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Thermodynamic analysis of an urban water system with reclaimed water as supplemental water resource

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ABSTRACT

The natural water system maintains its dynamic equilibrium through a hydrological cycle that involves a series of natural processes. Such a natural water cycle has been much disturbed by human activities in the process of water use. An urban water system was thus modeled in this paper as a series of artificial water cycles overlaid upon the natural water cycle. The system was thermodynamically analyzed by calculating the entropy budget as $\Delta S = \Delta_i S + \Delta_e S$ where $\Delta_i S$ and $\Delta_e S$ are the entropy increases due to natural and artificial contributions, respectively. The natural water cycle free from human disturbance should possess the nature of self maintenance of water and materials balance and could be assumed as a pseudo-reversible process with $\Delta_i S \to 0$. $\Delta_e S$ was then supposed as to be contributed by artificial disturbances on water quantity such as by water withdrawal, and on water quality such as by pollutant discharge. A series of models were developed for calculating $\Delta_e S$. As a result of scenario analysis of urban water system in Xi'an, a metropolitan in northwestern China, using these models, it was indicated that under the current condition of water supply and wastewater treatment, if 20% of the treated wastewater could be reused, $\Delta_e S$ would be decreased by 15.22% from the current level, while if the percent of treated wastewater reuse could be increased to 40%, $\Delta_e S$ would be decreased by 29.93%. Thermodynamic analysis thus provided a tool for quantitative evaluation of the effect of urban wastewater reclamation and reuse.

Keywords: Urban water system; Thermodynamic analysis; Entropy; Pseudo-reversible process; Water reclamation

1. Introduction

Urbanization is a common trend in most of the fast developing countries. Taking China as an instance, its urbanization rate (percent of urban population) was only 17.92% in 1978 but rapidly increased to 45.7% in 2008 [1]. Such a high rate of urbanization resulted in a rapid expansion of existing cites and growth of new cities from small towns and/or villages. This inevitably required more concentrated supply of energy and resource, as well as increased discharge of pollutants to the environment because measures taken for pollution control may not always be sufficient to keep pace with the urbanization rate [2]. In the field of water environment, there are increasing debates on the simultaneous occurrence of water shortage and water pollution due to urbanization

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[3]. The conventional mode of urban water system design is questioned because it is based on a human-centric philosophy of water supply to meet the demand of water use and sewerage work to collect and discharge the used water quickly and smoothly for protecting human health, while the sustainability of the resource and environment has seldom been taking into consideration [4–6]. From an ecological viewpoint, a city can be considered as an enlarged human settlement which in the primary time was like an "ecological niche" for human beings, a special species of organism that depended so much on the availability of natural resources [7]. It was only when human beings mastered advanced technologies, especially in the era of industrial revolution that the way for acquiring and processing the resources was much changed. Facing the worldwide water crisis, it becomes extremely necessary for us to change our standpoint from human-centric to nature-centric and find a new approach for assessing the impact of human activities on natural waters.

For the assessment of natural waters, entropy theory has provided a useful tool. The basic approach, as proposed by Aoki in 1983 [8], was to calculate the entropy production on the earth by using balance equations of radiation energy and entropy. The method was used for evaluating the annual entropy fluxes associated with direct, diffuse and reflected shortwave radiation in Lake Biwa, Japan [9]. In aquatic ecosystems such as lakes and estuaries, 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 [10]. By using data of biomass and respiration in trophic compartments in aquatic food webs, entropy production could be well evaluated [11] and a set of indices related to entropy production were proposed as useful indicators of the eutrophication state [12]. Based on the overproduction of entropy by crops from excessive use of organic fertilizers, a thermodynamic indicator was developed for assessing the sustainability of agro-ecosystems [13].

An urban water system, as to be discussed in the following sections, can be taken as an originally natural aquatic system but much artificially modified to meet human needs. In such a case, the thermodynamic approach abovementioned can be well referred but should be modified or extended for the calculation of entropy production closely related to human activities. It thus becomes the task of the present study to develop thermodynamic models in which the reversible property of a natural water system free from human disturbance is set as the baseline and the entropy production due to human disturbance is viewed as a quantitative measure of the "irreversibility" on the urban water system. Water reclamation and reuse, as is required and/or being practiced in many cities, is also taken as an important activity in the analysis.

2. Theoretical considerations

2.1. Conceptual model of an urban water system

Let us consider firstly the natural hydrological cycle and its disturbance by human activities. In a worldwide scale, the natural hydrologic cycle is the cycling of water through a series of natural phenomena including (i) precipitation, the process for moisture in the atmosphere to condense into droplets and fall to the Earth as rain or snow, (ii) runoff, the process for water to flow over the Earth as surface water or through the soil as groundwater and finally return to the oceans, (iii) evaporation, the process under the action of solar energy for water to evaporate from the ocean surface and return to the atmosphere. Such a water cycle is important for keeping a worldwide or regional circulation of water in various water bodies such as rivers, lakes, and groundwater aquifers. On the other hand, the water cycle is also a process of water purification that ensures the provision of fresh water resources in the cycle by a series of physical, chemical, and biological reactions [14].

