Thermodynamic analysis of an ecologically restored plant community:Process and diversity

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Abstract

The experimental data used for testing the applicability of the thermodynamic equations presented in the theoretical section were obtained from an ecological restoration project implemented at a manganese tailing site. Restoration of the plant community was shown to be an irreversible process characterized by spontaneous increases in its total biomass CT and total number of plant species N associated with increases in its enthalpy H, Gibbs free energy G and entropy S. Species enrichment was the cause for the decease in mass ratio xi (biomass of a species Ci divided by CT) and biomass growth potential μ i (the partial derivative of Gi with respect to Ci). The increase in s/CT (s denoting the ratio of S to gas constant R) associated with decrease in f/CT (f denoting the ratio of G to RT) with increasing N confirmed that the restored plant community possessed natural trends towards increase in its species richness and evenness. The observed trends gave support to use of the thermodynamic functions for describing the productivity-biodiversity relationship. The present analysis did not fully prove the use of the Shannon form of information entropy as a biodiversity index for the investigated plant community could not be uniquely determined by its individual numbers. In comparison, the entropy factor s was shown to be a suitable biodiversity index. The fact that N is the key factor that determines the changes in s/CT and f/CT makes N > 0ause fulindex for determining the direction f spontaneous changes for allopensystems with continuous input of matter and energy. Asameasureo

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Abstract. The experimental data used for testing the applicability of the thermodynamic equations presented in the theoretical section were obtained from an ecological restoration project implemented at a

manganese tailing site. Restoration of the plant community was shown to be an irreversible process characterized by spontaneous increases in its total biomass $C_{\rm T}$ and total number of plant species N associated with increases in its enthalpy H, Gibbs free energy G and entropy S. Species enrichment was the cause for the decease in mass ratio x_i (biomass of a species C_i divided by $C_{\rm T}$) and biomass growth potential μ_i (the partial derivative of G_i with respect to C_i). The increase ins $/C_{\rm T}$ (s denoting the ratio of S to gas constant R) associated with decrease inf $/C_{\rm T}$ (f denoting the ratio of G to RT) with increasing N confirmed that the restored plant community possessed natural trends towards increase in its species richness and evenness. The observed trends gave support to use of the thermodynamic functions for describing the productivitybiodiversity relationship. The present analysis did not fully prove the use of the Shannon form of information entropy as a biodiversity index for the investigated plant communities. Because of the presence of significant differences in individuals among species, the biodiversity of the plant community could not be uniquely determined by its individual numbers. In comparison, the entropy factor swas shown to be a suitable biodiversity index. The fact that N is the key factor that determines the changes ins $/C_{\rm T}$ and $f/C_{\rm T}$ makes N > 0ause ful index for determining the direction of spontaneous changes for all opensystems with continuous input of matter and

Key words: ecological restoration; metal contamination; thermodynamic functions; spontaneous changes; biodiversity.

Introduction

The objective of this study is to examine the applicability of the thermodynamic equations presented in the theoretical section (Theoretical basis) for description of a plant community ecologically restored at a manganese tailing site. Remediation of a damaged ecosystem should be a manipulated process welldesigned with proper measures and explicit targets (Baldera et al., 2018; Laughlin, 2014; Zhao et al., 2016; Haapalehto et al., 2017; Tongkoom et al., 2018) that can maximize the benefits and minimize the damages that are currently existed and that can possibly be brought into the site due to use of improper methods (González et al., 2014; Wallace et al., 2017; Garrouj et al., 2019). Performing a thermodynamic analysis focusing on changes in individual, population and community traits in the restoration process can provide useful information not only for assessment of the remediation effect but also for development of relevant knowledge and technology (Hesse et al., 2018; Kollmann & Mahy, 2018; Fiedler et al., 2018).

Biomass quantity C, individual number m and species number N are the three basic parameters that can be directly used as indicators for, respectively, productivity, species abundance and species richness. Other parameters developed for describing a specific state of an ecosystem, such as the Shannon-Wiener and Simpson indexes (Ricklefs & Relyea, 2014), exergy (Jørgensen, 2010; Jørgensen et al., 2016) and entropybased indicators (Laner et al., 2017; Ludovisi & Scharler, 2017), etc., are all presented as functions of C ,m or N , or a combination of them. Accounted for by their additive nature, $\,C\,$, $\,m\,$ and $\,N\,$ are extensive properties of an ecosystem. Thus, as primary state variables of an ecosystem, C, m and N all have fixed values at a given state and their changes can be uniquely determined by their difference between states regardless of the process history. It follows that all indexes presented as functions of either C, m or Nare also state variables with defined meanings in thermodynamics. The conventional indexes are useful and sufficient if one is only interested in assessing the remediation effect. They are not, however, sufficient enough if one is also interested in revealing their related mechanisms and apprehending their significances in ecology. The difference, for an example, in mathematical expressions between the Shannon-Wiener index (or the Shannon form of information entropy) as a function of m and N (Harte & Newman, 2014; Newman et al., 2014) and entropy S as a function of C and N will lead to differences in advantages and disadvantages of their applications. Analysis of their difference using the obtained experimental data can offer a better understanding of the restoration process reflected by the changes in C, m and N.

