# Thermodynamic entropy of organic oxidation in the water environment: experimental evaluation compared to semi-empirical calculation

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## Abstract

Residual organic matters in the secondary effluent are usually less biodegradable in terms of the total organic carbon content, and when discharged into a receiving water body, their further decomposition most likely mainly occurs due to chemical oxidation. Using this scenario, a semiempirical method was previously developed to calculate the thermodynamic entropy of organic oxidation to quantitatively evaluate the impact of organic discharge on the water environment. In this study, the relationship between the entropy increase (ΔSC) and excess organic mass (ΔTOC) was experimentally verified via combustion heat measurement using typical organic chemicals and mixtures. For individual organic chemicals, a linear relationship was detected between ΔSC and ΔTOC with the same proportionality coefficient, 54.0 kJ/g, determined in the previous semi-empirical relationship. For the organic mixtures, a linear relationship was also identified; however, the proportionality coefficient was 69.2 kJ/g, indicating an approximately 28 % increase in the oxidation heat required to decompose the same organic mass. This increase in energy can likely be attributed to the synergistic effects of hydrogen bonding, hydrophobic interactions, π–π interactions, and van derWaals interactions between functional groups of different organic compounds. Intermolecular interactions may result in 17–32 % more dissociation energy for organic mixtures compared to the organic components' chemical structures. Because organics discharged into a water body are always a mixture of organic compounds, the proportionality coefficient obtained using organic mixtures should be adopted to modify the previously proposed semi-empirical equation.

**Keywords**: Organics . Chemical oxidation . Entropy increase . Synergistic effects . Water environment

## Introduction

Effluent discharged from wastewater treatment plants (WWTPs) is the major source of organic matter in aquatic environments (Lee and Rasmussen 2006). The contribution of discharged organic matter to rivers and streams is particularly significant in the low-flow summer season, especially in arid areas where the discharged effluent may dominate the stream-flow during an extremely dry period (Quaranta et al. 2012). Therefore, there is an urgent need to quantitatively evaluate the impact of organic matter discharged from secondary effluent on the water environment.

Secondary effluent from a WWTP usually contains a relatively high concentration of COD that has not been effectively removed by a biological treatment process, such as the activated sludge process. This residual organic matter generally belongs to a less or non-biodegradable fraction (Katsoyiannis and Samara 2007). The residual organic concentration, in terms of total organic carbon (TOC), can be as high as 10 to 40 mg/L (Michael et al. 2015). In contrast, the biodegradable fraction is often very low in the secondary effluent, and the assimilable organic carbon (AOC) concentration may only be at μg/L or even ng/L level (Pramanik et al. 2015; Thayanukul et al. 2013).

The direct impact of effluent discharge to a receiving water body is an increase in pollutant concentration in part of or in the whole water body. If pollutant loading does not exceed the carrying capacity of the water body, excess pollutants will be gradually removed through natural processes, leading to a recovery of water quality to its background level (Wang et al. 2015). Depending on the properties of the excess organic substances, self-purification may be achieved through biological actions to decompose biodegradable fractions following the Streeter-Phelps equation (Wang et al. 2015) or via chemical oxidations to decompose the non-biodegradable fractions (Gotovtsev 2010). Under natural conditions, the main pathways for the degradation of the less or non-biodegradable organic substances are oxidation assisted by solar radiation, called the photolysis process (Dong et al. 2015; Tijani et al. 2013). Through such kind of oxidation process, the bulk concentration of organic matter can eventually return to background levels. Therefore, it can be reasonably assumed that chemical oxidation might be the sole process responsible for the decomposition of excess organics from secondary effluent.

From the thermodynamic viewpoint, the degradation of excess organics by chemical oxidation would be accompanied by an irreversible energy dissipation. According to the Second Law of Thermodynamics, entropy can be used to determine the irreversibility of a thermodynamic process (Atkins and de Paula 2002). The reaction of organic matter decomposition in surface water is considered to occur under constant pressure (atmospheric pressure, if the influence of water depth is ignorable) in a closed system, so a series of irreversible reactions for the decomposition of pollutants will cause the entropy to increase. Consequently, the entropy increase ($\Delta S$) can be used to directly and quantitatively evaluate the impact of organic matter discharged into the water environment. However, few studies have reported entropy increases in aquatic systems due to the intrusion of organic pollutants.

