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ORIGINAL ARTICLE

Effect of petroleum on carbon and hydrogen isotopic composition of long-chain *n*-alkanes in plants from the Yellow River Delta, China

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Abstract Carbon and hydrogen stable isotope ratios of *n*-alkanes are presented for *Suaeda salsa* and *Phragmites australis* from the Yellow River Delta (YRD), China. Under unpolluted conditions, *S. salsa* has lighter, mean carbon isotopic composition and heavier, mean hydrogen isotopic composition than those of *P. australis*. The $\delta^{13}C$ and δD variation of *n*-alkane in *S. salsa* and *P. australis* between unpolluted conditions and petroleum-polluted soil conditions, is small ($\Delta^{13}C_{S.\ salsa} = 0.7 \pm 0.6$ ‰, $\Delta^{13}C_{P.\ australis} = 0.8 \pm 0.7$ ‰, $\Delta D_{S.\ salsa} = 6.4 \pm 11.9$ ‰ and $\Delta D_{P.\ australis} = 4.8 \pm 8.6$ ‰). The plants in the contaminated area have a lighter, mean carbon and hydrogen isotopic compositions than those measured in the unpolluted area of the YRD. The lighter values of δD and $\delta^{13}C$ of individual *n*-alkanes in plants from petroleum soil may be due to the reduction of photosynthesis and slowness of water usage effectiveness caused by petroleum pollution. Therefore, the δD and $\delta^{13}C$ values of the plants *S. salsa* and *P. australis* could be used as proxies for evaluation of petroleum-polluted environments.

Keywords Carbon and hydrogen isotope · Individual *n*-alkanes · Plant · Petroleum pollution · Yellow River Delta

Introduction

n-Alkanes are one of the most abundant lipid molecules biosynthesized by terrestrial plants, aquatic plants and certain algae. *n*-Alkanes of terrestrial plants are characterized by strong odd predominance in C_{25}–C_{35} carbon-number range (Collister et al. 1994; Chikaraishi and Naraoka 2003), whereas aquatic plants are characterized by enrichment of C_{23} and C_{25} *n*-alkanes (Ficken et al. 2000). Relatively short-chain *n*-alkanes (C_{15}, C_{17} and C_{19}) are often attributed to algae and cyanobacteria (Chikaraishi and Naraoka 2003). Therefore, the distributions of *n*-alkanes in geological samples can indicate organic matter sources (Meyers 2003; Pancost and Boot 2004; Duan et al. 2012) and paleoenvironmental conditions (Ohkouchi et al. 1997; Pancost and Boot 2004).

Carbon and hydrogen isotopic ratios of individual *n*-alkanes are becoming increasingly popular for tracing organic sources (Rieley et al. 1991; Freeman and Colarusso 2001; Duan et al. 2005; Duan and He 2011) and paleoenvironmental reconstructions (Huang et al. 2002; Smith and Freeman 2006). Most studies have shown carbon and hydrogen isotopic variations between C_3 and C_4 plant groups (Collister et al. 1994; Chikaraishi et al. 2004; Smith and Freeman 2006; Duan et al. 2012) and within C_3 higher plants (Chikaraishi et al. 2004; Pedentchouk et al. 2008). Carbon and hydrogen isotopic ratios of long-chain *n*-alkanes in plants are controlled by isotopic

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fractionation during photosynthesis (Hayes 1993; Chikaraishi et al. 2004). C_3 plants are relatively ^{13}C-depleted (*n*-C_{24} to *n*-C_{35} typically range from $\delta^{13}C = -31$ to -39 ‰) and C_4 plants are ^{13}C-enriched ($\delta^{13}C = -18$ to -25 ‰) (Bi et al. 2005). The crassulacean acid metabolism (CAM) plants had an intermediate $\delta^{13}C$ range (-29.5 to -21.5 ‰), which were consistent with the utilization of both C_3 and C_4 carbon fixation pathways. At the same time, hydrogen isotopic compositions of long-chain *n*-alkanes in plants primarily reflect the isotopic composition of precipitation and the D-enrichment of the source water is caused by transpiration and soil evaporation (Sachse et al. 2004; Smith and Freeman 2006). Sternberg (1988) found that D/H ratios of plant lipid fractions were correlated with D/H ratios of environmental water. Furthermore, Xie et al. (2000) used a vertical δD profile of C_{23} *n*-alkane derived from Sphagnum species in a peat core sample for a paleoclimatic study.