Two fast-growing tree species *P. fortunei* and *K. bipinnata* were used as dominant species in the implemented restoration project. Analysis of their thermodynamic behaviors and the changes in their contribution rates with increase in species richness and abundance should be a meaningful approach to determine the causes that lead to the changes in the internal energy state of the restored plant community. Due to limited scope, the present analysis will be focused on identification of the key thermodynamic factors related to spontaneous

Methods

Applied remediation measures

Screening of metal-tolerant species known as hyper-accumulators applied for remediation of a metal contaminated site has been a worldwide hotspot of research (García et al., 2009; Tie et al., 2005; Zhang et al., 2015). A hyper-accumulator does not only tolerate high concentrations of a metal element in its tissue but also possesses high under-ground to above-ground metal transfer rates (Abreu et al., 2102; Adamo et al., 2014). The demerits for use of most of the reported hyper-accumulators, however, are their low levels of biomass growth associated thus with low levels of total metal uptake. In addition, the nature of their tolerance to a specific metal element also limits their application on multiple metal contaminated sites. Attentions in related fields have been paid to use of tree species (Bidwell et al., 2002; Yang et al., 2008; Wang et al., 2010) . As most of the fast-growing tree species cannot survive under heavily metal contaminated conditions, the commonly applied methods for forestation at a metal tailing site are either to seal its upper layer with an uncontaminated soil (Gomez-Ros et al., 2013) or to use an immobilization reagent to reduce its upper layer's metal toxicity (Vargas-García et al., 2012, Yang et al., 2017). The disadvantages of soil sealing and metal immobilization are mainly their high costs.

The experimental site under study was a manganese tailing wasteland located at Xiangtan, Hunan, China. The site was poor in nitrogen and phosphorus but very high in contents of manganese, lead, zinc, copper, cadmium and chromium. The applied remediation strategy was a combination of the above mentioned methods using tree species, metal-tolerant species and remediation reagent. Two fast-growing tree species (*Paulownia fortunei* and *Koelreuteria bipinnata*) screened from the native species naturally distributed in the uncontaminated region nearby the tailing site were used as dominant phyto-remediation species. Before transplanting their seedlings, a bacteri-rich organic manure specifically prepared for the tailing site was amended to their rhizospheric areas. The enrichment of the site's biodiversity was counted on natural germination of the native metal tolerant plant species based on the soil seed bank theory (Tang et al., 2006). To prevent the spread of metal contamination to surrounding areas, an ecological interception belt along the border of the tailing site was established and its outlet was connected to a constructed wetland system for treatment of runoff.

Detailed experimental information has been presented in previous work (Ouyang et al., 2016; Wu et al., 2017). The experiment plots, sample analysis and equations for calculation are briefly described below.

Experimental plot

The total experimental area was 4.4 hectares consisting of the three plots:

(I): 4.0 hm², manganese tailing site amended with an organic manure as a base fertilizer to increase the nutrient availability and reduce the metal toxicity in the rhizosphere before transplanting one-year old seedlings of *P. fortunei* and *K. bipinnata* (spacing 2-2.5m, 1000 plants of each species/hm²).

(II): 0.2 hm^2 , manganese tailing site amended with equivalent amounts of chemical fertilizers in the rhizosphere before transplanting one-year old seedlings of the same tree species (spacing 2-2.5m, 1000 plants of each species/hm²) and

(III): 0.2 hm², uncontaminated site in the vicinity of the tailing wasteland, a plant community naturally developed under normal soil conditions.

Sample collection and analysis

Plant and soil samples were collected from three fixed standard blocks (approximately 667 m^2 each) in each plots in June and October each year from 2009 to 2016 and analyzed following standard procedures (GB15618-1995; GB3838-2002; GB18918-2002, People's Republic of China). The numbers of individual plant and plant species were counted on-site. The relative standard deviations in duplicate sample analyses ranged between 8.4%-16.4% in biomass measurement and 5.1%-18.3% in metal uptake determination. The average values of the measurements were used for further calculation. The differences in related values between treatment plots were compared with LSD analysis of variance.

Calculation

For comparison, the Shannon-Wiener index (the Shannon form of the information entropy) was calculated by

 $SI=[?](m_i/M)\ln(M/m_i) = [?]p_i\ln(1/p_i) M = [?]m_i, p_i=[?]m_i/M, i = 1, 2, ..., N (1)$

where m_i denotes the number of individuals of the ith plant species, M denotes the total number of individuals of the plant community, N denotes the total number of species of the plant community and p_i stands for the relative abundance of the ith plant species (Eq. 1 referring to Eq. 15 in the theoretical section).