For a chemical reaction under constant pressure, if the work done on the system simply results in an expansion of the volume, the heat of the reaction ($\Delta Q$) is numerically equal to the enthalpy change of the reaction ($\Delta rH$) but with the opposite sign (−). Therefore, $\Delta rH$ can be used as a surrogate parameter for ΔQ in the ΔS calculation (Lukas et al. 2007). For organic substances of known molecular structures, ΔrH can be theoretically calculated according to the oxidation reactions, which results in complete decomposition to $CO_2$, $H_2O$, and other simple inorganic elements. When a water body receives excess organic pollutants, the endpoint is the return of the organic carbon concentrations to their background level, as long as the pollutant loading does not exceed the carrying capacity of the water body. This is equivalent to the complete oxidation of excess organic pollutants. In addition, the oxidation process for excess organics is also accompanied by energy consumption, thereby increasing the entropy of the water body, a higher energy consumption will result in a higher entropy increase. As complete oxidation of organics requires the highest level of energy consumption, the endpoint of oxidation is supposed to be the complete removal of excess organics from the water body (Matilainen and Sillanpää 2010). Following the thermodynamic principle, the ΔrH calculation can be conducted by taking into account the initial state (intrusion of excess organics) and the final state (recovery to the background condition) without considering the detailed reaction pathways.

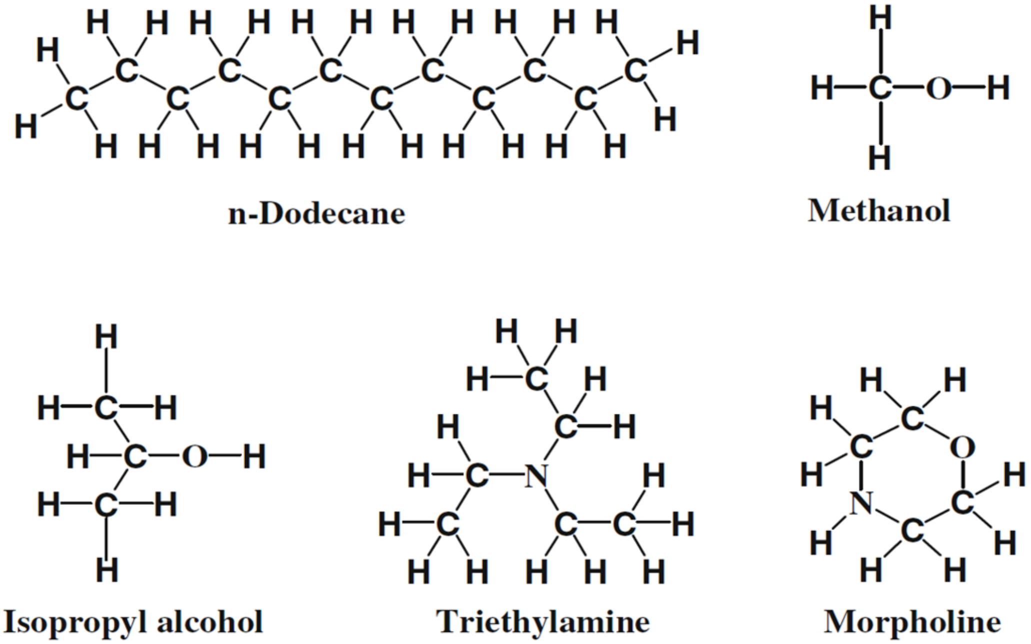
Under the assumption that excess organic pollutants were completely decomposed by chemical oxidation, more than 200 organic substances with known molecular structures were used to calculate the standard molar enthalpy change of the reaction ($\Delta rH^0$) (Luo et al. 2012). As a result, a proportional relationship was found between the calculated $\Delta rH^0$ values and the TOC content, and the proportionality coefficient was determined to be 54.0 kJ/g. On this basis, a semi-empirical relationship was obtained to calculate the entropy increase ΔSc due to excess organic decomposition. Using this semiempirical relationship, it is possible to evaluate the impact of effluent discharge on the water environment based on ΔTOC. However, such a simple method has not been experimentally verified. Because the final products of complete oxidation for each organic substance are the same as those in a combustion reaction, the heat produced by complete oxidation is equal to the combustion heat. In this case, the calculated ΔrH0 can be verified by a heat of combustion measurement. Under the same assumption, several typical organic chemicals with known structures can be selected to measure both the combustion heat ΔQ and TOC, and a relationship between ΔQ and TOC can be established. However, the composition of organic substances in the secondary effluent varies with the content of the organic components. There are different major components in the different secondary effluent streams, including alkanes, organic acids, esters, alcohols, amides, proteins, fats, and oils (Wang et al. 2014). It is difficult to measure the combustion heat of the organic substances in the secondary effluent because of its complicated composition, which was sometimes unable to be separated from the secondary effluent. On the other hand, excess organics due to effluent discharge are in fact organic mixtures, and there may inevitably exist interactions between different organic molecules that have not been taken into account in this calculation. Thus, to simulate organic compounds in the secondary effluent, organic mixtures with a broad range of carbon contents have been prepared based on the organic chemicals that commonly exist in the secondary effluent. To develop a ΔSc method that is more suitable for practical use, this study was conducted to experimentally verify the ΔSc-ΔTOC relationship and to illuminate the mixture effects between different organics.

