Internal energy ratios as ecological indicators for description of the phytoremediation process on a manganese tailing site

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ABSTRACT

A plant community is an open thermodynamic system. In accordance with the first and second laws of thermodynamics, the total internal energy U of a plant community before reaching equilibrium will increase under natural conditions because of solar energy intake and nutrient uptake. As state functions of a thermodynamic system, enthalpy H, entropy S and Gibbs free energy G are related to U by $G + TS = H = U + PV$. Increase in U will lead to increases in H, S and G since given volume V and temperature T or pressure P, $dG + TdS = dH = dU > 0$. The experimental data collected from the plant communities restored on a manganese tailing site confirmed the potential trend of increase in H, S and G of the plant communities with increase in their biomass quantity and biodiversity. The traditional criterion "$\Delta G < 0$" would then be no longer valid as a spontaneity index for description of the ecological process of a growing and developing plant community. Since $G/H = 1-T(S/H)$, given T, G/H will be negatively related to S/H. The number of plant species N is an essential property of a plant community, and as a function of N, the S/H ratio is expected to increase with increase in species richness under natural conditions, resulting in $d(S/H) \geq 0$ and $d(G/H) \leq 0$. The change in G/H can thus be applied as a thermodynamic parameter to judge the spontaneity of plant community growth and development. The results obtained from the present study showed that both G/H and S/H ratios were useful indicators for description of the ecological restoration process.

1. Introduction

Thermodynamics of ecosystems has become one of the foundational areas supporting the continuous development of systems ecology (Jørgensen et al., 2016; Notte et al., 2017; Patten, 2016; Puzachenko et al. 2016). The contributions made in this area include the work of Jørgensen (1992, 1995, 2000, 2010), his co-workers (Jøgensen et al., 1995, 2005; Jørgensen and Nielsen, 2007; Jørgensen and Marques, 2001), and many other researchers (Draganovic et al., 2013; Molozzi et al., 2013; Perryman and Schramski, 2015; Tang et al., 2015). Most recent studies in related fields are focused on analysis of emergy (Berrios et al., 2017; Ferraro and Gagliostro, 2017; Fonseca et al., 2017; Ohnishi et al., 2017; Shal and Hurme, 2017) used as an environmental accounting factor (Franzese et al., 2017; Pattersona et al., 2017; Picone et al., 2017; Vassallo et al., 2017) and determination of eco-exergy (Banerjee et al., 2017; Linares et al., 2017; Veríssimo et al., 2017) applied as a thermodynamic-oriented indicator. A few studies have also been carried out on entropy-based indicators in ecological network analysis (Laner et al., 2017; Ludovisi and Scharler, 2017).

Plant growth and development are essentially processes of matter and energy transformation. A plant community is thus an open thermodynamic system with plant species as key components, and its state changes can be determined by thermodynamic functions (Rodríguez et al. 2016, 2017). The total internal energy U of a thermodynamic system contains three interrelated components, enthalpy H, entropy S and Gibbs free energy G (Engel and Reid, 2006), of which all are quantitatively related to those commonly applied ecological indices, such as primary productivity as a function of biomass, and biodiversity as a combination of species richness, abudance and evenness (Molles, 2016; Ricklefs and Relyea, 2014). Analysis of H, S and G of a plant community restored on a metal contaminated site should be of high value in implementation of phyto-remediation projects and assessment of their effects.
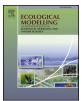
Determination and prediction of the direction of matter and energy flows in ecosystems can provide useful information for ecological management. According to the second law of thermodynamics (Direction of change), energy is transformed spontaneously in one direction only towards decrease in intensity gradient (Engel and Reid,

2006), which means that the direction of natural changes is determined by intensity factors. When it comes to the third law of thermodynamics (Quantification of entropy), however, decrease in Gibbs free energy, "$\Delta G < 0$", becomes a criterion for judging the spontaneity of various reactions in fundamental physics and chemistry (Engel and Reid, 2006; Brown et al., 2006). Since G is a capacity factor, the precondition and limitation for using ΔG as a direction indicator needs to be clarified to avoid the conflict between the second and third laws of thermodynamics. Results from previous studies (Wu et al., 2017) showed that following the first and second laws of thermodynamics, U, H, S and G of a restored plant community all increased in the observed period under natural conditions because of solar energy intake and nutrient uptake. The criterion "$\Delta G < 0$" would then be no longer valid as a spontaneity index for description of the ecological process of a growing and developing plant community.

Subject to the basic relation, $H = G + TS$, the G/H ratio will be negatively related to the S/H ratio. As a function of species richness of an ecosystem, the S/H ratio is expected to increase with increasing number of bio-species. Biodiversity has been shown to stabilize a number of ecological processes (Rinella and James, 2017). If, according to the equilibrium theory in ecology (Molles, 2016; Ricklefs and Relyea, 2014), an ecosystem possesses a natural trend towards increase in its species richness before reaching equilibrium, there should be a potential trend of decrease in its G/H towards increase in its number of species.

The main objective of this study is to evaluate the rationality of using G/H and S/H ratios as ecological indicators for description of ecological restoration processes. In our previous work (Wu et al., 2017), the conventional expressions for description of various reactions in gas, liquid, solid and mixed systems have been applied to determine H, S and G of the plant communities under study. The discussions in the following theoretical section will give further support to the general applicability of the conventional functions for all types of systems including ecosystems.