As human beings depend on natural water for sustaining life, the scale of human disturbance on the natural hydrological cycle became stronger and stronger with urban development. From ancient time people found traditional ways to take water from various water bodies for daily use and then discharge the used water that goes back to the water bodies through various routes. Because the scale of the traditional water use is very small, the disturbance on the natural water cycle is minor. However, in a modern city the human disturbance is no longer negligible and a large scale artificial water cycle is added to the natural water system. The pollutant loading from the artificial cycle to the natural cycle may be beyond the self-purification capacity for the water bodies to maintain "healthy". For these reasons, human beings have nothing to do but to take engineering measures to "protect" or "cure" the natural water bodies, such as to practice water purification and wastewater treatment [6].

Now we consider the composition of an urban water system. From what discussed above, the urban water system can be considered as many artificial water cycles overlaid upon a natural water cycle. From a nature-centric viewpoint, these artificial cycles that are related to various human activities for water utilization expose both disturbances on water quantity through water withdrawal and on water quality through pollutant discharge. In this way, a very simple conceptual model of the urban water system can be depicted as shown in Fig. 1.

2.2. Thermodynamic principles

According to the second law of thermodynamics, the entropy increase in a system can be written as

$$\Delta S = \oint_B \frac{\partial q}{T} \tag{1}$$

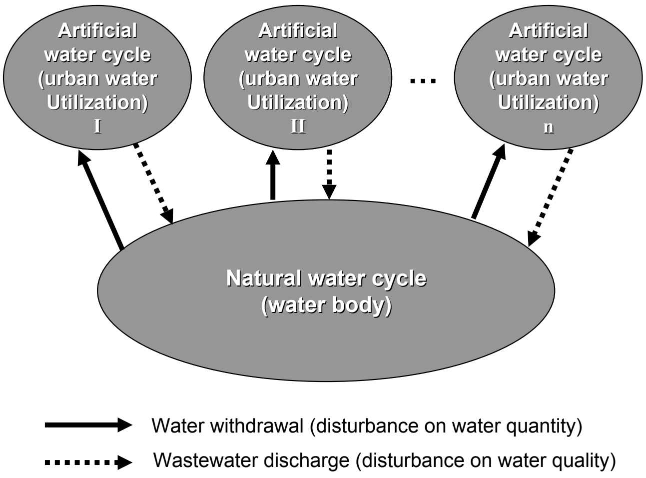

Fig. 1. Conceptual model of an urban water system.

where ΔS is entropy increase, B is the system boundary, ∂q is any small change of energy or heat, and T is absolute temperature.

An isolated system is considered to be reversible if $\Delta S = 0$, or irreversible if $\Delta S > 0$. However, since no ecosystem could ever exist as an isolated system, the second law of thermodynamics cannot be applied without adaptation. One prevailing method is to consider that the change in entropy for a non-isolated ecosystem is composed of two parts: an endogenous contribution due to the internal processes as $\Delta_i S$ and an external contribution from outside as $\Delta_e S$ [12]. Therefore, the total entropy increase can be written as

$$\Delta S = \Delta_i S + \Delta_e S \tag{2}$$

From a worldwide viewpoint, all the natural processes in the hydrological cycle can be considered as internal processes that bring about endogenous contribution to changes in entropy, i.e. $\Delta_i S$ within the large natural aquatic ecosystem, while the external contribution of $\Delta_e S$ is considered to be from human disturbances. Based on this consideration, Eq. (2) can be used as the basic equation for evaluating the entropy increase in the urban water system shown in Fig. 1, with $\Delta_i S$ as the entropy increase due to natural processes and $\Delta_e S$ as that due to human activities.

Although any natural process can only progress in a direction which results in an entropy increase [12], it may be reasonable to assume that the natural hydrological cycle as discussed in 2.1 would be a pseudo-reversible process by its nature of self maintenance of water and materials balance. Of course, such an assumption should be restricted to a comparatively short time span (e.g. the time scale of human life) but not a long time span (e.g. the time scale of natural evolution). We can thus assume that the following condition almost holds for the natural hydrological system, as well as the natural part of the urban water system:

$$\Delta_i S \to 0 \tag{3}$$

In this way, the task for evaluating the total entropy increase in the urban water system will become a work for evaluating $\Delta_e S$, the entropy increase due to human disturbances.

