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ORIGINAL ARTICLE

Characteristics of CO_2 in unsaturated zone (~90 m) of loess tableland, Northwest China

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Abstract In order to observe CO_2 characteristics in the unsaturated zone of loess tableland and further understand the carbon cycle, a series of tubes for gas monitoring and sampling were installed in an approximately 90-m deep Qiushe loess section of Lingtai County, Northwestern China. The results show that the concentration of CO_2 was higher in loess than in the atmosphere, reaching a maximum of 6970 $\mu mol \cdot mol^{-1}$. CO_2 concentrations in loess were higher in summer than in winter. The CO_2 in loess was related to organic carbon decomposed by microbes, and to the $CaCO_3$–H_2O–CO_2 system in the interface between the saturated and unsaturated zones.

Keywords Unsaturated zone · Soil CO_2 · Carbon stock in deep loess · Quantitative paleoclimate reconstruction · Loess

1 Introduction

Carbon stock in subsoil or deep soil has lately been attracting more attention. The Chinese Loess Plateau (CLP) with an area of 640000 km^2, has loess deposits with a thickness up to 200 m (Liu 1985). The CLP is a huge carbon sink in China (Wan and Wang 2000), storing 197 Pg of organic carbon (Qin et al. 2001), more than 850 Pg of inorganic carbon (Liu et al. 2001), and 0.067 Pg of gaseous carbon (Liu et al. 2001), in addition to absorbing about 0.02 Pg of carbon yearly (Qin et al. 2001). However, the carbon cycle in deep loess is still not well understood. The significant link of CO_2 in deep loess to the carbon cycle has been inadequately studied and reported, a notable exception being the report of Liu et al. (2001) on loess CO_2 concentrations and their $\delta^{13}C$ in Puxian, Pianguan, Xingxian, Lishi, and Jishan sections. However, the deepest layer observed by Liu et al. (2001) was only the 7th paleosol layer in the Puxian section. Further observations are necessary to understand the control factors of CO_2 and the dynamics of the carbon cycle in deep loess.

In order to observe CO_2 concentration in deeper loess over the long-term, and to further understand the carbon cycle in the interface between the unsaturated and saturated zones of loess tableland, a series of tubes for CO_2 monitoring and sampling were buried in a typical loess section (the Qiushe) of the central CLP. Here, we report observed temporal and spatial characteristics of CO_2 in deep loess ($\sim$90 m).

2 Methods

The study area is located in Qiushe (107°41′08.79″E; 35°10′08.13″N), Lingtai County of Pingliang City, Gansu Province, China (Fig. 1). The landscape consists of a flat, long strip of loess tableland with a width of 1.1–1.5 km and numerous gullies. The elevation of the tableland is about 1225 m above sea level. A perennial spring exists at the bottom of most gullies, including at LGQ (0.45 l/s discharge), HMQ, CZQ, and YYQ (Fig. 1). The thickness of

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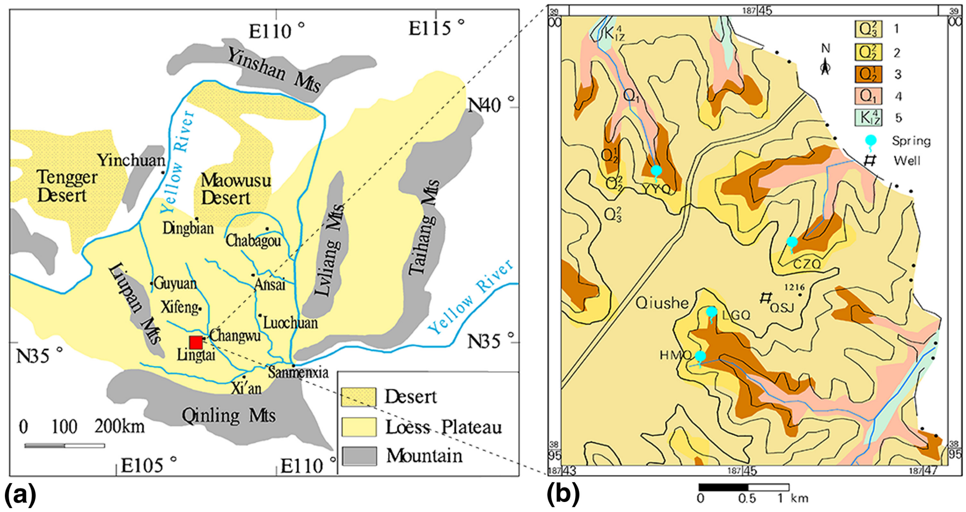

