ always remained lower than δ¹³C₃₁, and the difference between them, denoted as Δδ_{31–29}, changed toward lower values over the time before 1980.

3. Discussion

3.1 C₃ plant-dominated ecosystem in the catchment

The odd-over-even carbon number predominance of long-chain *n*-alkanes in our study samples reflects the input of fewer altered leaf waxes of vascular plants from land (Eglinton and Hamilton, 1967; Pearson and Eglinton, 2000). Our study cores are just outside the PRE, through which about 80 million tons of terrestrial materials are delivered

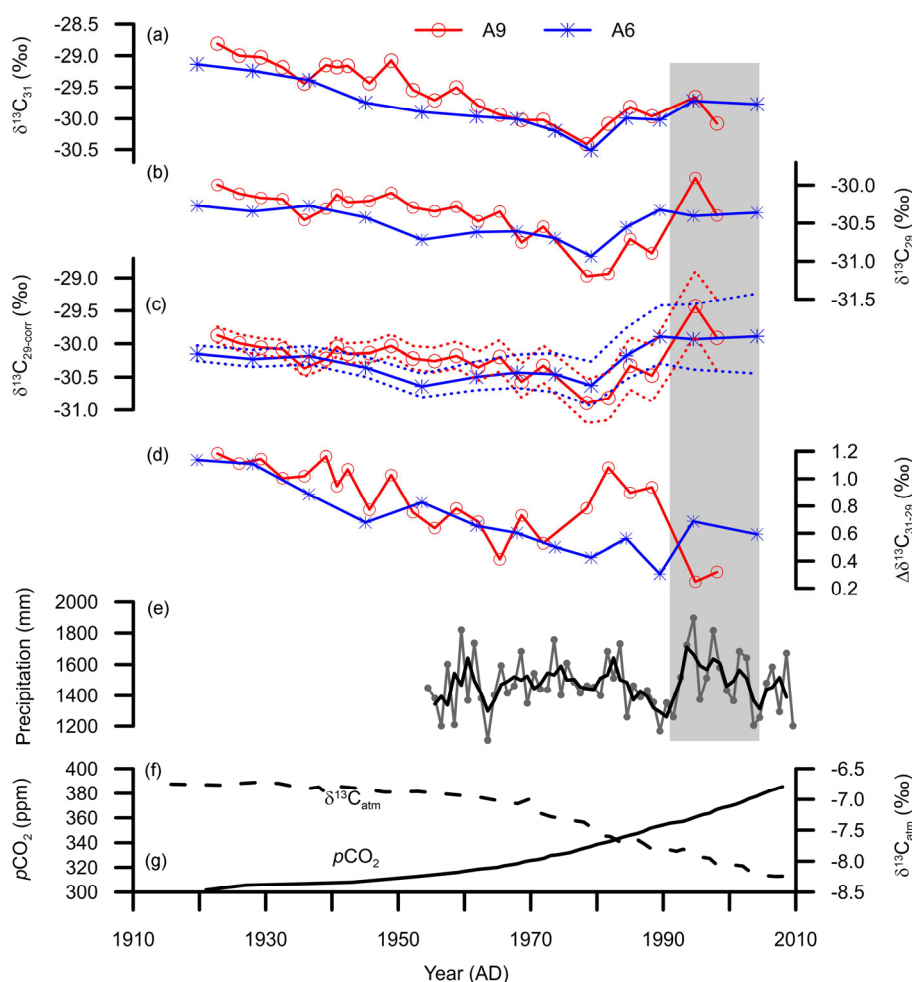


Figure 2 Profiles of δ¹³C₃₁, δ¹³C₂₉, δ¹³C_{29-corr}, Δδ_{31–29} ((a)–(d)) from the two cores presented in this study, and their comparisons with precipitation in the Pearl River catchment (e) (Wu et al., 2012), δ¹³C values of atmospheric CO₂ (δ¹³C_{atm}) (f), and atmospheric CO₂ concentration (g). Data for δ¹³C_{atm} before 1978 were from Francey et al. (1999), and those after 1980 were taken from (<http://cdiac.ornl.gov/trends/co2/iso-sio/iso-sio.htm>). To calculate δ¹³C_{29-corr}, the change of δ¹³C per unit increase in the atmospheric CO₂ was set as 0.014 ± 0.007‰ ppm^{–1}.

into the SCS every year (Zhang et al., 1999), so the inferred land-derived long-chain *n*-alkanes should be predominantly from the Pearl River catchments and their $\delta^{13}\text{C}$ values may reflect environmental changes in the catchments.