3. Mathematical models for $\Delta_e S$ calculation

The human disturbance to the water body may consist of the disturbance on water quantity from water withdrawal and the disturbance on water quality from wastewater discharge, so $\Delta_e S$ can be expressed as

$$\Delta_e S = \sum \Delta_e S_1 + \sum \Delta_e S_2 \tag{4}$$

where subscripts 1 and 2 denote the disturbance on water quantity and that on water quality, respectively.

3.1. Entropy increase due to disturbance on water quantity

The calculation of $\Delta_e S_1$, i.e. the entropy increase due to the disturbance on water quantity is under a consideration that any inflow or outflow from the water body is associated with an entropy flow that can be calculated from the gain or loss of heat and water temperature [12]:

$$\Delta_e S_1 = \frac{Q}{T} \tag{5}$$

where Q is the change of heat caused by an inflow or outflow (J), T is the corresponding water temperature (K). The heat carried by a certain quantity of water can be physically calculated as the product of its specific enthalpy and mass [12]. In a case when water is withdrawn for urban water supply from a river basin at one location (usually in the upstream) and after use the wastewater is then discharged back to the same basin at another location (usually in the downstream), Q will be caused by the heat transfer from the water mass with higher temperature to that with lower temperature. If the temperature difference is ΔT, then Q can be calculated as:

$$Q = \rho(T) \cdot V \cdot h(T) = \rho(T) \cdot V \cdot C_p(T) \cdot \Delta T \tag{6}$$

where $\rho(T)$ is the water density (kg·m^{-3}), V is the quantity of water flow with higher temperature (m^3), $h(T)$ is the specific enthalpy of water (J·kg^{-1}), $C_p(T)$ is the constant-pressure heat capacity of water (J·K^{-1}·kg^{-1}), T is the water temperature (K).

The $\Delta_e S_1$ calculated by Eq. (5) and Eq. (6) can be either positive or negative according to the direction of heat transfer. However, in most cases the water temperature will be increased after its use for various purposes. Therefore, heat will be transferred from the mass of the discharged wastewater to the mass of the bulk water in the receiving water body and result in an increase in $\Delta_e S_1$ which equivalents to a change of the background condition (i.e. water temperature increase) of the water body. On the other hand, the calculated $\Delta_e S_1$ can also be viewed as the energy (heat) required for the bulk water to recover its background condition (i.e. returning to the original water temperature).

3.2. Entropy increase due to disturbance on water quality

3.2.1. Basic methods

In order to evaluate $\Delta_e S_2$, i.e. the entropy increase due to the disturbance on water quality that is caused by pollutant discharge to the water body, exergy is used as a surrogating parameter for avoiding the difficulty of direct calculation of heat or energy flow. Exergy (E_x) can be defined as an effective measure of the potential of a substance to impact the environment [15]:

$$E_x = T_0(S_0 - S) \tag{7}$$

where T_0 is the absolute temperature of the environment (K), S_0 is the entropy of the environment, and S is the entropy of the system at thermodynamical equilibrium state. As the system under consideration has the same temperature as the environment, its entropy change ΔS can be expressed as:

$$\Delta S = \frac{E_x}{T_0} \tag{8}$$

For a chemical substance, we can use its chemical exergy to express its exergy at ambient temperature and pressure [16], while for chemical compounds, their chemical exergy expresses the amount of energy that will be released when they react and the products reach equilibrium with the surroundings [17]. The sum of various shocks of environment by pollutants due to chemical potential imbalance will be equal to the chemical exergy of all the substances [18], which results in the following equation for calculating the entropy increase $\Delta_e S_2$ caused by various substances discharged into the water body:

$$\Delta_e S_2 = \sum \frac{E_{ch,j}}{T_0} \tag{9}$$

where $E_{ch,j}$ is the chemical exergy of substance j.

The chemical exergy of a substance is composed of two components, namely the reaction exergy $E^1_{ch,j}$ resulting from the chemical reactions necessary to produce substances existing as stable components in the environment, and the concentration exergy E^2_{chj}, resulting from the necessary processes to match the chemical concentration of the produced substances to their chemical concentration in the environment [16]. $E^1_{ch,}$ and E^2_{chj} can be calculated by the following equations [19,20]:

$$E^1_{ch,j} = n_j \cdot W_{id} = n_j \cdot \left(-\Delta_r G^\theta\right) \tag{10}$$

$$E^2_{ch,j} = n_j R T_0 \ln \frac{c_j}{c_{j,0}} \tag{11}$$

where n_j is the mole number of substance j (mol), W_{id} is the ideal work (J·mol^{-1}), ΔrG^θ is the standard Gibbs free energy (J·mol^{-1}), R is the gas constant (J·K^{-1}·mol^{-1}), T_0 is the standard absolute temperature of the environment (298.15 K), c_j is the concentrations of substance j discharged into the environment, and $c_{j,0}$ is the concentration of substance j in the environment.

