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New thermodynamic entropy calculation based approach towards quantifying the impact of eutrophication on water environment

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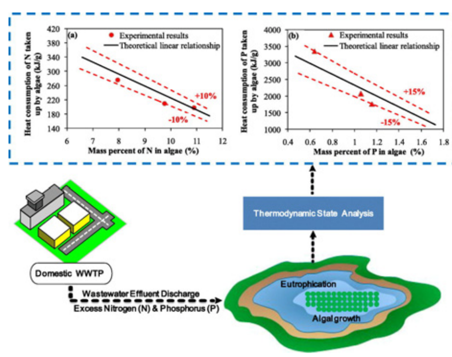
GRAPHICAL ABSTRACT



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ABSTRACT

Although the eutrophication phenomenon has been studied for a long time, there are still no quantifiable parameters available for a comprehensive assessment of its impacts on the water environment. As contamination alters the thermodynamic equilibrium of a water system to a state of imbalance, a novel method was proposed, in this study, for its quantitative evaluation. Based on thermodynamic analyses of the algal growth process, the proposed method targeted, both theoretically and experimentally, the typical algae species encountered in the water environment. By calculating the molar enthalpy of algae biomass production, the heat energy dissipated in the photosynthetic process was firstly evaluated. The associated entropy production (ΔS) in the aquatic system could be then obtained. For six algae strains of distinct molecular formulae, the heat energy consumed for the production of a unit algal biomass was found to proportionate to the mass of nitrogen (N) or phosphorus (P) uptake through photosynthesis. A proportionality relationship between ΔS and the algal biomass with a coefficient circa 44 kJ/g was obtained. By the principle of energy conservation, the heat energy consumed in the process of algae biomass production is stored in the algal biomass. Furthermore, by measuring the heat of combustion of mature algae of *Microcystis flos-aquae*, *Anabaena flos-aquae*, and *Chlorella vulgaris*, the proportionality relationships between the heat energy and the N and P contents were validated experimentally at 90% and 85% confidence levels, respectively. As the discharge of excess N and P from domestic wastewater treatment plants is usually the main cause of eutrophication, the proposed impact assessment approach estimates that for a receiving water body, the ΔS due to a unit mass of N and P discharge is 268.9 kJ/K and 1870.1 kJ/K, respectively. Consequently, P discharge control would be more important for environmental water protection.

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1. Introduction

Eutrophication associated with nutrients in the effluent from wastewater treatment plants (WWTPs) has become a serious problem in aquatic environments (Cai et al., 2013). Of the many nutrients required for plant growth, inorganic nitrogen (N) and phosphorus (P) are known to limit the growth of phytoplanktons, and so their input and enrichment in water are the main factors inducing eutrophication (Statham, 2012). It has been demonstrated that the potential eutrophication impact of WWTPs is mainly related to the discharge of sewage effluent to water bodies, especially the N and P content in sewage effluent (Gallego et al., 2008). Secondary effluent from WWTPs still contains nutrients, with total N (TN) and total P (TP) concentrations ranging from 15 to 35 mg N/L and 4 to 10 mg P/L, respectively (Carey et al., 2013). The eutrophication threshold for N-limited aquatic systems is 0.50–1.00 mg N/L, and that for P-limited systems is 0.02–0.10 mg P/L (Lin et al., 2008). Moreover, inorganic N and P play significant roles in algal cell growth and metabolism because N is needed for protein synthesis, while P is required for DNA, RNA, and energy transfer (Conley et al., 2009; Cai et al., 2013). Thus, the release of excess N and P from municipal WWTP effluent into the environment leads to eutrophication, which consequently, cause excessive algal growth.

Cultural eutrophication, the process by which a freshwater ecosystem becomes over-enriched with dissolved nutrients as a result of point and nonpoint source pollutant inputs, can cause environmental effects that are directly related to algal proliferation (Strokal et al., 2017). Nevertheless, although the eutrophication phenomenon has been studied for long, there is still no quantifiable parameters available for a comprehensive assessment of its impact on the water environment. The environmental impact of excessive nutrients discharge into a water body can be measured as eutrophication, but the substantive issue is the change of the thermodynamic equilibrium conditions of the water body. A water body in a healthy state is considered as an ecosystem in chemical and thermodynamic equilibrium (Diaz-Mendez et al., 2013). When secondary effluent containing excess N and P is discharged into the water body, the original state of thermodynamic equilibrium will be altered. If the nutrient load exceeds the carrying capacity of the water body, it can cause eutrophication due to a sharp increase in algal growth. In this case, the water body is no longer in equilibrium, and the thermodynamic state shifts from a balanced to an imbalanced status. Thus, by analyzing the thermodynamic state of the water body and by identifying a thermodynamic indicator to evaluate this state quantitatively, the environmental impact of excess nutrients discharge to the water body can be quantitatively assessed. The disequilibrium of a system can become irreversible as a result of fluctuations in physical and chemical factors, which destabilize the system and result in the production of entropy (Lucia, 2012). From a thermodynamic standpoint, the entropic distance from thermodynamic equilibrium is the key quantity to consider when describing the state of an ecosystem (Ludovisi, 2014). According to the second law of thermodynamics, entropy quantifies the system's evolutionary course towards increasingly more probable states, while entropy production describes its irreversibility. Moreover, the entropy production and the export of that entropy are considered to belong to the most important controlling factors of the ecosystem (Mauersberger, 1996). Thus, entropy production could represent the basis of a new approach to the impact assessment and be used as a promising indicator to evaluate eutrophication caused by excessive nutrients discharge quantitatively. Thermodynamics has some important features that allow it to be used to assess the impact of pollutants. First, the thermodynamic approach provides a universal language to compare different pollutants, which overcomes problems due to the individual characteristics of pollutants (Ludovisi and Poletti, 2003). Second, it provides a general theoretical framework based on the state of a system, which overcomes the problems of subjectivity.