The Yellow River Delta (YRD), in the northeast of Shandong Province, China, is one of the most active land–ocean interaction regions among the large river deltas in the world. However, Shengli Oilfield, the second largest oilfield of China, is located in the YRD and threatens the ecosystem of the YRD due to oil well blowouts, leaks and spills from underground tank, pipelines and illegal disposals (Wang et al. 2011). As a matter of fact, *Suaeda salsa* is not only a typical, protective, salinity- and alkali-resistant plant, but also a pioneering species spreading from the inland area to the coast of the YRD. In addition, *Phragmites australis* is one of the most important, widespread and constructive wetland plant species over the YRD. *S. salsa* and *P. australis* from YRD belong to C_3 plants (Ding et al. 2011). It has long been known that oil spills can have significant, negative impacts on coastal plant community. Crude oil spills lead to insufficient aeration, a reduction in the level of available plant nutrients and a rise in toxic levels of certain elements such as manganese and iron (Ekundayo et al. 2001). However, few studies have reported the interactive effects of petroleum-hydrocarbon spillage on the distribution of δD and $\delta^{13}C$ of *n*-alkane in plant–soil systems (Lichtfouse and Eglinton 1995). In this study, the carbon and hydrogen isotopic compositions of *n*-alkanes in *S. salsa* and *P. australis* from the YRD were measured in order to: (1) understand the carbon and hydrogen isotopic variations of plant in petroleum-polluted soil system and (2) evaluate the effect of petroleum on the fractionation of these isotopes.

Samples and analysis

Samples

The samples of *S. salsa* and *P. australis* were collected from the unpolluted area of the YRD, November 2013. In addition, the samples of *S. salsa* (P-*S. salsa*) and *P. australis* (P-*P. australis*) growing on the petroleum-polluted soils around the oil well were also collected in order to analyze the effect of petroleum pollution on the δD and $\delta^{13}C$ distributions of *n*-alkanes in *S. salsa* and *P. australis*. Furthermore, unpolluted soil samples (Soil-JP, Soil-LW) and the petroleum-polluted soil sample (P-soil-JP, P-soil-LW) around the oil well cultivated with *S. salsa* and *P. australis* were also collected. The physical and chemical properties of topsoil (0–10 cm) close to the plant samples are shown in Table 1. As little sampling intervals, the difference of physical and chemical properties of topsoil is not significant. However, the contamination of soil with crude oil resulted in an increase in pH and phosphorus, which is consistent with the findings of the studies of Ekundayo et al. (2001).

Analytical methods

Immediately after collection, the plant samples were washed repeatedly with tap water and then rinsed with distilled water. All plant samples (*S. salsa,* P-*S. salsa, P. australis and* P-*P. australis*) and freeze-dried sediment samples (P-soil) were dried at room temperature, crushed to a fine powder, and kept frozen until analysis. Soluble organic matter was extracted from about 8–15 g of the dried biomass using a Soxhlet apparatus with a mixture of dichloromethane–methanol (2:1, v/v). The extracts were filtered and evaporated to dryness, and fractionated using column chromatography on alumina over silica gel (Duan et al. 2005, 2012). The saturated hydrocarbon, aromatic hydrocarbon fractions were obtained using successive elution with *n*-hexane, dichloromethane, respectively.

The *n*-alkanes in the hydrocarbon fraction were identified by way of 6890 N gas chromatograph/5973 N mass spectrometer (GC–MS) equipped with a HP-5 column (30 m × 0.32 mm i.d., 0.25 l m film thickness). The GC oven temperature was programmed from 80 to 300 °C (held 30 min) at 4 °C min^{-1}. MS was run with helium as a carrier gas and its electron ionization was at 70 eV with an ion source temperature of 250 °C. The mass spectrometer was operated in the full scan mode from *m*/*z* 20 to 300.

Analyses of carbon and hydrogen isotopes of individual *n*-alkanes were performed by gas chromatography combustion-isotope ratio mass spectrometry using a Finnigan Delta plus XP mass spectrometer interfaced to a Thermo Finnigan GC Combustion III interface (for $\delta^{13}C$) and a high-temperature conversion system (for δD) (Duan et al. 2012). The combustion was performed in a micro-volume ceramic tube with CuO, NiO and Pt wires at 850 °C. Pyrolysis was performed in a micro-volume ceramic tube with graphite at 1450 °C. Individual *n*-alkanes were separated using a SE-54 fused silica capillary column

Table 1 Physical and chemical properties of topsoil for *Suaeda salsa* and *Phragmites australis* planting