The chemical exergy of substance j can thus be calculated as:

$$E_{ch,j} = E^1_{ch,j} + E^2_{ch,j} = n_j \left(RT_0 \ln \frac{c_j}{c_{j,0}} - \Delta_r G^\theta \right) \tag{12}$$

By substituting Eq. (12) to Eq. (9), the entropy increase caused by pollutant discharge can be calculated. In the calculation, the background concentration of a pollutant in the bulk water is taken as the termination of chemical reactions to decompose the pollutant. The calculated $\Delta_e S_2$ is thus equivalent to the energy needed for the recovery of the bulk water to its background condition (i.e. returning to its original water quality).

3.2.2. Entropy calculation for typical pollutants in wastewater

In this study, we take biodegradable organic matter (BOM), nitrogen, and phosphorous as three typical pollutants in wastewater which, when discharged into the water body, may result in an entropy increase $\Delta_e S_2$. In order to utilize Eq. (12) for calculating the chemical exergy, and then to utilize Eq. (8) for obtaining $\Delta_e S_2$, we need to set a series of assumptions regarding the molecular formula and associated chemical reaction for each pollutant as shown in Table 1.

For calculating the chemical exergy of each pollutant, the background concentration of each pollutant in the environment, i.e. in the water body, has to be set according to the case of investigation. Under a consideration that the pollutant discharged to the water body is often of higher concentration than the background level, the chemical reaction shown in Table 1 would terminate as the pollutant concentration reaches the background level.

4. Case study

4.1. Case description

The mathematical models discussed above are utilized to the case of the central city area of Xi'an, a large metropolitan in northwestern China. In the year of 2010, a centralized water supply and sewerage system is provided in the central city serving a population of 2.14 million. The city is located in the Weihe River basin which is the largest tributary of the Yellow River. For water supply, the source water is mainly from a dam across a branch river upstream of the city. The used water, including the treated and untreated, is ultimately discharged to the

Table 1
Assumed molecular structure and associated chemical reaction of typical pollutants in water

Typical pollutant	Molecular formula	Chemical reaction	Gibbs free energy ($\Delta_r G^\theta$)	Reference
BOM	CH_2O	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-584.0×10^3 J·mol^{-1}	[21]
Nitrogen	NH_4^+	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	-268.2×10^3 J·mol^{-1}	[22]
Phosphorous	PO_4^{3+}	$PO_4^{3-} + 2H^+ \rightarrow H_2PO_4^-$	-109.6×10^3 J·mol^{-1}	[19]

Weihe River downstream of the city. Therefore, the urban water system for this study can be depicted as Fig. 2 where its natural part is the Weihe River system that provides source water to the city and receives drainage from the city, and its artificial part is the centralized water supply and sewerage system.

As of 2010, the average per capita water consumption is 0.6 m^3·person^{-1}·d^{-1}, including water for all purposes of urban use such as domestic, industrial, municipal and gardening etc. and the population served by water supply facilities is 2.14 million (100% coverage in the central city). The percent of population served by sewerage facilities is estimated as 88% while the percent of wastewater treatment is 80%.

Because the Weihe River basin is within the water deficient area in northwestern China, water reclamation and reuse has been set as an important countermeasure for mitigating water shortage. Several wastewater treatment plants (WWTP) in Xi'an have already installed or begin to construct water reclamation facilities, but the current rate of reclaimed water supply is only about 2% through the centralized system. However, the local government has set a goal of 20% water reclamation and reuse by 2015 and 40% by 2020.

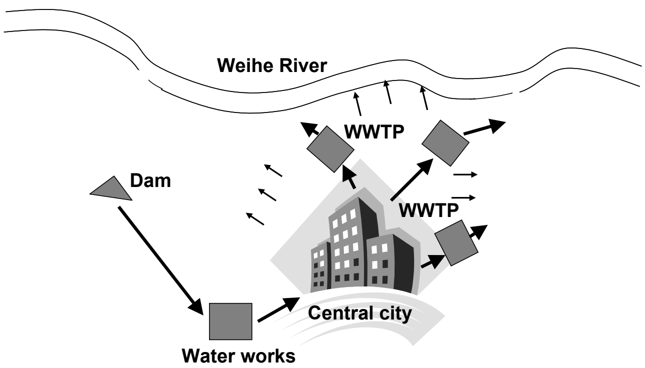

Fig. 2. Urban water system in the central city area of Xi'an.

4.2. Scenarios for case analysis

Three scenarios are set as shown in Table 2 for analyzing the abovementioned urban water system in central city area of Xi'an. The objective of the analysis is to evaluate the environmental benefit from practicing water reclamation and reuse in the study area under a condition of current water consumption and wastewater treatment scale but different level of water reuse.