The thermodynamic factors h, s and f (enthalpy H, entropy S and Gibbs free energy G divided, respectively, by gas constant R and temperature T) were calculated by

$$h = H /(RT) = C_{\rm T} \ln(N_{\rm m}) = C_{\rm T} \ln(66) \ C_{\rm T} = [?] C_{\rm i} (2)$$

$$s = TS /(RT) = S /R = [?] C_{\rm i} \ln(1/x_{\rm i}) x_{\rm i} = C_{\rm i} / C_{\rm T}, C_{\rm i} = [?] c_{\rm ij}, j = 1, 2, ..., m_{\rm i} (3)$$

$$f = G /(RT) = h - s = C_{\rm T} \ln(66) - [?] C_{\rm i} \ln(1/x_{\rm i}) (4)$$

$$s / C_{\rm T} = (1/C_{\rm T})[?] C_{\rm i} \ln(C_{\rm T} / C_{\rm i}) = [?] x_{\rm i} \ln(1/x_{\rm i}) (5)$$

$$f / C_{\rm T} = \ln(N_{\rm m}) - s / C_{\rm T} = \ln(66) - s / C_{\rm T} (6)$$

where c_{ij} denotes the net dry biomass quantity of the jth plant for the ith species, C_i denotes the total net dry biomass quantity of the ith species, C_T denotes the total net dry biomass quantity of the plant community, x_i denotes the mass ratio for the ith species, and N_m stands for the maximum number of plant species (Eqs. 2-4 referring to Eqs. 11-13, 24 in the theoretical section). As an upper limit of $N_{,N_m}$ for a given habitat is a constant. The enthalpy factor h is a linear function of C_T and use of any N_m value will not change its basic relation with the Gibbs free energy factor f and entropy factor s. Since, as a potential limit, N_m is a parameter related to regional species richness, the highest number of plant species 66 observed in the non-polluted surrounding area nearby the metal contaminated site was used as N_m for calculating h.

For comparing the difference among plant species, the standard deviation for relevant parameters was calculated by

$$SD = [?][(Z_{i} - Z)^{2}/(N - 1)]^{1/2} Z = [?]Z_{i}/N$$
 (7)

where Z_{i} denotes a parameter for the ith species and Z denotes its mean value.

Results and analysis

Dynamic changes in the restoration process

The total net dry biomass $C_{\rm T}$ and total number of species N of the plant communities in Plots I (amended with organic manure), II (amended with chemical fertilizer) and III (uncontaminated site) obtained in the period 2010 - 2016 are given in Table 1. Basic data for plant species are presented in Appendix 1. The values of h, s, f, s / C T and f / C T in Table 1 were calculated, respectively, by Eqs. 2-6. As a record of the restoration process history of the plant community, the data show the dynamic changes in its ecological and thermodynamic states. The effect of the applied restoration method has been partly discussed in previous papers (Wu et al., 2017; 2018). Some of the main results are briefly summarized below:

(1) The applied methods had not only enhanced the biomass growth and metal uptake of the plant community but also enriched its species composition (Table 1, Appendix 1). In the later period, both $C_{\rm T}$ and N of the plant community in Plot I (amended with organic manure) were all several folds greater than those

in Plot II (amended with chemical fertilizers) and their differences were highly significant (P < 0.01). In addition to supply of nutrients and improvement of soil properties, the remediation effect of the organic manure was mainly attributed to its incorporation with plant roots, microorganism and substrates, forming an integrated system of chelation, oxidation, adsorption and absorption in reduction of the metal toxicity in the rhizosphere. The significant differences in $C_{\rm T}$ and N between years 2015 and 2016 in Plot I indicated that the plant community was still undergoing fast development. The species enrichment in both Plots I and II after land preparation was attributed to the natural germination of the native metal-tolerant species from the soil seed inventory while the difference in N between plots was mainly caused by the applied fertilizers.

(2) The highest N value 66 was observed in Plot III for the plant community naturally developed under uncontaminated soil conditions (Table 1). The C_T value in Plot III was much lower than that in plot I and the difference was attributed to the significant contribution of the transplanted P. fortunei and K. bipinnata in plot I. The total metal uptake quantities for all measured metals were very low in Plot III (Wu et al., 2018) and the correlation between its biomass quantity and metal uptake was insignificant ($\mathbb{R}^2 < 0.20$), indicating that metal toxicity was not the factor limiting the plant growth. The species number N in Plot III remained unchanged in years 2015 and 2016 and the difference in C_T between these two years was insignificant (Table 1), showing that the plant community had reached a relatively steady state.

It is noted in Table 1 that the thermodynamic factors, h, s, f and $s/C_{\rm T}$, all increased with time in both Plots I and II with $f/C_{\rm T}$ as a unique exception. Unlike h, which is independent of N, both s and f are functions of $C_{\rm T}$ and N. If s reaches its maximum, $s = s_{\rm m} = C_{\rm T} \ln(N)$ (Eq. 19 in theoretical section), Eq. 6 becomes

 $f/C_{\rm T} = \ln(N_{\rm m}) - s/C_{\rm T} = \ln(N_{\rm m}) - \ln(N_{\rm r})$ (8)

showing that $f/C_{\rm T}$ will decrease while $s/C_{\rm T}$ will increase with increasing N. The observed changes in $f/C_{\rm T}$ and $s/C_{\rm T}$ were thus expected results, indicating that N is the key factor that governs the internal energy flow and distribution. Since the inverse relationship between $f/C_{\rm T}$ and $s/C_{\rm T}$ holds in nature, Eqs. 6 and 8 can be applied to analyze the productivity-species richness relationship.