Fig. 1 Location and hydrogeological map of study area. **a** Loess Plateau of Northwestern China: *red square*—the location of the study area; **b** hydrogeological map: *1* Late Pleistocene loess (sand loam); *2 orange-yellow* Middle Pleistocene loess with light *red* paleosols (sand loam with clay layers); *3 deep orange* Middle Pleistocene clay with calcic concretion layers; *4* light *red* Early Pleistocene clay with calcic concretions; *5 light gray*, *brown-gray*, *brown-yellow* Cretaceous conglomeratic coarse sandstones, conglomerate

the groundwater aquifer is up to 25 m. The East Asia monsoon influences the climate of the Lingtai area, providing a semi-humid, warm-to-temperate, continental monsoon climate, characterized by relatively hot, humid summers and cold, dry winters. Lingtai station meteorological data from 1959 to 2008 show a mean annual temperature of 15.3 °C, with monthly mean temperatures in July and January of 22.1 and −4.7 °C, respectively. Mean annual precipitation is 605 mm, with rainfall concentrated in the summer and autumn. Mean annual latent evaporation reaches 1492 mm.

A series of horizontal monitoring holes were drilled in the Qiushe loess section, and polypropylene random (PPR) tubes (gas-storing tube: L = 80 cm, Ø = 45 mm; airway tube: L = 1.0 m, Ø = 1 cm) were buried in each hole. Soil CO_2 concentration was measured with the ATX620 m (Industrial Scientific Corp., Oakdale, PA, USA).

3 Results and discussion

3.1 The characteristics of CO_2 concentration in loess

The CO_2 concentrations from different loess and paleosol layers are listed in Table 1. CO_2 concentrations in loess were up to twelve times atmospheric levels. There was no distinct pattern of CO_2 concentration with depth, consistent with the results from Liu et al. (2001). CO_2 was highest—6970 parts per million by volume (μmol·mol^{-1})—in the S_{14} layer, which is the interface between the unsaturated and saturated zones in this loess section. This observation is consistent with many others around the world that soil CO_2 concentrations are highest near the water table (Arora et al. 2016; Keller 1991; Reardon et al. 1979; Walvoord et al. 2005; Wood et al. 1993; Wood 1985). Loess and paleosol CO_2 concentrations in summer were generally higher than in winter (Table 1).

3.2 The origin and controlling factors of CO_2 in deep loess

3.2.1 Organic matter: microbial effect

The $\delta^{13}C$ value of organic matter in the loess-paleosol is −24.9‰ to −14.6‰ (Lin and Liu 1992). If we consider that CO_2 in loess derives from the respiration of organic matter, $\delta^{13}C$–CO_2 should be in the range of −20.5‰ to −10.2‰ because the $\delta^{13}C$ value of CO_2 in soil is usually 4.4‰ higher than that of soil respiration CO_2 (Cerling et al. 1991), which is similar to the $\delta^{13}C$ value of organic matter (Liu et al. 2001). $\delta^{13}C$–CO_2 varied from −15.48‰ to −11.14‰ in the Puxian section, suggesting that the CO_2 mainly derived from microbial decomposition of stable organic matter (Liu et al. 2001).

Organic matter in the loess-paleosol sequence has been proven to have a positive relationship with magnetic susceptibility (Hu 2004; Jia and Lin 1993), where the paleosol layers often have higher organic matter content and greater magnetic susceptibility than the loess layers [see (1) and (2) in Fig. 2]. CO_2 concentrations and magnetic susceptibility were plotted to analyze the controlling factors of organic matter (Fig. 2). CO_2 concentration shows no obvious correlation with magnetic susceptibility, indicating that soil CO_2 in the deep loess unsaturated zone may be independent of organic matter and possess complicated control factors. The most important factor determining the decomposition of organic matter seems to be related to the spatially heterogenous distribution of fresh carbon and to soil microbial biomass (Rumpel and Kögel-Knabner 2011).

Table 1 CO_2 concentration in different loess and paleosol layers of the Qiushe loess section ($\mu mol \cdot mol^{-1}$)