In this case, the Weihe River including its main channel and branch streams as a whole is taken as the natural part of the urban water system, and to simplify the analysis, variation of water quality in different section or location of the river system is ignored. It is thus assumed to be a river with quality in accordance with Class IV standard that is the minimum requirement for river water quality in this basin. If other conditions are unchanged, the impact of water reclamation and reuse can be envisaged from two aspects: one is the mitigation of the disturbance on water quantity of the river system because of the substantial decrease of source water withdrawal as well as the drain-

Table 2
Scenarios set for analyzing the urban water system in Xi'an

Scenario	Circumstances	Background surface water quality
I	Current level of water consumption, current capacity of wastewater treatment, none water reclamation and reuse	Class IV as set by the Chinese Environmental Quality Standard for Surface Waters (GB3838-2002)
II	Current level of water consumption, current capacity of wastewater treatment, 20% water reclamation and reuse	
III	Current level of water consumption, current capacity of wastewater treatment, 40% water reclamation and reuse	

age back to the river, and another is the mitigation of the disturbance on water quality in the river system because of less amount of pollutants discharged to the river.

4.3. Analysis results

Table 3 is a list of the parameter values used for the analysis. Empirical data are used for the temperature of river water and wastewater, and untreated wastewater quality.

By putting the parameters listed in Table 1 and Table 3 into Eqs. (5)–(6) for evaluating $\Delta_e S_1$ due to the disturbance on water quantity, and Eqs. (8)–(12) for evaluating $\Delta_e S_2$ due to the disturbance on water quality, a set of equations for the case analysis can be obtained as shown in Table 4. According to the empirical data, the annual average temperature of river water in the study area is about 12°C (285.15 K) and the wastewater finally discharged to the river through the urban drainage is about 14°C (287.5 K), it can be considered that as a result of wastewater discharge, heat will be transferred from the wastewater to the river system, and the calculated $\Delta_e S_1$ value should be positive, i.e. an entropy increase in the river system, by using the equations shown in Table 4 and taking $\Delta T = 2$ K.

Fig. 3 shows the water budget for the case analysis. From the source water, a volume of $V_{w,0}$ is supplied for fresh water supply to the city. As water reclamation and reuse is also considered, the total quantity of water supply will be $V_{w,0} + V_R$. In the case study, 88% of the water used is supposed to be collected by the centralized urban sewage system. Of this amount, 80% is treated in the wastewater treatment plants while the remaining 20% with a volume as $V_{d,1}$ is directly discharged to the river system without treatment. The effluent from the wastewater treatment plants is either reclaimed for urban reuse (volume as V_R) or discharged to the river system (volume as $V_{d,2}$). The total quantity of wastewater discharged to the river system is supposed to be V_w which is the sum of $V_{d,1}$ and $V_{d,2}$. To simplify the analysis, any lose of water quantity in the process of wastewater collection, treatment, and reclamation is not taken into account.

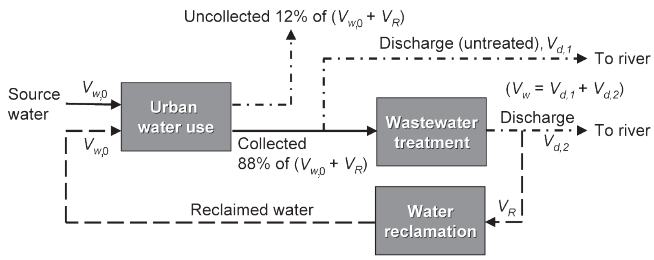

Fig. 3. Water budget for the case analysis.

The analysis results are summarized in Table 5. In the case of Scenario I, i.e. current level of water use and wastewater treatment without water reclamation, the total annual entropy increase is calculated as 1.38×10^{13} J·K^{-1} of which $\Sigma\Delta_e S_1$, i.e. the contribution of the disturbance on water quantity, takes about 87.0% while $\Sigma\Delta_e S_2$, i.e. the contribution of the disturbance on water quality, takes about 13.0%. When 20% of the treated wastewater is reclaimed for urban water use while the other conditions are unchanged (Scenario II), $\Delta_e S$ can be decreased by 15.22% or 2.1×10^{12} J·K^{-1} of which the decrease of $\Sigma\Delta_e S_1$ takes about 90.48%. If the water reclamation rate is increased to 40% (Scenario III), then $\Delta_e S$ can be decreased by 29.93% or 4.13×10^{12} J·K^{-1} comparing with Scenario I, of which the decrease of $\Sigma\Delta_e S_1$ takes about 92.25%.