Samples no.	Bulk density ($g\ cm^{-3}$)	pH	Soil moisture ($cm^3\ cm^{-3}$)	Total nitrogen ($mg\ kg^{-1}$)	Total phosphorus ($mg\ kg^{-1}$)
Soil-JP	1.30	7.75	0.301	591.0	480.25
P-soil-JP	1.28	8.08	0.298	670.5	486.23
Soil-LW	1.32	7.68	0.309	608.5	482.89
P-soil-LW	1.31	8.12	0.312	585.6	485.62

Reference Sun et al. (2013)

Soil-JP unpolluted soil for *Suaeda salsa* planting; *P-soil-JP* petroleum-polluted soil for *Suaeda salsa* planting; *Soil-LW* unpolluted soil for *Phragmites australis* planting; *P-soil-LW* petroleum-polluted soil for *Phragmites australis* planting

Table 2 Plants, carbon fixation modes, and *n*-alkane parameters

Samples no.	Plant	Region	Carbon fixation pathway	Chain length range	C_{max}	CPI	ACL
S. salsa	*Suaeda salsa*	YRD	C_3	15–32	*n*-C_{27}	2.46	27.61
P–*S. salsa*	*Suaeda salsa*	YRD	C_3	15–32	*n*-C_{29}	2.03	27.62
P. australis	*Phragmites australis*	YRD	C_3	15–32	*n*-C_{27}	2.84	27.54
P–*P. australis*	*Phragmites australis*	YRD	C_3	15–32	*n*-C_{27}	4.95	28.59
[a]CPL-1	*Phragmites australis*	Qaidam basin	C_3	16–31	*n*-C_{27}	4.55	26.91
[a]KP-1	*Phragmites australis*	Kunming	C_3	17–31	*n*-C_{29}	14.9	27.83
[a]GP-1	*Phragmites australis*	Nanning	C_3	19–35	*n*-C_{31}	14.0	30.35

S. salsa unpolluted *Suaeda salsa* sample; *P-S. salsa* petroleum-polluted *Suaeda salsa* sample; *P. australis Phragmites australis* sample; *P-P. australis* petroleum-polluted *Phragmites australis* sample

C_{max} *n*-alkane with maximum abundance, *CPI* carbon preference index = Σodd C_{21}–C_{31}/Σeven C_{20}–C_{30}, *ACL* average chain length = $[\Sigma(c_i) \times i]/[c_i]$ for i = 23–31, where i is the concentration of the *n*-alkane containing i carbon atoms

[a] Data of CPL-1, KP-1 and GP-1 refer to Duan and He (2011)

(60 m × 0.32 mm i.d., 0.25 μm film thickness) and helium as carrier gas with a flow rate of 1 ml min^{-1}. The GC oven temperature was isothermal for 5 min at 80 °C and then programmed from 80 to 300 °C at 3 °C min^{-1}. $\delta^{13}C$ and δD values are expressed relative to the PDB and VSMOW, respectively. The reproducibility and accuracy of the analysis were evaluated routinely using laboratory standards of known δD and $\delta^{13}C$ values (C_{18}, C_{23}, C_{28}, C_{32} *n*-alkanes). Samples were analyzed once to three times. For most of the *n*-alkanes, the standard deviation of carbon and hydrogen isotope analyses was better than 0.5 and 5 ‰, respectively.

Results and discussion

Compositions of *n*-alkanes in plants

Compositions of *n*-alkanes are reported in Table 2 and Fig. 1. *n*-Alkanes from C_{15}–C_{33} were identified in *S. salsa* and *P. australis* collected from the YRD. Such plant species showed strong odd carbon-numbered predominance with carbon preference index (CPI) values ranging from 1.99 to 3.72. Average chain length (ACL) values varied from 27.61 to 28.59. *n*-C_{27} and *n*-C_{29} were found abundantly in every studied samples (Fig. 1), which is in some sort inconsistent with C_{max} at C_{29} or C_{31} of the grass, C_{27}, C_{29} or C_{31} of the reed and C_{27} or C_{29} of the tree leaves, as previously reported (Duan and He 2011). In this study, it is found that the same type plant (*P. australis*) from low latitudes (GP-1) has higher carbon-number maxima than those from high latitudes (LW, CPL-1), as shown in Table 2. One possible explanation is that plants at low latitudes have a longer growth period and more potential incoming radiation that protects their leaves with longer chain *n*-alkanes from water loss.