Contribution of plant species

The contributions of P. fortunei and K. bipinnata to relevant indices are compared in Table 2. The two transplanted species were shown to be fast-growing tree species with high growth and metal uptake rates under the improved site conditions. The sum of their number of individual plants in Plot I was only 0.104% of that of the plant community while that of their biomass, Mn uptake and land coverage contributed, respectively, 84.77%, 67.63% and 56.30% to the plant community. The high contribution percentage of the two species to s, h and f showed their importance in matter and energy transformation and conservation (Table 2).

Positive correlations between biomass and uptake of all measured metal elements among species were observed in both Plots I and II at high levels of significance ($\mathbb{R}^2 > 0.95$) (Wu et al., 2018), indicating that the accelerated growth of the plant community enhanced its metal uptake rates. Accordingly, the significant contribution of the transplanted species to total metal uptake was accounted for by their high growth rates. In comparison, the average contents of Mn in *P. fortunei* and *K. bipinnata* (0.1302, 0.1530 mg/g, calculated using the data in Appendix 1) were much lower than that in *Radix Phytolaccae* (0.9990 mg/g) in Plot I. The average net dry biomass quantity per plant of the two tree species (31.77, 2.23 kg) was, respectively, 369.5 and 25.92 times higher than that of *R. Phytolaccae* (0.0860 kg), and their average Mn uptake per plant (4.1373, 0.3410 g) was thus 48.16 and 3.97 times higher than that of this commonly acknowledged hyper-accumulator (0.0859 g) (Xua et al., 2015; Zhang et al., 2015).

The key factor that led to the differences in $C_{\rm T}$ and N between Plots I and II was the type of applied fertilizers. However, as the organic manure was only addressed to the rooting area of the transplanted species in Plot I for reducing the remediation cost (Wu et al., 2017), the rapid increase in the number of native plant species spreading over the entire area of Plot I suggested that the root growth and metabolic

activities of the transplanted species and decomposition of their fallen branches and leaves had also played important roles in promoting the growth of other native species and enhancing the species richness of the plant community particularly in later years.

Despite their important functions as dominant species in the restored plant community, the contributions of *P. fortunei* and *K. bipinnata* to the Shannon-Wiener index *SI* were extremely low and the sum of their percentage values was less than 0.3% (Table 2). The *SI* index (Eq. 1) is a single function of the number of individual plants m_i while the sum of the survived number of individual plants of the two transplanted tree species (1700/hm², Appendix 1) was negligible compared to the total individual number of the community (1633974.9/hm²), giving thus extremely low*SI* i or p_i values for these two tree species. This means that the *SI* i index will not take into account the important roles of the dominant species if they have small individual numbers.

Another phenomenon depicted in Fig. 1. was that the contribution percentage of the two transplanted species to $C_{\rm T}$ (Fig. 1a) and M (Fig. 1b) decreased while that of the other species increased with increasing N. The contribution percentage of a species to $C_{\rm T}$ or M is equal to its $x_{\rm i}$ (biomass ratio) or $p_{\rm i}$ (individual number ratio) given in percentage. The curves in Fig. 1 thus show clearly the negative effect of species richness (N) and abundance (M) on $x_{\rm i}$ and $p_{\rm i}$ of the transplanted tree species.

Difference between thermodynamic entropy and information entropy

It is noticed in Table 2 that the highest SI value was 2.97 observed for Plot I, followed by 2.86 for Plot III and 1.75 for Plot II. It is understandable for Plot II to have the lowest SI value but it is not fully explicable for Plot I to have a higher SI than Plot III. As a commonly applied biodiversity index, SI is thought to be presented as a function of species richness and evenness (Molles, 2016), namely that the higher the level of species richness and evenness, the higher the level of biodiversity. Compared to Plot I, Plot III had a higher maximum $SI_m = \ln(N)$ associated with much lower standard deviation SD values for C_{TB} , C_{TU} , Cov, s, h and f among the species of the community (Table 2). As a statistical parameter given by Eq. 7, SD can be used as an indicator for species evenness. The trend will be that the lower the SD value, the higher the species evenness in related physical quantities. As seen in Table 2, the SD values for C_{TB} , C_{TU} , Cov, s, h and f were all in confirmative with the on-site field sensation that Plot III had a higher level of species richness and evenness than Plot I. The unique factor left that actually lowered the SI value of Plot III was its highly significant difference in the number of individual plants m_i among species as being indicated by the largest SD value for M (Table 2).

The significant differences between SI_{i} and s_{i} crossing plant species are illustrated in Fig. 2 using the data obtained from the year 2016. The number on the horizontal axis in Fig 2 corresponds to the rank number of species (ranked in an ascending order of m_{i} or SI_{i}) listed in Appendix 1. The generally observed trend was that a great number of species possessing lower SI_{i} values had relatively higher s_{i} values. The typical case in Plot I depicted in Figs. 2a was that the two transplanted tree species (*P. fortunei* and *K. bipinnata*) had extremely low SI_{i} values (0.0038; 0.0040) associated with the highest s_{i} values (6.2368; 5.5120 ton/hm²). The species that had the highests i value was *P. acinosa* (0.5142 ton/hm²) in Plot II (Fig. 2b) and *B. papyrifera* (3.4985 ton/hm²) in Plot III (Fig. 2c) but their SI_{i} values (0.1306; 0.1105) were relatively low. The two transplanted species were not the strongest competitors under natural conditions in this region. Among the native species in Plot III, *B. papyrifera* was found to be the one possessing the highest s_{i} value though its SI_{i} value was comparably low (Fig. 2c).

