The thermodynamics stability of soil humic and fulvic acids

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Abstract
The formation and transformation of humus is mainly a process of soil biochemical changes. However, it belongs to a thermodynamics stability field if we pay attention to the energy changes for initial and terminal states in humus. There are many factors that affect humus stability in soil. However, to calculate the reaction equilibrium constant ($\log K_R$) and the changes of standard Gibbs formation free energy ($\triangle G^o{}_f$), only the following three factors, capillary water activity ([H_2O]), oxygen partial pressure (pO_2) and carbon dioxide partial pressure(pCO_2), are taken into consideration supposing the temperature is 25^{o}C. By utilizing the $\log k_R$ and $1/n\triangle G^o{}_R$, we can calculate the thermodynamics stability range of FA and HA. The sequence of stability to ［H_2O］ and PCO_2 is FA > HA, and the stability to PO_2 is HA> FA. Under the controlled incubation experiments, more moisture, relatively low temperature, low oxygen concentration and high carbon dioxide concentration generally lead to the formation of FA.

Key Words
Thermodynamics stability, humic acid, fulvic acid, elemental composition formula, soil condition parameter

Introduction
Compared with live organic components (e.g. micro-organisms and plants), soil humus is more inert. In the sense, the soil humus and clay have similar properties and behaviors, such as the space-time continuity in composition, polymerization or degradation, being assembled and scattered, hydration or dehydration. Like clay, soil humus can adapt to themselves, constantly change into each other, be destroyed and newly formed in response to soil water, gas, heat and soil solution composition. Thus, it is possible to handle more complex soil humus the same as mineral elements from the perspective of thermodynamic stability (Tardy *et al.*， 1997). In soils, there are a number of factors, such as type and content of clays, vegetation, microorganisms, moisture, temperature, air composition, chemical composition and concentration of solution, acidity, status of redox, can affect the formation and transformation of soil humus. But from the aspect of thermodynamics, the above soil conditions can be simplified into three parameters, i.e. water activity ([H_2O]), oxygen partial pressure (p_{O2}) and carbon dioxide partial pressure (p_{CO2}), in order to calculate the reaction equilibrium constant ($\log K_R$) and Gibbs formation energies ($\Delta G^o{}_f$) at a given temperature of 25℃. As what we know, all organic substances are composed of the three elements and would eventually be decomposed into H_2O and CO_2 that contain the three elements. Owing to different conditions, various organic components are in different stages of the equilibrium system, and have different energy level (Dou， 2001).

Methods
Black soil (Typic Hapludoll) collected from the cultivated topsoil (0-20 cm) on the eastern side of Chang-Yi Road, Jilin Agricultural University Farm Changchun, Jilin, China (E125°23′45″, N43°48′44″), in April, 2000, was used to prepare HA and FA. Aeolian soil (Quartzipsamments) collected from the cultivated topsoil (0-20 cm) on Yaojingzi Grassland Research Station, Northeast Normal University, Changling, Jilin, China (E123°45′, N44°45′), in April, 2001, was used in the incubation experiment. The soil samples were air-dried and passed through 2 mm mesh sieve. The soil moisture was adjusted to 70%-80% of the field capacity. Then they were incubated preliminarily for 7 days before adding corn stalk. The corn stalk was dried at 50-70^{o}C, ground and passed through 0.25 mm mesh sieve. The OC content, total nitrogen and C/N of the corn stalk was 442.3 g kg^{-1}, 5.6 g kg^{-1} and 79, respectively. The C/N ratio was adjusted to 25:1 by mixing 6 g corn straw and 0.53 g $(NH_4)_2SO_4$ with 175 g aeolian soil. Eleven treatments with 3 repetitions were carried out in this experiment. The temperature treatments included 4 treatments: 10^{o}C, 25^{o}C, 40 ^{o}C and 55 ^{o}C. The moisture treatments included 4 treatments: 20 % (20W), 70 % (70W), 90 % (90W) of the field capacity, respectively, and waterlogged (Y). The oxygen (O_2) treatments included 3 treatments: 5 % O_2 (O1), 21 % O_2, 50 % O_2 (O3) treatments. The carbon dioxide (CO_2) treatments included 3 treatments: normal CO_2 concentration

(C0), 3 % CO_2 (C1), 30 % CO_2 (C2). At the same time, control experiments for these 11 treatments mentioned above were done without corn straw (CK). Sampling times were on days 1, 3, 7, 15, 30, 60, 90, 120 and 180d, respectively. The method for preparing HA and FA was the same as previously reported (Dou *et al.* 1991). The elemental composition of HA and FA was measured with a Vario EL.CHN analyzer. The reaction equilibrium constant ($\log K_R$) and Gibbs formation free energy ($\triangle G°_f$) of HA and FA were measured by "the elemental composition-soil condition parameter method". The method of humus composition modification was used in HA and FA quantitative analysis (Dou *et al.*, 2007). Organic carbon was measured by $K_2Cr_2O_7$-H_2SO_4 method, CO_3^{-2} HCO_3^- was measured by double-indicator method, and NO_3^- and NH_4^+ were measured by the electrode method. Other analyses were measured by conventional methods (Lao, 1998).