Carbon isotopic composition of alkane in *S. salsa* and *P. australis*

Distinct isotopic patterns were evident for the plants having different carbon dioxide metabolisms. In general, C_3 plants are more enriched in ^{12}C than C_4, while C_4 plants are more enriched in ^{13}C. The $\delta^{13}C$ values for C_4-derived *n*-alkanes are all within the range of −25 to −18 ‰, while C_3 plants are depleted in ^{13}C with an overall $\delta^{13}C$ range of −39 to −31 ‰ (Bi et al. 2005). *S. salsa* and *P. australis* collected from the YRD belong to C_3 plants (Ding et al. 2011). Their $\delta^{13}C$ values range from −37.6 to −33.5 ‰ and from −31.3

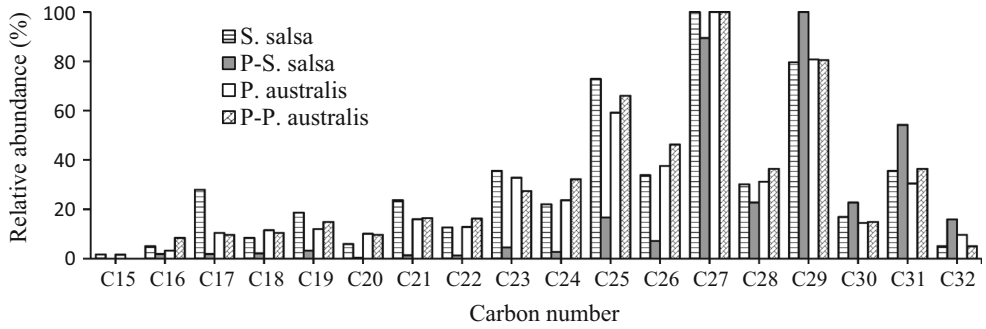

Fig. 1 *Histograms* of the molecular distributions of *n*-alkanes in the studied samples. *S. salsa* unpolluted *Suaeda salsa*; *P-S. salsa* petroleum-polluted soil *Suaeda salsa*; *P. australis Phragmites australis*; *P-P. australis* petroleum-polluted soil *Phragmites australis*

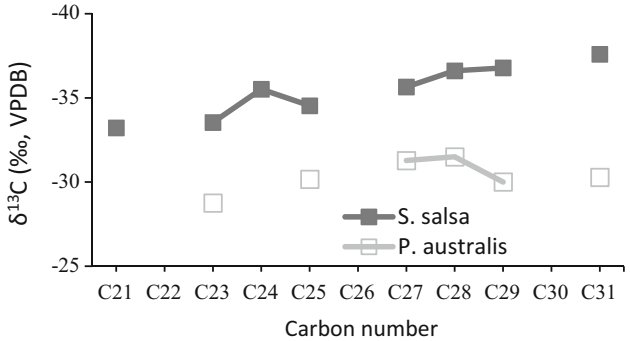

Fig. 2 $\delta^{13}C$ values of *n*-alkane in *Suaeda salsa* and *Phragmites australis* vs. *n*-alkane carbon number

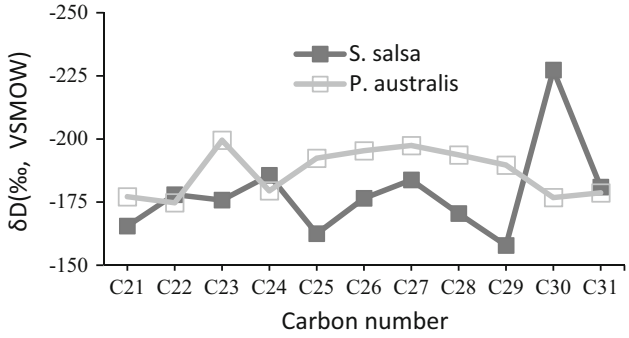

Fig. 3 δD values of *n*-alkane in *Suaeda salsa* and *Phragmites australis* vs. *n*-alkane carbon number

to −28.8 ‰, respectively, which is consistent with the general $\delta^{13}C$ distribution of lipid molecules in the C_3 higher plants.

As mentioned above, loss of the low molecular weight target compounds during the GC-IRMS sample preparation procedure (such as drying procedure) resulted in some $\delta^{13}C$ data deficient. *n*-C_{25}–C_{35} congeners were the major compounds in the studied plant samples. Here, carbon isotopic composition of the studied *n*-C_{25}, *n*-C_{27}, *n*-C_{29} and *n*-C_{31} was reported in details. The mean $\delta^{13}C$ values of *n*-C_{25} in unpolluted *S. salsa* and *P. australis* are −34.53 and −30.17 ‰, respectively, showing that *S. salsa* has a lighter mean carbon isotopic composition than *P. australis*. A similar difference in the $\delta^{13}C$ value for *n*-C_{27}, *n*-C_{29} and *n*-C_{31} also exists in this study (Fig. 2). $\delta^{13}C$ values of *S. salsa* and *P. australis* from the YRD were consistent with the literature values (Bi et al. 2005).