The inconsistence of the variation in m_i and C_i among species is the reason for the difference between SI_i and s_i given, respectively, as $(m_i/M)\ln(M/m_i)$ (Eq. 1) and $C_i\ln(C_T/C_i)$ (Eq. 3). Since most species possessing high C_i values in Plot I had relatively low m_i values, the levels of the correlations of s, h and f with SI crossing species were extremely low as indicated by their correlation coefficient R values (Table 2). The reason for the slightly higher R values of the correlations between SI and s in Plots II and III was attributed to their lower SD values in C_i among species.

The present study does not give full support to use of SI as a biodiversity index for describing the investigated

plant communities simply because SI is a single function of the individual plant number. Biodiversity of an ecosystem should be in principle a macroscopic property or a state function of the ecosystem describing the state of its composition and structure linked to its matter and energy transformation. The *s* factor defined by Eq. 3 meets this criterion as a biodiversity index as it is not a probability variable but a state function interrelated with another two thermodynamic factors *h* and *f*. It is noted in Table 2 that though the $C_{\rm T}$ value was much higher in Plot I than in Plot III, the *s* value of Plot I (34.77 ton/hm²) was still lower than that of Plot III (35.05 ton/hm²). This was in agreement with what was observed in the field that Plot I had a higher level of biomass productivity while Plot III had a higher level of biodiversity.

Difference between entropy and maximum entropy

As illustrated in Fig. 3, the ratio of the entropy factor to total mass quantity s / C_T was positively related to $\ln(N)$ at high levels of correlation in both Plots I ($\mathbb{R}^2 = 0.9449$, Fig. 3a) and II ($\mathbb{R}^2 = 0.9950$, Fig. 3b). Since $s_m/C_T = \ln(N)$, the difference between the observed s / C_T and $\ln(N)$ was resulted from the difference between s and its maximum s_m . Combining the linear regression equation with Eq. 5 gives

$$s / C_{\rm T} = [?] x_{\rm i} \ln(1/x_{\rm i}) = a \ln(N) = a (s_{\rm m}/C_{\rm T}) (9)$$

The logical variation range of the proportional factor a will be 0 [?] a [?] 1 as a = 0, $s / C_T = \ln(N^0) = 0$, which is a special case for a single species system while $a = 1, s / C_T = \ln(N) = s_m / C_T$, which is the potential limit at which s reaches its maximum s_m .

The increase in s / C_T with increasing $\ln(N)$ is a process of increase in species richness while the approach of s to s m is a process of increase in species evenness. The proportional factor a can thus be regarded as an index for species evenness. The higher value of a found for Plot II (0.7059) than that for Plot I (0.2218) indicated that the level of species evenness was much higher in Plot II than in Plot I. The cause for the smaller difference between s and s m in Plot II was its metal contaminated condition that inhibited the growth of the species and reduced the difference among them.

Discussions

Spontaneous changes

Because of matter and energy input, the growth and development of a plant community should be in principle a natural process characterized by spontaneous increases in its total biomass quantity $C_{\rm T}$ and total number of plant species N. The enthalpy H, Gibbs free energy G and entropy Sof a plant community are state functions all positively related to $C_{\rm T}$ and N. Their increments, $^{H}, ^{G}and^{S}shouldbegreater than zero subject to ^{C}{}_{\rm T}>0 and ^{N}>0. Such changes shown by the experimental data in Table 1 thus followed$

In contrast, the observed decrease in $f/C_{\rm T}$ due to increase in $s/C_{\rm T}$ with increasing N (Table 1) obeys the 2nd law of thermodynamics that the spontaneous change in the state of a system is an irreversible process towards the direction of decrease in its intensity factor (Engel & Reid, 2006). For a given system, $\ln(N)$ and $\ln(N_{\rm m})$ are intensity factors related to the average chemical potential μ , weighted standard chemical potential μ^0 and average mass ratio x, respectively, by

$$[?]f / [?]C_{\rm T} = [?]h / [?]C_{\rm T} - [?]s_{\rm m} / [?]C_{\rm T} = \mu / (\rm RT) = \mu^{0} / (\rm RT) - \ln(1/x) = \ln(N_{\rm m}) - \ln(N) (10)$$

(Eq. 25inthe theoretical section). Given temperature Т $\ln(N)$ is m) We a constant while increasing Nwill reduce x since x = 1/Nshall have . $x < 0 and \mu < 0 as long as^N > 0, indicating that the change of an ecosystem is essentially a process of species enrichment that leads to the decease initis intensity factors of the second second$

The observed changes in s / C_T and f / C_T (Table 1) also obeys the 3rd law of thermodynamics regarding the principle of entropy increase (Engel & Reid, 2006). As been discussed in the previous paper, there can be two spontaneous changes related to entropy increase, of which one is increasing s with increasing N and the other one is increasing s towards s_m at a given N. The general trend of increasing s with increasing Nis clearly demonstrated by the positive correlation between s/C_T and $\ln(N)$ in Fig. 3. The decrease in the mass ratio of the transplanted species with increasing N illustrated in Fig. 1a shows the potential trend of increasing s towards s_m. The increase in the contribution of new species naturally geminated in the plot to the total biomass quantity $C_{\rm T}$ reduced the contribution ratio of the dominant species, which in turn reduced the difference between the peak x_i and average x. In accordance with the maximum entropy theorem, $s = s_{\rm m}$ at $x_{\rm i} = x_{\rm j} = x = 1/N$, s will get closer to $s_{\rm m}$ at higher N levels subject to the constraint [?] $x_{\rm i} = 1$.