Name	Layers	Depth (m)	20131106	20140131	20140725	20150223
	Atmosphere		450	450	430	450
QS1	S_0	1.00	3310	1750	6740	1730
QS2	S_0	1.40	3280	1710	6180	1790
QS3	S_0	1.80	2860	1750	5200	1810
QS4	S_1	11.45	720	440	1220	680
QS5	L_2	13.25	1020	1130	1390	750
QS6	S_2	15.98	1520	2820	1700	1150
QS7	S_2	17.65	3730	2820	4350	2690
QS8	S_2	18.20	3060	1960	4160	1540
QS9	S_2	20.20	2860	1920	3810	2690
QS10	L_3	23.59	2240	770	2410	1090
QS11	L_3	25.14	1640	790	1920	830
QS 12	S_3	26.54	1270	660	1680	720
QS13	L_4	30.94	1890	1250	2120	1170
QS14	S_4	32.14	980	560	1520	550
QS15	S_4	33.85	1900	1360	2490	1220
QS16	L_5	35.30	3330	2370	3570	2430
QS17	L_5	36.72	3530	2310	3550	2300
QS18	S_5	39.56	3730	2550	4290	2610
QS19	S_5	41.66	3590	2330	3790	2280
QS20	L_6	44.59	2180	1650	2570	1870
QS21	L_6	45.69	2750	1870	3070	1920
QS22	L_6	46.99	2850	2000	2950	1960
QS23	S_6	48.37	3100	2160	3380	1820
QS24	S_8	57.17	2330	1390	3240	1400
QS25	L_9	59.98	1550	1060	2030	1100
QS26	L_9	61.65	1760	1180	2070	1040
QS27	L_9	63.40	4120	3360	2860	3180
QS28	L_9	65.29	2490	1650	2580	1780
QS29	S_9	67.68	2630	1610	2530	1560
QS30	L_{10}	70.83	1810	1170	2000	1090
QS31	L_{12}	75.66	1200	730	1490	680
QS32	L_{13}	79.42	2010	1460	2130	1310
QS33	S_{14}	83.58	4110	4460	6970	4180

L loess layer, *S* paleosol

3.2.2 The impact of water

Consistent with observations from other areas (Arora et al. 2016; Keller 1991; Reardon et al. 1979; Walvoord et al. 2005; Wood et al. 1993; Wood 1985), the CO_2 concentration near the saturated zone had the highest value in this study, indicating that CO_2 distribution in loess is impacted by water. On the one hand, the layer near water has high soil moisture, resulting in increased organic matter decomposition compared to the layer with less moisture. On the other hand, past studies have shown that the dissolution and precipitation of carbonate mineral is a key geochemical process in loess. Such study results include: (1) the hydro-chemical type of groundwater in this study area is HCO_3–Ca·Mg; (2) the saturation index of calcite (SIc) in spring water varies from 0.31 to 0.40, demonstrating that the springs are saturated with respect to $CaCO_3$; and (3) the $CaCO_3$ content is 12%–16.1% in the loess layer and 49%–62% in the illuvial horizon (Zhao 2000), 79.2%–98% (89.7% on average) of which is secondary carbonate (Wen 1989). These results also indicate that the high CO_2 concentration of nearby groundwater in