Carbon isotopic composition of *n*-alkanes from unpolluted *S. salsa* and *S. salsa* that grew in petroleum-polluted soil ranged from −37.59 to −33.22 ‰ with the average of −35.43 ‰, and −38.15 to −34.87 ‰ with the average of −36.67 ‰, respectively. On the other hand, carbon isotopic composition of *n*-alkanes in unpolluted and polluted soil *P. australis* samples ranged from −31.50 to −28.76 ‰ with the average of −30.33 ‰, and −32.10 to −30.42 ‰ with the average of −31.29 ‰, respectively. Based on this, the average carbon isotopic composition of *n*-alkanes from plants growing in petroleum soil is slightly lighter than that of plant under unpolluted condition.

Hydrogen isotopic composition of *n*-alkane in *S. salsa* and *P. australis*

The distribution of hydrogen isotopic composition of *n*-alkanes in *S.salsa* and *P. australis* from the YRD are presented in Fig. 3. *S. salsa* exhibited a zigzag pattern in δD value dependent on carbon number. The δD values of *S. salsa* and *P. australis* range from −227.3 to −157.9 ‰ and from −120.4 to −28.8 ‰, respectively. Moreover, the hydrogen isotopic compositions of the studied *n*-C_{25}, *n*-C_{27}, *n*-C_{29} and *n*-C_{31} were also analyzed in detail. The mean δD values of *n*-C_{25} in *S. salsa* and *P. australis* samples are −162.50 and −192.40 ‰, respectively. A similar difference in the δD value for *n*-C_{27}, *n*-C_{29} and *n*-C_{31} also exists in this study. *n*-Alkanes in *P. australis* have lighter mean hydrogen isotopic composition than those in *S. salsa*. This indicates that different kinds of plants have different hydrogen isotopic compositions

Table 3 $\delta^{13}C$ (‰, VPDB), and δD (‰, VSMOW) composition of C_{15}–C_{31} *n*-alkanes isolated from samples

n-alkane	P-soil		*S. salsa*		P-*S. salsa*		*P. australis*		P-*P. australis*	
	$\delta^{13}C$	δD	$\delta^{13}C$	δD	$\delta^{13}C$	δD	$\delta^{13}C$	δD	$\delta^{13}C$	δD
n-C_{15}	−30.49	−157.62	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n-C_{16}	−30.31	−150.96	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	−130.34
n-C_{17}	−29.03	−100.41	n.d.	−199.49	n.d.	n.d.	n.d.	−120.40	n.d.	−129.45
n-C_{18}	−31.33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	−120.63	n.d.	−126.64
n-C_{19}	−31.06	n.d.	n.d.	−182.38	n.d.	n.d.	n.d.	−165.83	n.d.	n.d.
n-C_{20}	−29.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	−150.12	n.d.	−170.72
n-C_{21}	−30.11	n.d.	−33.22	−165.52	n.d.	n.d.	n.d.	−177.14	n.d.	−178.75
n-C_{22}	−30.01	n.d.	n.d.	−177.97	n.d.	−190.60	n.d.	−174.75	−30.42	−179.68
n-C_{23}	−29.06	n.d.	−33.54	−175.82	−34.87	n.d.	−28.76	−199.52	−30.62	−190.98
n-C_{24}	n.d.	n.d.	−35.52	−185.62	n.d.	−180.50	n.d.	−179.46	n.d.	−193.29
n-C_{25}	n.d.	n.d.	−34.54	−162.50	−36.26	−175.08	−30.17	−192.40	−31.67	−199.21
n-C_{26}	n.d.	n.d.	n.d.	−176.52	n.d.	−185.79	n.d.	−195.35	n.d.	−197.95
n-C_{27}	n.d.	n.d.	−35.65	−183.80	−36.61	−188.21	−31.28	−197.44	−31.98	−194.96
n-C_{28}	n.d.	n.d.	−36.61	−170.48	−37.40	−188.19	−31.50	−193.70	−32.10	−193.17
n-C_{29}	n.d.	n.d.	−36.79	−157.87	−36.72	−177.99	−30.01	−189.68	−31.39	−195.66
n-C_{30}	n.d.	n.d.	n.d.	−227.32	n.d.	−209.29	n.d.	−176.83	n.d.	n.d.
n-C_{31}	n.d.	n.d.	−37.59	−180.99	−38.15	−184.99	−30.29	−178.69	−31.29	−199.09

n.d. not determined, *P-soil* petroleum-polluted soil sample, *S. salsa,* P-*S. salsa, P. australis and* P-*P. australis* refer to note of Table 2

possibly related to the hydrogen isotopic fractionation during plant growth. *S. salsa* has thin leaves and grows clinging to ground, while *P. australis* has wide leaves and grows far from the ground. This is likely to lead *S. salsa* leaf water to have smaller evaporation compared to *P. australis* leaves, so *S. salsa* leaf is enriched in ^{2}H.