The $\delta^{13}\text{C}$ values of C_{29} and C_{31} *n*-alkanes in all study samples are close to the typical values for C_3 plants that are generally in a range between -28‰ and -39‰ with a mean of -34‰ (Collister et al., 1994; Chikaraishi and Naraoka, 2003). As a comparison, those for C_4 plants range between -18‰ and -25‰ with a mean of -19‰ (Collister et al., 1994; Chikaraishi and Naraoka, 2003). Therefore, our values are indicative of C_3 -dominated ecosystems in the Pearl River catchment. This is consistent with the present regional vegetation type of subtropical evergreen broad-leaved forest and some soil $\delta^{13}\text{C}_{\text{org}}$ analyses (Chen and Jia, 2009; Yu et al., 2010; Zhang et al., 2014).

3.2 Corrections for the effects of anthropogenic CO_2

Variations of vegetational $\delta^{13}\text{C}$ values may be caused by several factors, such as precipitation, atmospheric CO_2 , and the relative contribution of C_4 and C_3 plants (Castaneda et al., 2007; Farquhar et al., 1982; Meyers, 2003). However, the change of $\delta^{13}\text{C}$ in atmospheric CO_2 ($\delta^{13}\text{C}_{\text{atm}}$), which is the basis for the $\delta^{13}\text{C}$ of higher plant-photosynthesized organic matter, should be taken into account first when interpreting the changes of vegetational $\delta^{13}\text{C}$ values (e.g., Jia et al., 2012). Since the beginning of the industrial revolution in the 17th century, $\delta^{13}\text{C}_{\text{atm}}$ has decreased by $\sim 2\text{‰}$ due to emission of ^{13}C -depleted CO_2 from human activities, such as the burning of fossil fuels and the clearing of land (Druffel and Benavides, 1986), referred to as the so-called Suess effect. The $\delta^{13}\text{C}_{\text{atm}}$ Suess effect was subtle before 1970, with a slow decreasing rate of ca. -0.006‰ yr^{-1} , but has increased to a rate of ca. -0.03‰ yr^{-1} since 1970 (Figure 2f). This changing pattern of $\delta^{13}\text{C}_{\text{atm}}$ is well exhibited in our $\delta^{13}\text{C}_{29}$ and $\delta^{13}\text{C}_{31}$ records, showing a persistent decreasing trend before 1980, and suggesting that the Suess effect might be responsible for the downcore changes observed in $\delta^{13}\text{C}_{29}$ and $\delta^{13}\text{C}_{31}$ spanning most of last century. However, the changing rates of $\delta^{13}\text{C}_{29}$ and $\delta^{13}\text{C}_{31}$ in our results were higher than that of $\delta^{13}\text{C}_{\text{atm}}$ during the periods before 1970 and during 1970–1980. Moreover, the concurrent rise in atmospheric CO_2 could also be taken into account. For C_3 plants, the specific leaf area and stomatal conductance decrease in response to elevated CO_2 , leading to a lower intercellular CO_2 concentration (C_i) (Ainsworth and Long, 2005; Beerling and Woodward, 1995). As C_i falls, the $\delta^{13}\text{C}$ of the CO_2 inside the leaf is progressively enriched, thus reducing the fractionation factor between leaf lipids and the atmospheric CO_2 (Farquhar et al., 1989). Therefore, an increase of CO_2 may play an opposite role in modulating the $\delta^{13}\text{C}$ of C_3 plants relative to the Suess effect; similarly, the decrease of $\delta^{13}\text{C}_{29}$ and $\delta^{13}\text{C}_{31}$ due to the Suess effect could be partly offset by the increased CO_2 . However, the influ-

ence of increased atmospheric CO_2 on isotopic fractionation is poorly constrained and different values have been proposed for the change of $\delta^{13}\text{C}$ in trees per unit increase in the atmospheric CO_2 ($\Delta\delta$), ranging from 0.007‰ to 0.02‰ ppm^{-1} (Feng and Epstein, 1995; Kürschner, 1996; Treydte et al., 2001).