Table 3
List of the parameter values for the analysis

Category	Parameter	Value	Remarks
River water	Organic matter (BOD_5), $c_{C,0}$	6.0 mg·L^{-1}	Chinese standard[1]
	Nitrogen (NH_3-N), $c_{N,0}$	1.5 mg·L^{-1}	Chinese standard[1]
	Phosphorous (P), $c_{P,0}$	0.3 mg·L^{-1}	Chinese standard[1]
	Water temperature	12°C (285.12 K)	Annual average[3]
Untreated wastewater	Organic matter (BOD_5), $c_{C,1}$	200 mg·L^{-1}	Empirical data
	Nitrogen (NH_3-N), $c_{N,1}$	40 mg·L^{-1}	Empirical data
	Phosphorous (P), $c_{P,1}$	10 mg·L^{-1}	Empirical data
	Wastewater temperature	14°C (284.12 K)	Annual average[3]
Treated wastewater	Organic matter (BOD_5), $c_{C,2}$	20 mg·L^{-1}	Chinese standard[2]
	Nitrogen (NH_3-N), $c_{N,2}$	8 mg·L^{-1}	Chinese standard[2]
	Phosphorous (P), $c_{P,2}$	1.5 mg·L^{-1}	Chinese standard[2]
	Wastewater temperature	14°C (284.12 K)	Annual average[3]

[1]Chinese Environmental Quality Standard for Surface Waters (GB3838–2002), Class IV.
[2]Chinese Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18919-2002), Class I-B.
[3]Empirical data.

Table 4
List of equations for case analysis

Equations[1]	Parameter explanations[2]
(1) $\Sigma\Delta_e S_1$ due to quantitative disturbance $$\Delta_e S_1 = \frac{Q_w}{T_w} = \frac{\rho(T_w)\cdot V_w \cdot C_p(T_w)\cdot \Delta T}{T_w}$$	Q_w — Heat transfer from the discharged wastewater to the water body
	V_w — Annual volume of wastewater discharge
$$\rho(T) = 1000.3 - 9.2\times10^{-3}(T-273.15) - 4.8\times10^{-3}(T-273.15)^2$$ $$C_p(T) = 4.2154\times10^{3} - 3.1(T-273.15) + 8.0\times10^{-2}(T-273.15)^2 - 8.0\times10^{-4}(T-273.15)^3$$	ΔT — Temperature difference between the discharged wastewater and water body $\Delta T = T_w - T_0$
(2) $\Sigma\Delta_e S_2$ due to organic discharge ($\Sigma\Delta_e S_2^{C}$) Through untreated wastewater discharge $$\Delta_e S_2^{C,1} = \frac{E^1_{ch,C}}{T_0} = \frac{V_{d,1}}{T_0}\left(c_{C,1} - c_{C,0}\right)\left(18.25 + 0.077\ln\frac{c_{C,1}}{c_{C,0}}\right)\times10^3$$	$\Delta_e S_2^{C,1}$ — Entropy increase due to organic discharge through untreated wastewater inflow
Through treated wastewater discharge $$\Delta_e S_2^{C,2} = \frac{E^2_{ch,C}}{T_0} = \frac{V_{d,2}}{T_0}\left(c_{C,2} - c_{C,0}\right)\left(18.25 + 0.077\ln\frac{c_{C,2}}{c_{C,0}}\right)\times10^3$$	$\Delta_e S_2^{C,2}$ — Entropy increase due to organic discharge through treated wastewater inflow
(3) $\Sigma\Delta_e S_2$ due to nitrogen discharge ($\Sigma\Delta_e S_2^{N}$) Through untreated wastewater discharge $$\Delta_e S_2^{N,1} = \frac{E^1_{ch,N}}{T_0} = \frac{V_{d,1}}{T_0}\left(c_{N,1} - c_{N,0}\right)\left(19.16 + 0.177\ln\frac{c_{N,1}}{c_{N,0}}\right)\times10^3$$	$\Delta_e S_2^{N,1}$ — Entropy increase due to nitrogen discharge through untreated wastewater inflow
Through treated wastewater discharge $$\Delta_e S_2^{N,2} = \frac{E^2_{ch,N}}{T_0} = \frac{V_{d,2}}{T_0}\left(c_{N,2} - c_{N,0}\right)\left(19.16 + 0.177\ln\frac{c_{N,2}}{c_{N,0}}\right)\times10^3$$	$\Delta_e S_2^{N,2}$ — Entropy increase due to nitrogen discharge through treated wastewater inflow
(4) $\Sigma\Delta_e S_2$ due to phosphorous discharge ($\Sigma\Delta_e S_2^{P}$) Through untreated wastewater discharge $$\Delta_e S_2^{P,1} = \frac{E^1_{ch,P}}{T_0} = \frac{V_{d,1}}{T_0}\left(c_{P,1} - c_{P,0}\right)\left(3.535 + 0.08\ln\frac{c_{P,1}}{c_{P,0}}\right)\times10^3$$	$\Delta_e S_2^{P,1}$ — Entropy increase due to phosphorous discharge through untreated wastewater inflow
Through treated wastewater discharge $$\Delta_e S_2^{P,2} = \frac{E^1_{ch,P}}{T_0} = \frac{V_{d,2}}{T_0}\left(c_{P,2} - c_{P,0}\right)\left(3.535 + 0.08\ln\frac{c_{P,2}}{c_{P,0}}\right)\times10^3$$	$\Delta_e S_2^{P,2}$ — Entropy increase due to phosphorous discharge through treated wastewater inflow
	$V_{d,1}$ — Annual volume of the untreated wastewater inflow
	$V_{d,2}$ — Annual volume of the treated wastewater inflow