In addition, δD values of *n*-alkane in unpolluted and polluted soil *S. salsa* ranged from −227.32 to −157.87 ‰ with the average of −178.58 ‰, and −209.29 to −175.08 ‰ with the average of −186.74 ‰, respectively. On the other hand, δD values of *n*-alkane in unpolluted and polluted soil *P. australis* ranged from −212.87 to −120.40 ‰ with the average of −183.67 ‰, and −246.48 to −126.64 ‰ with the average of −192.27 ‰, respectively. Based on this, the average hydrogen isotopic composition of *n*-alkanes in polluted plants *S. salsa* and *P. australis* is lighter than that of the same plants grew in unpolluted condition.

Effect of petroleum on the distribution of carbon and hydrogen isotopic composition in *n*-alkanes

The mean $\delta^{13}C$ values of *n*-C_{27} in *S. salsa* in unpolluted condition, *S. salsa* in petroleum-polluted soil condition, *P. australis* in unpolluted condition and *P. australis* in petroleum-polluted soil condition samples are −34.53, −36.26, −30.17 and −31.67 ‰, respectively. On the other hand, the mean δD values of *n*-C_{27} in such plant samples are −162.50, −175.08, −192.40 and −199.21 ‰, respectively. In this study, the $\delta^{13}C$ and δD variation between *S. salsa* in petroleum-polluted condition and *S. salsa* in unpolluted condition for *n*-alkane is small ($\Delta^{13}C = 0.7 \pm 0.6$ ‰ and $\Delta D = 6.4 \pm 11.9$ ‰). On the other hand, the $\delta^{13}C$ and δD variation between *P. australis* in unpolluted condition and *P. australis* in petroleum-polluted soil condition for *n*-alkane is also small ($\Delta^{13}C = 0.8 \pm 0.7$ ‰ and $\Delta D = 4.8 \pm 8.6$ ‰). Carbon and hydrogen isotopic compositions in the *P. australis* and *S. salsa* from the petroleum-contaminated area have relatively lighter isotopic composition (Table 3; Figs. 4, 5), indicating that these δD and $\delta^{13}C$ values may be used as indicators of a changing environment.

For the biosynthesis of *n*-alkanes, hydrogen and carbon isotopic fractionations occur during enzymatic reactions such as hydrogenation with nicotinamide adenosine dinucleotide hydrophosphoric acid (NADPH) (Sessions et al. 1999) and decarboxylation of pyruvate to form acetate (Monson and Hayes 1982). Generally, lipid compounds are biosynthesized from ^{13}C-depleted acetate precursors, and additional fractionations occur at biosynthetic branch points (Hayes 1993). However, the extent of hydrogen and carbon isotopic fractionation has not been clarified for each lipid molecule yet. Besides *n*-alkane biosynthesis, δD values of *n*-alkanes will be controlled by the isotopic composition of leaf water at the time they are formed. The δD of leaf water may vary relative to that of environmental water for a variety of reasons such as evaporation, use of groundwater and seasonality of precipitation (Dawson and Ehleringer 1993; Chikaraishi and Naraoka 2003).