Here, our $\delta^{13}\text{C}_{29}$ records down the two cores were corrected ($\delta^{13}\text{C}_{29\text{-corr}}$) for the effect of anthropogenic CO_2 , with CO_2 concentration of 285 ppm and a $\delta^{13}\text{C}_{\text{atm}}$ value of -6.4‰ in AD 1850 as the reference values. The correction was based on the following equation:

$$\delta^{13}\text{C}_{29\text{-corr}} = \delta^{13}\text{C}_{29} - (\delta^{13}\text{C}_{\text{atm}} + 6.4) - \Delta\delta \times (\text{CO}_2 - 285), \quad (1)$$

in which $\Delta\delta$ was set as $0.014 \pm 0.007\text{‰ ppm}^{-1}$. By applying historical annual values of atmospheric CO_2 concentration and $\delta^{13}\text{C}_{\text{atm}}$ to this equation, we obtained $\delta^{13}\text{C}_{29\text{-corr}}$ records down the two cores (Figure 2c). The decrease in the trend prior to 1980 is still observed to exist, albeit subtly. Moreover, the subsequent increase becomes more conspicuous in $\delta^{13}\text{C}_{29\text{-corr}}$ records. Therefore, the $\delta^{13}\text{C}_{\text{atm}}$ and atmospheric CO_2 concentration are not enough to account for the full range of our observed changes in leaf wax $\delta^{13}\text{C}$ records, suggesting that other eco-environmental factors would have played a part.

It should be noted that the above correction was on the assumption of a pure C_3 plant ecosystem in the Pearl River catchments, which is not strictly true despite approximating the actual conditions. Additionally and interestingly, the $\Delta\delta_{31-29}$ value, in which the effect of CO_2 concentration and $\delta^{13}\text{C}_{\text{atm}}$ are most likely removed, displayed a decreasing trend from the 1920s to 1970s. This pattern might also be associated with ecosystem changes, as discussed below.

3.3 Eco-environmental change inferred from $\delta^{13}\text{C}$ records

We speculate that changes of $\Delta\delta_{31-29}$ may be caused by vegetation dynamics within a C_3 ecosystem or changes in the C_3/C_4 ratio in the catchment vegetation. Our available data from East Asia have shown that mean $\Delta\delta_{31-29}$ values for C_3 plants change from -0.9‰ in the tropical-south subtropical to 0.2‰ in the north subtropical (Jia et al., 2015), significantly lower than the values between 0.2‰ and 1.2‰ observed here. This suggests that community change in terms of the pure C_3 ecosystem is unlikely to be the dominant factor for the $\Delta\delta_{31-29}$ trends. Alternatively, C_{29} *n*-alkane has been found to mainly be sourced from C_3 trees and shrubs, while the longer chain C_{31} counterpart has a greater contribution from C_4 grasses (Wang et al., 2013). Therefore, in a mixed C_3/C_4 ecosystem, $\delta^{13}\text{C}_{31}$ should be less negative than $\delta^{13}\text{C}_{29}$ (Wang et al., 2013; Jia et al., 2015). So, the decrease of $\Delta\delta_{31-29}$ values in our results could likely suggest a persistent decline of C_4 plants in the Pearl River catchments between the 1920s and 1970s. However, the full range of $\Delta\delta_{31-29}$ decrease is only $\sim 1\text{‰}$ in this work, much less than