2. Theoretical

2.1. Precondition for using "$\Delta G < 0$" as a spontaneity indicator

From the conventional relation (Engel and Reid, 2006),

$$G + TS = H = U + PV \tag{1}$$

V
T
P
G
S
H
U

$$dG + TdS = dH = dU = 0$$

Thus

$$dG = -TdS$$

Since $T \geq 0$, and according to the third law of thermodynamics, the sum of entropy of the system and surroundings increases in spontaneous processes, which is equivalent to say that the entropy of an isolated system increases in spontaneous processes, we can write

$$d(S_{sys} + S_{sur}) = dS_{\text{(isolated system)}} \geq 0$$

and thus

$$dG_{\text{(isolated system)}} \leq 0$$

It should be noted that both $dH = dU = 0$ and $dS \geq 0$ are essential conditions to ensure $dG \leq 0$. For example, in either open or closed

Table 1
Changes in thermodynamic functions between initial and final states of reactions taking place in isolated systems.

Reaction	Formula	Number of component (N)		Difference between states (Given V and T or P)
		Initial state	Final state	
Combination	A + B = = D	2 (A, B)	3 (A, B, D)	$\Delta U = 0$; $\Delta C_T = 0$; $\Delta H = 0$; $\Delta N \geq 0$; $\Delta S \geq 0$; $\Delta G \leq 0$
Decomposition	D = = A + B	1 (D)	3 (D, A, B)	$\Delta U = 0$; $\Delta C_T = 0$; $\Delta H = 0$; $\Delta N \geq 0$; $\Delta S \geq 0$; $\Delta G \leq 0$

systems, if $dH = dU \neq 0$, $dG \neq -TdS$, and both dG and dS can be either higher or lower than zero. In open and closed systems, one may have $dH = dU = 0$ when the exchange of matter and energy between systems and surroundings reaches equilibrium. The direction of the change in G in such systems, however, is still uncertain as the change in S of the systems, dS_{sys}, can be either positive or negative. When a system is isolated, its total internal energy U and mass quantity C_T will remain constant while various reactions can take place among its components. In general, reactions will reach dynamic equilibrium between reactants and products at the final state, which means that, generally, the reactants will not disappear from the system except for parts of their mass being transformed into products. Examples given in Table 1 show that the total number of the components N increases in both combination and decomposition reactions because of the formation of new products. Increase in N leads to increase in diversity or disorder of system composition (namely, S) while the energy available to perform net work (namely, G) is consumed in the reaction. Thus, given $\Delta C_T = 0$ and $\Delta U = \Delta H = 0$ in isolated systems, $\Delta N > 0$ leads to $\Delta S > 0$ and the unique direction for the change in G is $\Delta G < 0$. The conclusion will then be that the criterion "$\Delta G < 0$" can only be used as a spontaneity indicator for isolated systems subject to the condition $\Delta S_{\text{(isolated system)}} \geq 0$.

It is necessary to mention that the spontaneous decrease in G associated with increase in S in the reactions listed in Table 1 is due to the decrease in chemical potential μ of the reaction components, which, since μ is an intensity factor, obeys the second law of thermodynamics (Wu et al., 2009). Using the decomposition reaction (Table 1) as an example, the Gibbs free energy of the reaction system at the initial state will be,

$$G_0 = C_0 \mu_{Co}$$

where μ_{Co} denotes the initial chemical potential of D, while that at the final (equilibrium) state will be

$$G_e = C_1 \mu_D + C_2 \mu_A + C_3 \mu_B$$

where, for a unit volume reaction system, C_0 denotes the molar concentration of component D at the initial state while C_1, C_2 and C_3 stand for, respectively, that of components D, A and B at the final state. Since there is no loss of mass quantity in the reaction, $C_0 = C_1 + C_2 + C_3$, the change in G will be

$$\Delta G = G_e - G_0 = (C_1 \mu_D + C_2 \mu_A + C_3 \mu_B) - C_0 \mu_{Co} = (C_1 \mu_D + C_2 \mu_A + C_3 \mu_B) - (C_1 + C_2 + C_3)\mu_{Co} = C_1(\mu_D - \mu_{Co}) + C_2(\mu_A - \mu_{Co}) + C_3(\mu_B - \mu_{Co}) < 0$$

Molar concentration C_i and chemical potential μ_i are two positively related intensity factors. Since $C_1 \leq C_0$, $C_2 \leq C_0$ and $C_3 \leq C_0$, we have $\mu_D - \mu_{Co} \leq 0$, $\mu_A - \mu_{Co} \leq 0$, $\mu_B - \mu_{Co} \leq 0$ and thus $\Delta G \leq 0$. It follows that since $C_i \leq C_0$ and $\mu_i - \mu_{Co} \leq 0$ in all types of reactions that reach dynamic equilibrium under isolated conditions, the generalized relation holds

$$\Delta G = G_e - G_0 = \Sigma C_i(\mu_i - \mu_{Co}) = \Sigma C_i \Delta \mu_i \leq 0 \quad C_0 = \Sigma C_i$$