The fact that increasing N is the essential cause for $\mu < 0 makes^N > 0 a use ful indicator for judging the spontaneity of an ecological process as it is the essential cause for <math>\mu < 0 makes^N > 0$ and $\mu < 0$ makes $\lambda = 0$ and $\lambda = 0$.

System diversity

The SI data listed in Table 2 do not fully prove the use of the traditional applied Shannon-Wiener index SI for comparing the biodiversity among the investigated plant communities. The patterns in Fig. 2 indicate that SI i is not a proper parameter for species abundance in terms of mass quantity and internal energy. There is a theoretical flaw to use SI as a biodiversity index for description of an ecosystem simply because the biodiversity of an ecosystem is not a single function of the number of individuals m_i or its ratio p_i . According to the principle of invalidity of a single factor, a system state cannot be determined by a single factor unless some of other factors are kept constant. The relative abundance of a species on a habitat cannot thus be uniquely determined by m_i unless the individuals both within and across species are identical, or at least, with no significant differences in their concerned physical properties and quantities. As a matter of fact, use of p_i as a relative abundance index also disobeys the principle of additivity. The number of individuals of a herb species cannot be added to that of a tree species simply because a small grass is hardly comparable to a big tree with respect to their ecological functions in a plant community. The value of M would be in particular meaningless at an ecosystem approach if it should stand for the total number of individuals of all organisms co-existed in the ecosystem.

Unlike SI, which is a single function of individual number ratio p_i , s is a function of mass quantity C_i and mass ratio x_i . As been discussed in the theoretical section, the rationality for calculating x_i is based on the assumption that the biomass of different plant species possesses the same unit energy value in terms of standard chemical potential. If this criterion is not fulfilled, the weighted biomass quantity $C_{i\gamma}$ should be used for calculating the total equivalent mass quantity $C_{T\gamma}$. As a state function (rather than a probability variable), s is a system property linked to system composition, and can thus be generally applied as a system diversity index. Use of s for determining the diversity state of a system also follows the principle of relative validity of a single factor. From Eq. 5, we see that $\ln(N_m)$ is a constant, and given C_T , both f and s can be uniquely determined by x_i . The analytical results obtained in the present study give support to use of s as a system diversity index (Tables 1 and 2, Fig 2). Since the related principle holds in general with no exceptions, s can be used as a diversity index for all types of thermodynamic systems.

It is necessary to mention that SI can be a useful index in particular cases. Apart from that SI does not differ from s / C_T in both concept and quantity in systems with uniform individuals (see discussions in the theoretical section), the number of individuals m_i or SI_i is a meaningful index to reflect the ability of a species to reproduce at a given habitat. The SI_i patterns for different plots depicted in Fig. 2 show its importance for comparing the ability of species to survive under different site conditions. Reproduction is also an energy consumption process. It should take a longer time for a tree species with a larger body size to multiply its individual number since more energy is required in its reproduction.

Conclusions

(1) The change in the state of the restored plant community with time was an irreversible process characterized by spontaneous increase in its total biomass quantity $C_{\rm T}$ and total number of plant species N associated with increase in its enthalpy H, Gibbs free energy G and entropy S. Species enrichment was the cause for the decease in mass ratio $x_{\rm i}$ and biomass growth potential $\mu_{\rm i}$. The changes in the thermodynamic factors f/CT and $s/C_{\rm T}$ due to decrease in $x_{\rm i}$ with increasing N followed the basic laws of thermodynamics. The criterion N > 0 can be generally applied as an index for determining the direction of spontaneous changes in an open thermodynamic system w

(2) The conducted analysis did not fully prove the use of the Shannon-Wiener index as a biodiversity index for the investigated plant communities. The biodiversity of a plant community cannot be determined by the

number of individuals if there are significant differences in individuals among species of the plant community. In contrast, the entropy factor s was proven to be a suitable diversity index. As a state function related to system composition, s can be applied as a diversity index for all types of systems.

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Conflict of interest

None declared.

Author Contributions

Mingli Chen and Xiaofu Wu designed the study. Xinxi Fu and Zijian Wu conducted the statistical analysis and wrote the first draft of the manuscript. All authors contributed substantially to revision, field sampling and Lab analysis.

Data accessibility

The authors agree to deposit their data to a public repository. The basic experimental data used in the analyses have been presented in Appendix 1.