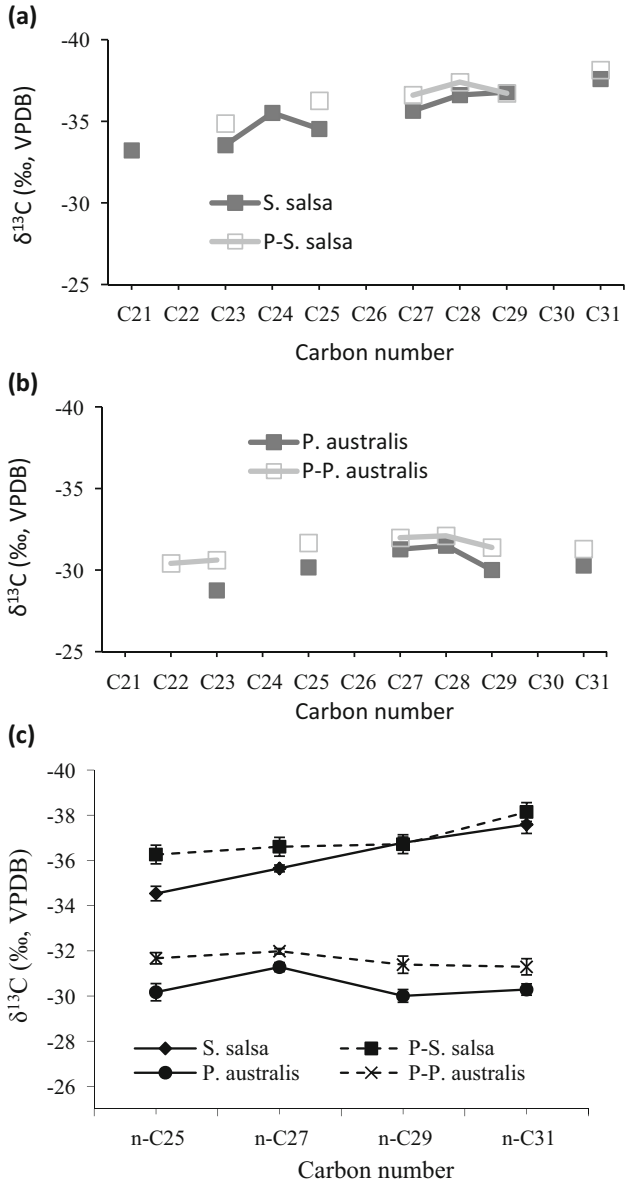

Fig. 4 $\delta^{13}C$ values of *n*-alkane vs. *n*-alkane carbon number

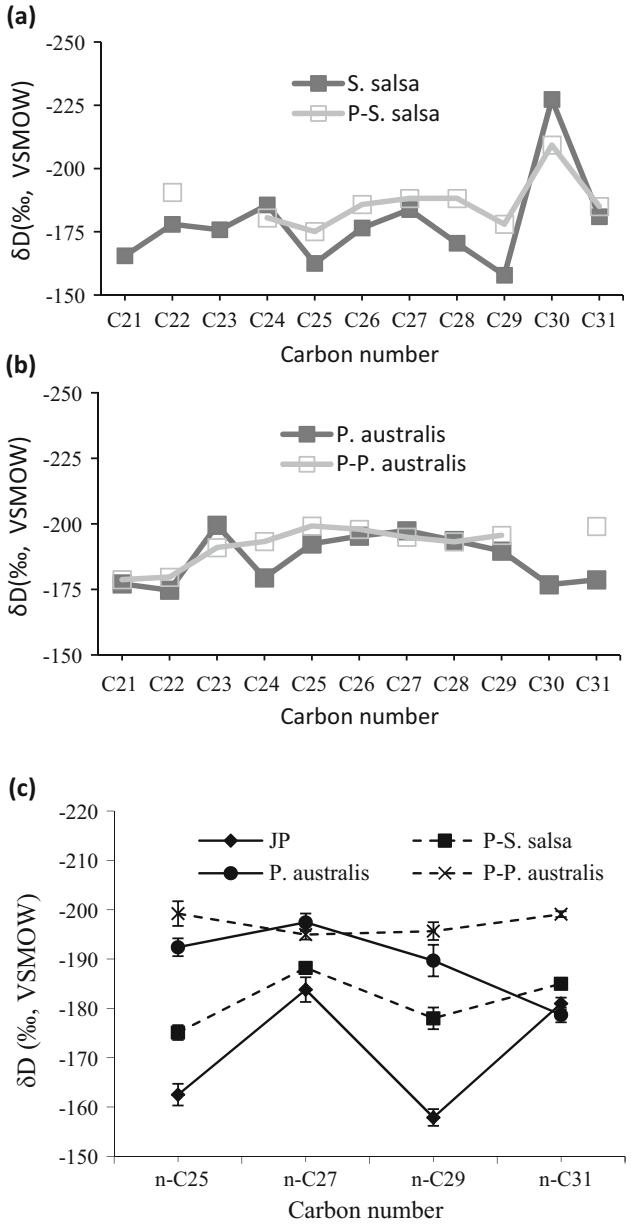

Fig. 5 δD values of *n*-alkane vs. *n*-alkane carbon number

It has been reported that photosynthesis was inhibited by high concentrations of hydrocarbon. Oil pollution affects the soil water condition, porosity and other physical properties; as well as soil carbon, nutrient and other chemical properties (Wang et al. 2011). The harmful effects of petroleum hydrocarbons in soils include inhibition of seed germination, reduction of photosynthetic pigments, slowdown of nutrient assimilation, water usage effectiveness (WUE) and shortening of roots and aerial organs (Peng et al. 2009). $\delta^{13}C$was mainly controlled by evapotranspiration and chemical fixation of carbon dioxide. Carbon isotopic composition ($\delta^{13}C$) values are positively correlated with WUE (Lucero et al. 2000). In general, δD values of biomolecules in plants are expected to be dependent on δD values of environmental water (e.g., Sternberg, 1988; Sauer et al. 2001). On the whole, the $\delta^{13}C$ value of crude oils (−34.4 ∼ −24.6 ‰; Shen and Xu 1998) was much lighter than the CO_2 (−7 ‰). In addition, δD of crude oils (−269 ∼ −93 ‰; Shen and Xu 1998) was also lighter than meteoric water (−80 ∼ −30 ‰) and soil water (−200 ∼ −160 ‰). Based on this, the lighter values of δD and $\delta^{13}C$ of individual *n*-alkanes in *S. salsa* and *P. australis* samples grew in petroleum-polluted soil may be due to the petroleum pollution.

Crude oil can exert acute or chronic toxicity or both on soil properties and *S. glauca* and *P. australis* (Wang et al. 2011). They also reported that petroleum hydrocarbon

utilizers can tolerate oil-contaminated environments because they may possess the capacity to utilize oil as energy sources. For example, a certain amount of crude oil may serve as fertilizer and stimulates the growth of *S. glauca*. Under petroleum-polluted conditions, plants or plant-associated microflora can convert hydrocarbons (HCs) to nontoxic forms. In this study, $\delta^{13}C$ values of *n*-alkane in polluted soil sample (P-soil) are within the range of −29.03 to −31.07 ‰, with the average of −29.85 ‰. $\delta^{13}C$ values of *n*-alkane in polluted soil *S. salsa* ranged from −38.15 to −34.87 ‰, with the average of −36.67 ‰. $\delta^{13}C$ values of *n*-alkane in polluted soil *P. australis* ranged from −32.10 to −30.42 ‰, with the average of −31.35 ‰. It suggested that there is not much correlation between the $\delta^{13}C$ values in petroleum-polluted soil and $\delta^{13}C$ values of *P. australis* and *S. salsa* in this study.