[1] The equations for $\rho(T)$ and $C_p(T)$ calculation are based on reference [23].
[2] Other parameters appeared in the equations are explained in other tables or the text.

In a large city such as Xi'an in this case, the withdrawal of large amount of source water for water supply seems to have much stronger impact than the discharged water quality on the local water system if the calculated entropy is used as a thermodynamic indicator. This is because under the condition of this case, the $\Delta_e S_1$ resulted from 1 m^3 water withdrawal is 2.56×10^4 J·K^{-1}·m^{-3} which is even higher than the $\Delta_e S_2$ of 1.54×10^4 J·K^{-1}·m^{-3} resulted from the discharge of 1 m^3 untreated wastewater. Therefore, with a substantial decrease of water withdrawal as a result of practicing water reclamation and reuse, the total $\Delta_e S$ can be effectively reduced.

Regarding the contributions of the three kinds of pollutants to $\Sigma\Delta_e S_2$, the discharge of untreated wastewater, though with smaller volume ($V_{d,1}$ in Table 5) than the discharge of treated wastewater ($V_{d,2}$ in Table 5) in each

Table 5
Results of case analysis ($J \cdot K^{-1}$)

$\Sigma\Delta_e S_1$	$\Sigma\Delta_e S_2$						$\Delta_e S = \Sigma\Delta_e S_1 + \Sigma\Delta_e S_2$
	$\Sigma\Delta_e S_2^{C}$		$\Sigma\Delta_e S_2^{N}$		$\Sigma\Delta_e S_2^{P}$		
	$\Delta_e S_2^{C,1}$	$\Delta_e S_2^{C,2}$	$\Delta_e S_2^{N,1}$	$\Delta_e S_2^{N,2}$	$\Sigma\Delta_e S_2^{P,1}$	$\Sigma\Delta_e S_2^{P,2}$	
Scenario I: $V_{w,0} = 4.69\times10^8\ m^3\cdot y^{-1}$, $V_w = 4.13\times10^8\ m^3\cdot y^{-1}$, $V_R = 0$, $V_{d,1} = 0.83\times10^8\ m^3\cdot y^{-1}$, $V_{d,2} = 3.30\times10^8\ m^3\cdot y^{-1}$							
1.20×10^{13}	1.05×10^{12}	2.97×10^{11}	2.21×10^{11}	1.46×10^{11}	1.08×10^{10}	5.09×10^{9}	1.38×10^{13}
Scenario II: $V_{w,0}= 4.03\times10^8\ m^3\cdot y^{-1}$, $V_w = 3.47\times10^8\ m^3\cdot y^{-1}$, $V_R = 0.66\times10^8\ m^3\cdot y^{-1}$, $V_{d,1} = 0.83\times10^8\ m^3\cdot y^{-1}$, $V_{d,2} = 2.64\times10^8\ m^3\cdot y^{-1}$							
1.01×10^{13}	1.05×10^{12}	2.38×10^{11}	2.21×10^{11}	3.34×10^{10}	1.08×10^{10}	4.07×10^{9}	1.17×10^{13}
Scenario III: $V_{w,0}= 3.37\times10^8\ m^3\cdot y^{-1}$, $V_w = 2.81\times10^8\ m^3\cdot y^{-1}$, $V_R = 1.32\times10^8\ m^3\cdot y^{-1}$, $V_{d,1} = 0.83\times10^8\ m^3\cdot y^{-1}$, $V_{d,2} =1.98\times10^8\ m^3\cdot y^{-1}$							
8.19×10^{12}	1.05×10^{12}	1.78×10^{11}	2.21×10^{11}	2.51×10^{10}	1.08×10^{10}	3.05×10^{9}	9.67×10^{12}

[1] $\Delta_e S$ calculation is on annual basis.
[2] $V_{w,0}$ is the annual source water withdrawal for urban water supply.
[3] V_w is the wastewater collected and finally discharged to the water body and takes 88% of total water used (including reclaimed water).
[4] $V_{d,1}$ is assumed to be 20% of V_w.
[5] $V_{d,2}$ is assumed to be 80% of V_w.