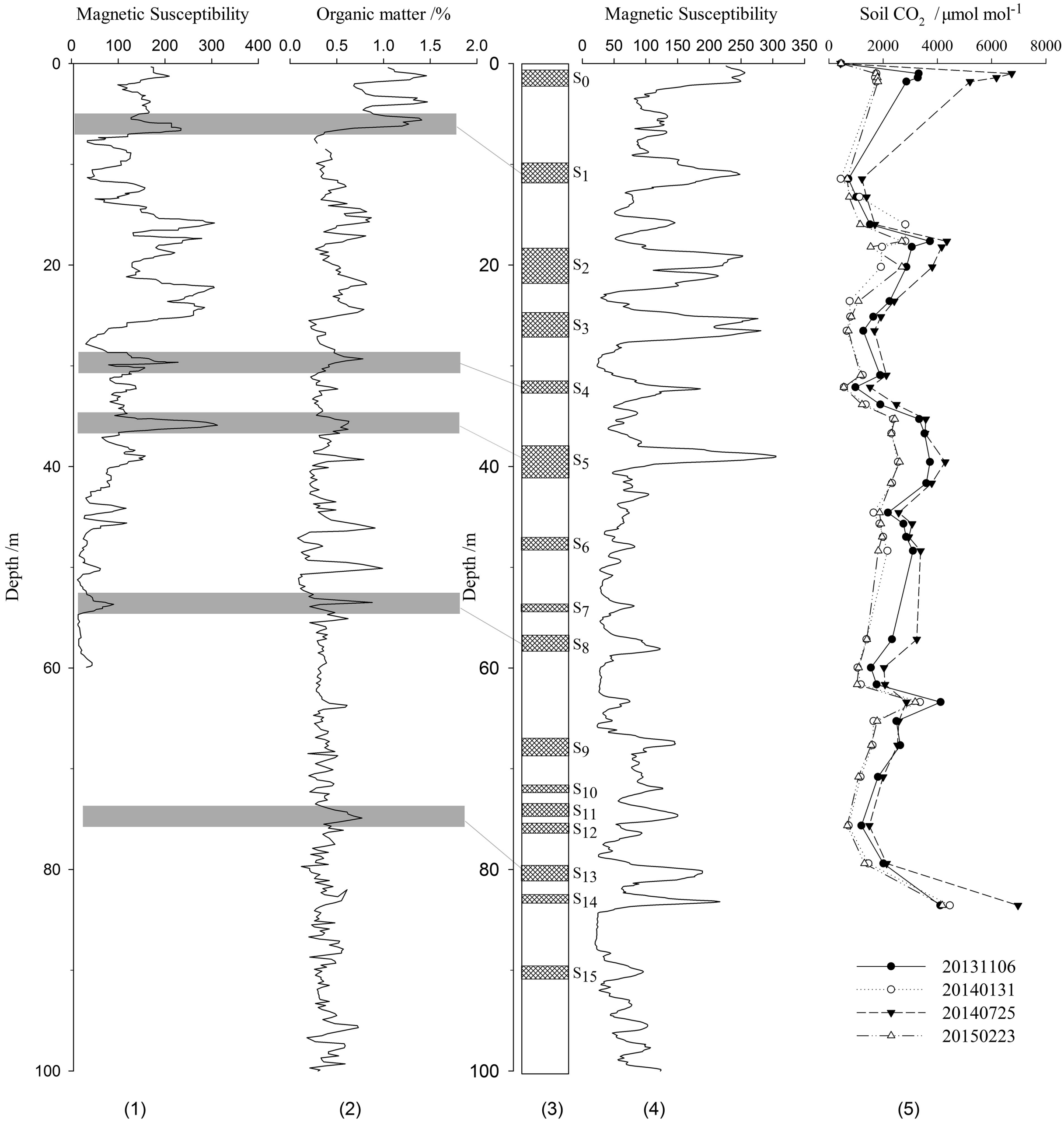

Fig. 2 CO_2 concentration in the unsaturated zone of loess. (*1*) magnetic susceptibility in Lantian loess section (Jia and Lin 1993); (*2*) organic matter in Lantian loess section (Jia and Lin 1993); (*3*) striped column: loess-paleosol sequence (*white*: loess; *gray*: paleosol); (*4*) magnetic susceptibility in Lingtai loess section (Sun et al. 2006); (*5*) concentration of soil CO_2 in Qiushe loess (this study)

this study is related to the degassing in groundwater described by the following equation: $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$, in a balanced system of $CaCO_3$–H_2O–CO_2 at the interface between the saturated and unsaturated zones. This can be partly proven by data from Liu et al. (2001) that show high CO_2 concentrations with high $\delta^{13}C$–CO_2 values. Moreover, scanning electron micrograph results from Walvoord et al. (2005) also indicate that at least part of the deep CO_2 is associated with calcite precipitation at a 110-m-deep water table.

3.3 The implication for quantitative reconstruction of paleoclimate using organic carbon proxy in loess

Organic carbon and/or its isotopic composition in the loess-paleosol sequence is often employed as a proxy in quantitative paleoclimate reconstruction (An 2014). A prerequisite for this analysis is that this proxy is invariable or at least a knowable variable. However, as discussed above, microbes and the groundwater cycle are two key factors driving the modern carbon cycle in loess, and affecting the carbon-related proxies. These effects need to be reexamined in further research.

4 Conclusions

CO_2 geochemical characteristics of deep loess ($\sim$90 m) were determined in the Qiushe section of Lingtai County, Northwestern China. The results show that the CO_2 concentration in loess was higher than in the atmosphere and reached a maximum of 6970 $\mu mol \cdot mol^{-1}$. CO_2 concentrations were higher in summer than in winter. The CO_2 in loess was not only related to microbial decomposition of organic carbon, but also to the balance of the $CaCO_3$–H_2O–CO_2 system in the interface between the saturated and unsaturated zones. Carbon fluxes (i.e., transportation and transformation) of deep loess carbon stock are posing a new challenge to quantitative paleoclimate reconstruction that uses proxies related to carbon in loess. Modern matter and energy cycle processes in deep loess need to be re-explored to unravel paleoclimate records. The research that remains to be conducted includes: (1) observing spatial and temporal characteristics of $\delta^{13}C$–CO_2 in deep loess; (2) characterizing different carbon stocks and their control factors (hydro, microbial) through drill cores; and (3) monitoring loess groundwater for dissolved inorganic carbon, dissolved organic carbon, particulate inorganic carbon, and particulate organic carbon, along with their isotopic variations.

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