the $\Delta\delta_{31-29}$ value of 3‰–4‰ observed for marked changes in the C_3/C_4 ratio (Wang et al., 2013; Jia et al., 2015) and again suggestive of a C_3 -dominated ecosystem—although not a pure C_3 ecosystem—in the river catchment. We therefore surmise that this scenario could be related to regional climate change (likely a wetting trend) during the period, because wetter climates generally favor C_3 species over C_4 species in tropical-subtropical settings. To say the least, a wetting climate change between the 1920s and 1970s is also a plausible explanation for the decrease of $\delta^{13}C_{29}$ and $\delta^{13}C_{31}$ due to significant negative correlation between the $\delta^{13}C$ value of C_3 plants and precipitation (Diefendorf et al., 2010; Kohn, 2010). Indeed, based on available observational data, a slight increase of precipitation in the Pearl River catchment between 1950 and 1980 has been reported (Figure 2e) (Wu et al., 2012). More than that, it is likely that climate change is also responsible for the subsequent increase of $\delta^{13}C_{29}$ and $\delta^{13}C_{31}$ between the mid-1980s and mid-1990s that corresponds to a period of severe drought in the observational data (Wu et al., 2012; gray area in Figure 2e). Under drought conditions in this subtropical region, C_4 grasses may struggle to survive and C_3 plants may adjust their stomatal conductance to weaken the ^{13}C discrimination, both of which would lead to an increase of $\delta^{13}C_{29}$ and $\delta^{13}C_{31}$.

Although precipitation change could be interpreted in our downcore $\delta^{13}C_{29}$ and $\delta^{13}C_{31}$ records, including the $\delta^{13}C$ shift changing direction at around 1980, the good match in time between the documented vegetation change and precipitation is largely unexpected, primarily because the vegetation shift may be slow to respond and lag behind climate change (Bertrand et al., 2011). As an alternative, we thought that human activity might be partly responsible for the positive shift in $\delta^{13}C$ around 1980, because this positive shift is persistent into the mid-1990s and does not match well with the drought event that shows a peak at around 1990. Since the early 1980s, like in other regions in China, agriculture and industry have been developing rapidly in the Pearl River catchment, causing increased deforestation and soil erosion (Wu et al., 2012). Deforestation may lead to replacement of C_3 forests by C_4 grasses or crops (Townsend et al., 2002), thus leading to the positive shift in plant wax $\delta^{13}C$ after 1980 as shown in our downcore records.

Our results demonstrate that leaf wax n -alkanes buried in the sediments off the PRE may act as suitable proxies for changes in the regional climate and/or human activity in the river catchment over the past century. This is an interesting result, because generally there would be a significant residence time in soils for plant leaf wax n -alkanes before entering the marine environment via river transport. For example, based on compound radiocarbon (^{14}C) analysis, the age of leaf wax n -alkanes in marine surface sediments has been found to be up to hundreds and thousands of years (Eglinton et al., 1997; Smittenberg et al., 2004). However, recent ^{14}C evidence has revealed that tropical rivers may rapidly export young terrestrial primary production from

catchments (Martin et al., 2013). Although no ^{14}C data were available for this study, our results may suggest that the residence time of leaf wax n -alkanes between their initial production and final burial in the near shore sediments of the PRE might be minimal. In other words, the buried leaf wax n -alkanes may be predominantly “fresh”, and the aged ones, if any, would be minor and do not confound the use of sedimentary n -alkane $\delta^{13}C$ as a valid short-time scale environmental proxy in this study. However, this is a tentative suggestion and needs to be verified in future ^{14}C studies. Besides, our results here do not necessarily mean that leaf wax n -alkanes in the outer shelf, slope, and deep sea sediments in the SCS have similar ages as the syndepositional materials, because their dispersion and transportation in offshore and open marine environments may be a long complex journey.

4. Conclusions

Our study demonstrates that $\delta^{13}C$ records of leaf wax n -alkanes off the Pearl River estuary adequately reflect climatic and environmental change in the river catchment over the past century. The atmospheric Suess effect and the increase of precipitation before around 1980 were nicely shown to correspond to the decreasing trends in the $\delta^{13}C$ records. Incidentally, the subsequent interval of dry climate and intensified human activities can be also traced by the $\delta^{13}C$ records. The capability of the downcore leaf wax $\delta^{13}C$ record to infer decadal scale catchment environmental change suggests that the buried leaf wax n -alkanes in the inner shelf of the coastal northern SCS are dominantly “fresh” and thus can be used as a valid short-time scale environmental proxy.

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