Results

Thermodynamic stability range of HA and FA

The Proportions of C, H, O, N in HA or FA of soil generally accounted for more than 97% of their elemental composition. This can be written to a simplified formula,that is nCxHyOzN. The tested element composition of HA and FA from black soil is shown in Table 1.

Table 1. The elemental composition of humic acid and fulvic acid in black soil (on an ash- and water-free basis).

Humus	C g/kg	H g/kg	N g/kg	O+S g/kg	C/H mol	C/N mol	O/C mol	simplified formula
HA	581.1	47.4	32.8	338.7	1.022	20.67	0.437	$nC_{21}H_{21}O_9N$
FA	473.8	54.8	23.2	448.2	0.720	23.83	0.709	$nC_{24}H_{33}O_{17}N$

According to the data in Table 1 and the simplified formula nCxHyOzN, the HA and FA of black soil can be expressed as $nC_{21}H_{21}O_9N$（$1/n$=431g/mol）and $nC_{24}H_{33}O_{17}N$（$1/n$=607g/mol）. It must be noted that the simplified formula does not represent the true size of molecules, as it is hard to determine the n. From the simplified formula, if the condensation degree of HA (C/H) is high, the oxidation degree of FA (O/C) is also high.

In addition, the soil conditional parameters and related thermodynamic data are also essential for the calculation of thermodynamic stability (see table 2).

Table 2. The soil conditional parameters and related thermodynamic data in the experi,mental black soil.

Item	P_{CO2} (g)	P_{O2} (g)	$[H_2O]$ (l)	e^-	H^+ (aq)	HCO_3^- (aq)	NO_3^- (aq)	NH_4^+ (aq)
log[mol L^{-1}] or log$P$ (0.1MPa)	-1.50	-31.54	-0.155	—2)	-7.0	-2.3	-3.46	-1.37
G^o_f（kJ mol^{-1}）	-394.4	0	-237.2	0	0	-587.1	-110.5	-79.5

1) log PCO_2= log[HCO_3^-]（mol L-1）－pH ＋7.8; log PO_2= log([NO_3^-]/2（mol L^{-1}）－log [NH_4^+])/2（mol L^{-1}）－pH－23.5; [H_2O] is calculated by 70% of soil relative humidity.2）not measured

Using the data listed in Table 2, we can calculate theΔG^o_f of HA and FA. The decomposition method can be used to calculate ΔG^o_f of FA.

$nC_{24}H_{33}O_{17}N$（FA）$_s$＋$4.5nH_2O_l$＋$26.75nO_{2\,g}$→$24nHCO_3^-{}_{aq}$＋$nNO_3^-{}_{aq}$＋$18nH^+_{aq}$ ……………..（1）

$\log K_R$ =660; $1/n\Delta G^o_R$=-5.707$\log K_R$=-3 765 kJ mol^{-1}; $1/n\Delta G^o_f$（FA）$_s$ =24ΔG^o_f（HCO_3^-）$_{aq}$＋ΔG^o_f（NO_3^-）$_{aq}$＋18ΔG^o_f（H^+）$_{aq}$－4.5ΔG^o_f（H_2O）$_l$－26.75ΔG^o_f（O_2）$_g$－ΔG^o_R=-10 983 kJ mol^{-1}

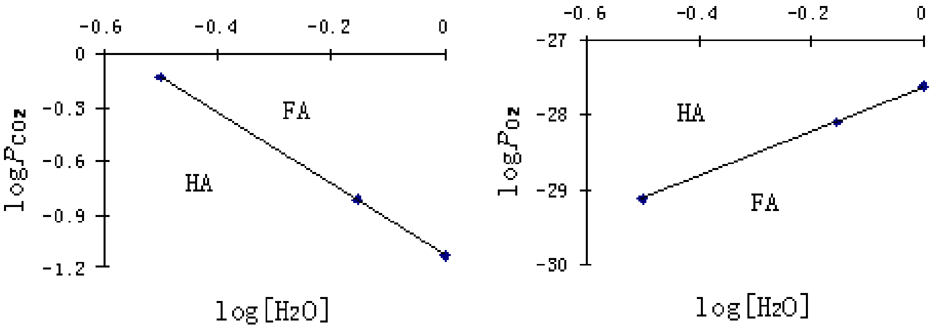
We can also use transformation method to calculate theΔG^o_f of HA.