scenario, has contributed much larger part, indicating that much energy is needed for the degradation of the pollutants in even a small volume of the untreated wastewater discharged into the water body and brings about a substantial entropy increase. It can also be seen from Table 5 that the $\Sigma\Delta_e S_2^{C,1}$ due to organic discharge is about 1 order higher than $\Sigma\Delta_e S_2^{N,1}$ due to nitrogen discharge and 2 orders higher than $\Sigma\Delta_e S_2^{P,1}$ due to phosphorous discharge. The higher Gibbs free energy $\Delta_r G^{\theta}$ for BOM as shown in Table 1 and its higher mole concentration n_j (related to the concentration c_j shown in Table 3) are the reasons for this.

5. Conclusions

This study tried to apply the entropy theory to the analysis of the urban water system with attention mainly paid to the disturbance of human activities, such as water withdrawal, wastewater discharge, and water reclamation and reuse, on the originally natural water system. By definition, an ecosystem, no matter natural or artificial, can never experience no entropy production [12]. Therefore, detailed calculation of the entropy increase from every aspect is often a complicated task. In order to simplify the analysis and find ways to evaluate and to compare the extent of entropy increase due to human activities, an assumption was made in this study that the natural hydrological cycle is a pseudo-reversible process by its nature of self maintenance of water and materials balance so that any entropy increase due to natural processes can be ignored in the analysis and the impact from human activities can be viewed as the artificial disturbance on the natural water system by using entropy as the thermodynamic indicator. The human disturbance was analyzed in two categories: one is related to the quantity of water withdrawal and discharge and another is related to the alteration of water quality due to the pollutants discharged. The models developed for calculating the corresponding entropy increase were based on the energy (heat/exergy as the equivalents) needed for the recovery of the water system to its background condition.

By using the developed models for analyzing the water system in the central city area of Xi'an under three sets of scenarios of current condition of water supply and wastewater treatment without water reclamation and reuse, 20% treated water reuse, and 40% treated water reuse, it was evaluated that by water reclamation and reuse $\Delta_e S$ could be effectively decreased. Comparing with the entropy increase due to qualitative disturbance, the entropy increase due to water withdrawal was found to be much larger in this case under the condition of temperature difference as $\Delta T = 2$ K between the discharged wastewater and water in the river system. As water reclamation and reuse could decrease the demand for fresh water withdrawal and reduce the quantity of wastewater discharge, its major effect was a remarkable decrease of $\Sigma\Delta_e S_1$. The effect of $\Sigma\Delta_e S_2$ reduction was minor but not ignorable. Thermodynamic analysis thus provided a tool for quantitative evaluation of the effect of urban wastewater reclamation and reuse although further improvement of these models and methods of calculation are still needed.

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Symbols

- ∂q — Energy or heat variation, J
- B — System boundary
- c_j — Concentration of substance j, mg·L^{-1}
- $C_P(T)$ — Constant-pressure heat capacity of water at temperature T, J·kg^{-1}·K^{-1}
- E_x — Exergy, J
- $E_{ch,j}$ — Chemical exergy of substance j, J
- $E^1_{ch,j}$ — Reaction exergy, J
- $E^2_{ch,j}$ — Concentration exergy, J
- $h(T)$ — Specific enthalpy of water at temperature T, J·kg^{-1}
- n_j — Mole number of substance j, mol
- $\rho(T)$ — Water density at temperature T, kg·m^{-3}
- Q — Heat of water body, J
- R — Gas constant, 8.314 J·mol^{-1}·K^{-1}
- S — Entropy of the system, J·K^{-1}
- S_0 — Entropy of the environment, J·K^{-1}
- ΔS — Entropy increase, J·K^{-1}
- $\Delta_i S$ — Entropy increase due to natural contributions, J·K^{-1}
- $\Delta_e S$ — Entropy increase due to artificial contributions, J·K^{-1}
- $\sum\Delta_e S_1$ — Entropy increase from quantitative disturbance, J·K^{-1}
- $\sum\Delta_e S_2$ — Entropy increase from qualitative disturbance, J·K^{-1}
- T — Absolute temperature, K
- T_0 — Absolute temperature of the environment, 298.15 K
- t — Water temperature, °C
- V — Quantity of water flow with higher temperature, m^3
- V_d — Volume of wastewater discharge, m^3
- V_R — Volume of water reclamation, m^3
- V_w — Volume of wastewater discharge, m^3
- $V_{w,0}$ — Volume of water withdrawal, m^3
- W_{id} — Ideal work, J·mol^{-1}
- $\Delta_r G^0$ — Standard Gibbs free energy, J·mol^{-1}

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