In using entropy production as a tool for water environmental analysis, the basic thermodynamics approach, as proposed in a previous study (Aoki, 1983), was to calculate entropy production on the earth by using balance equations for radiation energy and entropy. The method was used to evaluate the annual entropy production from entropy fluxes associated with direct, diffuse, and reflected shortwave radiation in lakes (Aoki, 1987). In surface waters, it was considered that chemical, physical, and organic activities would be supported by chemical energy released by decomposition of macro-molecules in organisms by respiration (Aoki, 2006a; Aoki, 2006b). Entropy production was successfully evaluated by using data of biomass and respiration in trophic compartments in aquatic food webs (Aoki, 2008). Another study focused on the correlation between entropy production indices and Carlson's trophic state index for several lake ecosystems (Ludovisi and Poletti, 2003). The data reported in Ludovisi and Poletti (2003) were used to calculate biotic and abiotic entropy production in lake ecosystems (Ludovisi, 2004). Later, the ratio between the entropy produced and the stored exergy, which is the maximum amount of useful work produced, by the biological component of an ecosystem was proposed as a thermodynamic indicator for elucidating the evolution of ecological systems (Ludovisi et al., 2005) and the developmental state of lake communities (Ludovisi, 2006). Furthermore, the net radiative entropy exchange showed a significant correlation with phytoplankton successional traits in the studied lakes (Ludovisi, 2012), and so entropy production was considered to indicate the extent of biological activity in a lake (Ludovisi, 2014). Similar principles have been applied to assess biological developmental states (Martyushev and Seleznev, 2006), the state and sustainability of ecosystems (Chakrabarti and Ghosh, 2009; Meysman and Bruers, 2010), the reduction and excessive consumption of resources (Diaz-Mendez et al., 2013), the utilization efficiency of natural resources (Samiei and Fröling, 2014), and the overall activity of ecosystems (Lin, 2015). Most of the studies as mentioned above have focused on the long-term natural evolution of the environment due to the shift in thermodynamic equilibrium conditions.

As cultural eutrophication is irreversible processes, they will result in entropy production according to the second law of thermodynamics. Therefore, more sophisticated thermodynamic analyses may be needed to estimate the impact of eutrophication due to excess N and P discharge on the receiving water body. However, there is no calculation method to quantitatively evaluate this impact based on thermodynamic principles. Considering that the impact of any contamination is the change in state of a water system from thermodynamic equilibrium to imbalance, this study presents, for the first time, thermodynamic analyses of algal growth processes. For quantitative assessment of the impact of eutrophication due to the discharge of excess N and P, we first establish a method for calculating entropy production in aquatic systems caused by nutrient pollution, and then experimentally validate and apply this method to a case study.

2. Theoretical calculation and experimental methods

2.1. Theoretical calculation methods

2.1.1. Calculation of standard molar enthalpy of formation of algae $\Delta_f H_{algae}$

The main causes of eutrophication in natural waters have been identified as N in the forms of ammonium-N (N-NH_4^+) and nitrate-N (N-NO_3^-), and P in the form of phosphates (PO_4^{3-}) (Zamparas and Zacharias, 2014). In secondary WWTP effluents, N occurs mainly as NH_4^+ and NO_3^-, while P is predominantly in the form of PO_4^{3-}. When the secondary effluent containing excess nutrients is discharged into a water body, the worst condition is that all of the N and P exist in the most biologically available forms. The most biologically accessible form of N is N-NH_4^+, because of its reduced state and energetically favorable assimilation. Thus, to assess the impact of eutrophication, NH_4^+ and PO_4^{3-} were used as the N and P sources for algal photosynthesis, respectively. The essential elements of carbon (C), hydrogen (H), oxygen (O), N and P, which provide the atomic-level skeletons for biomolecules constitute over 95% of phytoplankton by mass. So, a general molecular