$nC_{24}H_{33}O_{17}N$（FA）$_s$ ＋$2nO_2$→ $nC_{21}H_{21}O_9N$（HA）$_s$ ＋$3nCO_2$＋$6nH_2O$ …………………………（2）

$\log K_R$ =57.7; $1/n\Delta G^o_R$ =-5.707$\log K_R$=-329 kJ mol^{-1}; $1/n\Delta G^o_f$（HA）$_s$=-3ΔG^o_f（CO_2）$_g$－6ΔG^o_f（H_2O）$_l$＋ΔG^o_f（FA）$_s$ －2ΔG^o_f（O_2）$_g$＋ΔG^o_R= -8 268 kJ mol^{-1}

The equation (2) demonstrate that the transformation, from HA to FA, is a process of condensation, oxidation decarboxylation and dehydration, accompanied by decreased of C/N ratio. On the contrary, from HA to FA, it is a depolymerization, reduction and hydration process with an increased of C/N ratio.

In $1/n\Delta G^o_f$, n depends on the size of the molecular weight. If the molecular weight hardly determined, then we can just compare $1/n\Delta G^o_f$. If the average molecular weights for HA and FA are 6,000 and 1,500 respectively, the n value for HA and FA would be 14 and 2.5 respectively. Thus $1/n\Delta G^o_f$ of HA and FA are -115 752 kJ mol-1 and -27 458 kJ mol-1, respectively. If the given monomer model of HA is $C_{308}H_{335}O_{90}N_5$ and its molecular weight is 5541 g mol^{-1}, the n value is 13, and thus $1/n\Delta G^o_f$ is -107484 kJ mol^{-1}.With the $\log K_R$ values in reaction(2), the thermodynamic stability range of FA and HA can be calculated(Figure 1).As is shown,for $[H_2O]$and pCO_2, the stability order is FA ＞HA(Figure 1a); but for pO_2, the stability order is HA＞FA(Figure 1b).



a b

(a: $\log P_{CO2}$-$\log[H_2O]$, $\log P_{O2}$=-31.54; b: $\log P_{O2}$-$\log[H_2O]$, $\log P_{CO2}$=-1.5)

Figure1. Thermodynamics stability range of FA and HA in black soil (25°C).

It should be noted that although FA has high oxidation degree, it is more stable under the conditions of lacking of O_2, much moisture and high CO_2 concentration. HA is the opposite. In fact, under the conditions of bad ventilation, high moisture and acidity, such as cold podzols, tropical podzols and red soil, FA has more advantage than HA. On the contrary, in the environment of good ventilation, good drainage, much saline groups and lack of acidity, such as black soil, chernozem, it is beneficial to polymerization and thus HA is more stable. Of course, the opposite situation may exist. For example, the HA/FA in paddy soil is much higher than that in the corresponding upland soil. From hill to basin, the HA/FA in perennial cold soak field is higher than that in red soil, yellow-mud field and alluvial land.

Effect of temperature, moisture, O_2 and CO_2 on humus composition

To verify the method of thermodynamic stability offered above and to study on the effect of mono-environmental factors on the formation and transformation of HA and FA, PQ (the proportion of HA in extracted HS) of incubated soil under different temperature, H_2O, pO_2 and pCO_2 conditions was analyzed.

Considering the entire incubation period (Figure 2a), the effect of temperature on the values of PQ was not significant. But the values of PQ in the treatments of 40°C and 55°C were slightly but not significant higher than those in the treatments of 10°C and 25°C. This indicated that high temperature was beneficial to the formation of HA or the transformation from FA into HA.

Figure 2b shows that the change regularity of PQ under different moisture treatments had poor logical order during the entire incubation period. But on the average (A), the value of PQ of water-logged treatment (Y) was much lower.Thus, waterlogged condition is beneficial to transformate HA into FA, which coincides with the result that high moisture is beneficial to the formation of FA (Tardy *et al*., 1997; Dou, 2007).