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Table 1 Total net dry biomass $C_{\rm T}$ (kg/hm²), total number of species N and thermodynamic factors (h, s and f, ton/hm²) of the investigated plant communities (Plot I: tailing site amended with organic manure; Plot II: tailing site amended with chemical fertilizers; Plot III: uncontaminated site; h, s, f, $s/C_{\rm T}$ and $f/C_{\rm T}$: calculated, respectively, by Eqs. 2-6).

Plot	Year	2010	2011	2012	2013	2014	2015	2016
Ι	C_{T}^{*}	259.2 ± 21.3	566.2 ± 65.7	2187.4 ± 229.7	7763.2 ± 869.5	14915.2 ± 2013.6	23324.0 ± 2752.2	33498.7 ± 35
	N	5	8	17	36	44	48	51
	h	1.085	2.37	9.165	32.53	62.5	97.75	140.35
	s	0.092	0.26	1.33	5.63	11.2	20.01	34.77
	f	0.993	2.11	7.835	26.9	51.3	77.74	105.58
	$s/C_{\rm T}$	0.3549	0.4592	0.6080	0.7252	0.7509	0.8579	1.0380
	$f/C_{\rm T}$	3.8310	3.7266	3.5819	3.4651	3.4394	3.3330	3.1518
II	C_{T}	75.2 ± 8.8	$134.2{\pm}10.9$	267.1 ± 30.2	$475.2 {\pm} 48.5$	$786.7 {\pm} 80.2$	$1132.6{\pm}107.6$	$1468.8{\pm}171$
	N	5	5	7	8	11	13	15
	h	0.315	0.56	1.12	1.99	3.295	4.745	6.2291
	s	0.084	0.151	0.36	0.69	1.39	2.100	2.733
	f	0.231	0.409	0.76	1.3	1.905	2.645	3.4961
	$s/C_{\rm T}$	1.1170	1.1252	1.3478	1.4520	1.7669	1.8541	1.8607
	$f/C_{\rm T}$	3.0718	3.0477	2.8454	2.7357	2.4215	2.3353	2.3802
III	C_{T}						$9983.5 {\pm} 902.1$	10884.9 ± 87
	N						66	66
	h						83.66	91.21
	s						31.54	35.06
	f						52.12	56.15
	s/CT						0.3159	0.3221
	\dot{f}/CT						0.5221	0.5159

*: Significant difference in C $_{\rm T}$ between Plots I, II and III: P < 0.01

Table 2 Contribution percentage (*C.P.*) of *P. fortunei* and *K. bipinnata* to total net dry biomass (*C*_{TB}, kg/hm²), total Mn uptake (*C*_{TU}, g/hm²), total number of individual plants (*M*), Coverage (*Cov*.), Shannon-Wiener index (*SI*) and thermodynamic factors (*s*, *h* and *f*, ton/hm²); standard deviation (*SD*); and coefficient (*R*) of correlations of *s*, *h* and *f* with *SI* (Data: Year 2016)

Plot	Index	C_{TB}	C_{TU}	M	Cov	SI	s	h	f
Ι		33498.7	5532.6	1633974.9	298.0	2.970	34.77	140.35	105.57
II	Total	1468.8	2116.2	1449607.8	70.08	1.752	2.716	6.229	3.513
III		10884.9	698.4	11603893.4	316.4	2.86	35.05	91.21	56.16
Ι		84.77	67.63	0.1040	56.30	0.2648	33.79	84.77	87.20
II	C.P.~(%)	-	-	-	-	-	-	-	-
III		2.293	1.610	0.0023	0.7585	0.0090	3.1689	2.2933	1.7467
Ι		3704.6	483.2	61177.4	16.87	0.0688	1.3449	15.52	14.92
II	SD^*	184.3	334.4	166994.8	7.7928	0.1186	0.1377	0.7724	0.6628
III		328.8	17.3	391331.8	6.4990	0.0695	0.6470	2.7547	2.1502
Ι							-0.0197	-0.1136	-0.1185
II	R						0.4603	0.0672	-0.0173
III							0.4517	0.3281	0.2845

*: Standard deviation SD was calculated by Eq. 7.

Appendix 1 ($C_{\rm B}$: biomass quantity, kg/hm²; $C_{\rm U}$: Mn uptake, g/hm²; m: number of individuals. Rank No: arranged in an ascending order of m corresponding to $SI_{\rm i}$ in Fig. 2. Data: Year 2016)