Conclusions

In this study, a variation of the composition of *n*-alkanes and their carbon and hydrogen isotopic composition in *S. salsa* and *P. australis* from YRD of China has been observed. The distribution of *n*-alkanes is in the range of C_{15}–C_{33} with high odd over even predominance and carbon-number maxima (C_{max}) at C_{25}, C_{27}, C_{29} or C_{31}. Average chain length (ACL) values varied from 27.61 to 28.59. The $\delta^{13}C$ values of *S. salsa* and *P. australis* ranged from −37.6 to −33.5 ‰ and from −31.3 to −28.8 ‰, respectively. On the other hand, the δD values of *S. salsa* and *P. australis* range from −227.3 to −157.9 ‰ and from −199.52 to −120.40 ‰, respectively. *S. salsa* has a lighter mean carbon isotopic composition than *P. australis*. *P. australis* has a lighter mean hydrogen isotopic composition than *S. salsa*. In this study, the $\delta^{13}C$ and δD variations between *S. salsa* of unpolluted conditions and those of petroleum-polluted soil conditions for *n*-alkanes are small ($\Delta^{13}C_{S.\ salsa} = 0.7 \pm 0.6$ ‰ and $\Delta D_{S.\ salsa} = 6.4 \pm 11.9$ ‰). In addition, the $\delta^{13}C$ and δD variations between *P. australis* of unpolluted conditions and those of petroleum-polluted soil conditions for *n*-alkanes are also small ($\Delta^{13}C_{P.\ australis} = 0.8 \pm 0.7$ ‰ and $\Delta D_{P.\ australis} = 4.8 \pm 8.6$ ‰). The distribution of $\delta^{13}C$ and δD values *n*-alkanes clearly shows that plants living in the contaminated area have a lighter mean isotopic composition than those measured in unpolluted area of YRD. The lighter values of δD and $\delta^{13}C$ or individual *n*-alkanes in *S. salsa* and *P. australis* samples of petroleum-polluted condition may be due to the reduction of photosynthesis and slowness of WUE by the petroleum pollution. There is not much correlation between the $\delta^{13}C$ values in petroleum-polluted soil and $\delta^{13}C$ values of *P. australis* and *S. salsa* in this study.

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