Fig.3 shows the effect of O_2 and CO_2 concentration on HS, the values of PQ of various treatments became much lower with addition of corn straw. This indicated that the initial speed for FA formation was higher than that of HA formation in the decomposition period of corn straw. On different time points, most of PQ values were in the sequence of O3＞O2＞O1 among different O_2 concentration treatments (Figure 3a). This showed that high O_2 concentration favored the formation of HA or FA further transformation into HA. This is coincided with the result that soil with low moisture, good ventilation was beneficial to the formation of HA, but was unfavorable to the formation of FA (Tardy *et al*., 1997; Dou, 2007), although this issue needs further study.

From Figure 3b, it could be seen that the values of PQ of C2 treatments were almost the lowest in the entire process of incubation, but the PQ values of C1 and C0 were much higher than C2. Thus, the accumulation of HA under high CO_2 concentration treatment (C2) was lower than under low CO_2 concentration treatments (C1 and C0). Another possibility might be that FA was more stable under the condition of high CO_2 concentration, which coincided with the thermodynamic stability results mentioned above.

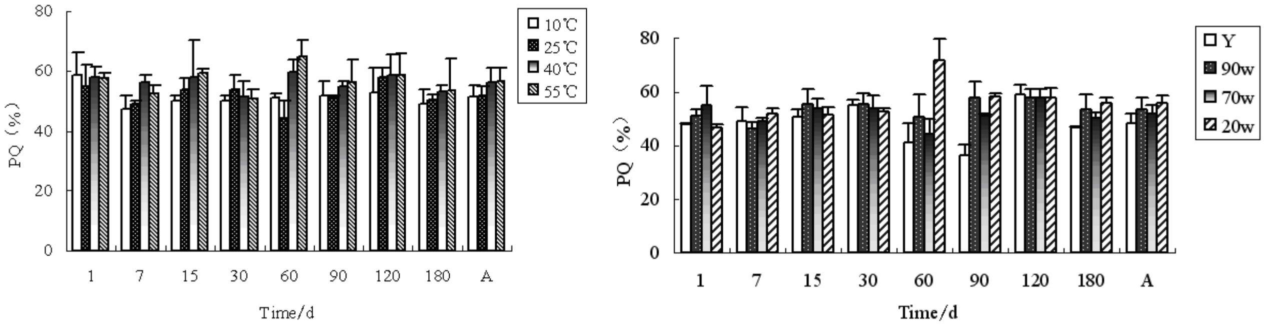


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Figure2. PQ values of soil humic substances under different temperatures and moistures ("A" is the average of PQ)
a : different temperatures ; b : moistures, 20W, 70W and 90W mean the 20%, 70% and 90% of field moisture capacity, respectively, and Y means waterlogged.

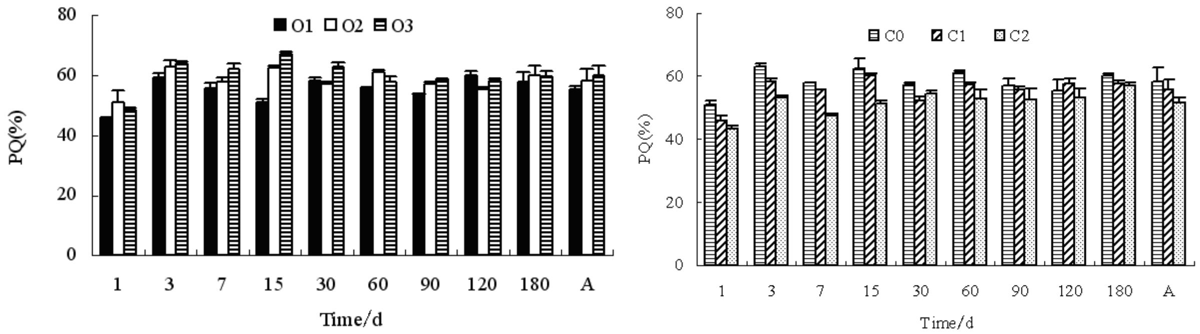

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Figure 3. PQ values of soil humic substances under different O_2 and CO_2 concentrations ("A" is the average of PQ)
a: different O_2 (O1:5%, O2: 21%, O3: 50%); b: different CO_2 (C0: normal CO_2 concentration, C1: 3% CO_2, C2: 30% CO_2)

Conclusion

The stability order of two HS fractions analyzed by this method was FA＞HA for [H_2O] and pCO_2, but was HA＞FA for pO_2. This indicates that high moisture and high CO_2 concentration were beneficial to the formation and stability of FA. Incubation experiments showed that low temperature, high moisture and high CO_2 concentration were more beneficial to the formation of FA, while low moisture and high O_2 concentration were more beneficial to the formation of HA.

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