Rank No	Plot I	Plot I	C_{B}	$C_{\rm B}$	$C_{\rm B}$
1	Ixeris denticulata	Ixeris denticulata	12.57	12.57	12.57
2	Achyranthes bidentata	Achyranthes bidentata	2.94	2.94	2.94
3	Pharbitis nil	Pharbitis nil	9.44	9.44	9.44
4	Paulownia fortunei	Paulownia fortunei	26465.71	26465.71	26465.71
5	Koelreuteria bipinnata	Koelreuteria bipinnata	1932.07	1932.07	1932.07
6	Pterocypsela formosana	Pterocypsela formosana	18.98	18.98	18.98
7	Kummerowia striata	Kummerowia striata	2.23	2.23	2.23
8	Chenopodium ambrosioides	Chenopodium ambrosioides	99.65	99.65	99.65
9	Mazus japonicus	Mazus japonicus	2.15	2.15	2.15
10	Imperata cylindrica	Imperata cylindrica	1.99	1.99	1.99
11	Polygonum flaccidum	Polygonum flaccidum	29.9	29.9	29.9
12	Artemisia carvifolia	Artemisia carvifolia	5.23	5.23	5.23
13	Solanum nigrum	Solanum nigrum	16.52	16.52	16.52
14	Clerodendrum cyrtophyllum	Clerodendrum cyrtophyllum	24.5	24.5	24.5
15	Phytolacca acinosa	Phytolacca acinosa	293.64	293.64	293.64
16	Eclipta prostrata	Eclipta prostrata	11.05	11.05	11.05
17	Rhus chinensis	Rhus chinensis	159.1	159.1	159.1
18	Oenanthe javanica	Oenanthe javanica	29.45	29.45	29.45
19	Broussonetia papyrifera	Broussonetia papyrifera	1811.46	1811.46	1811.46
20	Kalimeris indica	Kalimeris indica	45.3	45.3	45.3
21	Commelina communis	Commelina communis	3.57	3.57	3.57
22	Plantago depressa	Plantago depressa	6.87	6.87	6.87
23	Duchesnea indica	Duchesnea indica	3.02	3.02	3.02
24	Avena fatua	Avena fatua	8.93	8.93	8.93
25	Conyza bonariensis	Conyza bonariensis	279.69	279.69	279.69
26	Vicia hirsuta	Vicia hirsuta	11.02	11.02	11.02
27	Rosa multiflora	Rosa multiflora	29.85	29.85	29.85
28	Eragrostis pilosa	Eragrostis pilosa	1.18	1.18	1.18
29	Humulus scandens	Humulus scandens	217.78	217.78	217.78
30	Clematis hexapetala	Clematis hexapetala	92.3	92.3	92.3
31	Erigeron acer	Erigeron acer	4.9	4.9	4.9
32	$Xan thium \ sibiricum$	$Xan thium \ sibiricum$	58.02	58.02	58.02
33	$Pleioblastus \ amarus$	$Pleioblastus \ amarus$	2.55	2.55	2.55
34	Vicia sepium	Vicia sepium	49.7	49.7	49.7
35	Daucus carota	Daucus carota	63.3	63.3	63.3
36	Artemisia argyi	$Artemisia \ argyi$	36.21	36.21	36.21
37	$Gelsemium \ elegans$	$Gelsemium\ elegans$	40.79	40.79	40.79
38	Artemisia selengensis	Artemisia selengensis	24.73	24.73	24.73
39	$Miscanthus\ sinensis$	$Miscanthus\ sinensis$	403.01	403.01	403.01
40	Rubus howii	Rubus howii	98.24	98.24	98.24
41	41	Setaria viridis	Setaria viridis	39.47	25.21
42	42	Erigeron annuus	Erigeron annuus	98.91	145.62
43	43	Arthraxon hispidus	Arthraxon hispidus	12.94	7.40
44	44	$Clinopodium \ chinense$	$Clinopodium \ chinense$	10.79	3.36
45	45	Carex tristachya	Carex tristachya	21.46	18.17
46	46	Agrostis matsumurae	Agrostis matsumurae	26.04	18.02
47	47	Poa annua	Poa annua	121.66	71.57
48	48	$Oxalis \ corniculata$	Oxalis corniculata	31.35	24.62
49	49	Conyza canadensis	Conyza canadensis	135.14	38.75
50	50	Juncus effusus	Juncus effusus	92.42	82.71

Rank No	Plot I	Plot I	C_{B}	$C_{\rm B}$	$C_{\rm B}$
51	51	Cynodon dactylon	Cynodon dactylon	499.02	280.91
Sum	Sum			33498.7	5532.6
Rank No	Rank No	Plot II	Plot II	$C_{\rm B}$	C_{U}
1	1	Pharbitis nil	Pharbitis nil	6.40	0.75
2	2	$Chenopodium \ ambrosioides$	$Chenopodium \ ambrosioides$	42.37	21.59
3	3	Solanum nigrum	Solanum nigrum	12.42	16.49
4	4	Oenanthe javanica	Oenanthe javanica	46.05	30.45
5	5	Vicia hirsuta	Vicia hirsuta	8.37	1.32
6	6	$Clerodendrum \ cyrtophyllum$	$Clerodendrum \ cyrtophyllum$	28.14	61.10
7	7	Duchesnea indica	Duchesnea indica	4.71	1.89
8	8	Clematis hexapetala	Clematis hexapetala	107.13	6.79
9	9	Phytolacca acinosa	Phytolacca acinosa	745.54	1327.8
10	10	Artemisia argyi	Artemisia argyi	15.16	19.38
11	11	Setaria viridis	Setaria viridis	42.31	101.43
12	12	Poa annua	Poa annua	78.80	83.01
13	13	Daucus carota	Daucus carota	125.30	124.74
14	14	$Conyza\ canadensis$	Conyza canadensis	142.09	236.29
15	15	Erigeron acer	Erigeron acer	81.98	83.16
Sum	Sum			1486.8	2116.2

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