## Materials and methods

## Chemicals

### *Organic chemicals*

Organic compounds are normally composed of carbon, hydrogen, and oxygen, as well as nitrogen and sulfur. In natural water and the secondary effluent, they may include pure hydrocarbons and organic compounds containing additional elements. Common additional elements are oxygen and nitrogen, with structures varying form linear and branched to ring groups (Xue et al. 2011). In this study, several typical organic chemicals were selected to cover a range of different organic elements (C, H, O, and N) so that the combustion heat measurements could be more comprehensive. Furthermore, the selected chemicals contained a broad range of carbon content with structures of linear, branched, and ring groups; this was critical to capture because of the semi-empirical relationship calculated using these organic substances. As the TOC was used to quantify the organic mass, the selected chemicals also had to be soluble. Therefore, five organic chemicals from the lowest carbon content (methanol) to the highest carbon content (n-dodecane) were finally selected, as shown in Fig. 1. These chemicals can be classified into four types, namely pure hydrocarbons with only C and H; compounds with C, H and O; compounds with C, H and N; and compounds with C, H, O, and N. For all of the selected organic chemicals, the theoretical organic carbon (ThOC) and standard molar enthalpy change of reaction ($\Delta rH^0$) were first calculated, and then, the TOC and corresponding combustion heats were measured. The selected organic chemicals are n-dodecane ($C_{12}H_{26}$), methanol ($CH_4O$), isopropyl alcohol ($C_3H_8O$), triethylamine ($C_6H_{15}N$), and morpholine ($C_4H_9NO$). Among them, methyl alcohol and isopropyl alcohol belong to the type of compounds with C, H, and O, while the chemical structure of isopropyl alcohol is more complicated than that of methyl alcohol. Morpholine has C, H, O, and N, with a ring group structure. All of these chemicals are of analytical grade or chromatographic grade (purity $\geq$ 99 %).


n-Dodecane

Methanol

Isopropyl alcohol

Triethylamine

Morpholine

**Fig. 1** Structural formulae for 5 organic chemicals

Secondary effluent from biological wastewater treatment still contains a certain amount of organic compounds, and the effluent TOC concentrations typically range between 10 and 50 mg/L. Dissolved organic matter (DOM) in the secondary effluent is a heterogeneous mixture of aromatic and aliphatic hydrocarbon structures that have attached amide, carboxyl, hydroxyl, ketone, and various other minor functional groups (Leenheer and Croué 2003). These organic compounds mainly consist of low molecular weight (smaller than 1000 Da) organic components, including humic substances, proteins, lipids, carboxylic acids, saccharides, amines, amino acids, and hydrocarbons (Shon et al. 2006; Xue et al. 2011). Therefore, to simulate organic compounds in secondary effluent, in this study, some liquid reagents of pure organic substances, which contain most of the organic components, were selected for mixing. Meeting the requirements for combustion heat and TOC analysis, these organic substances include alkyls, olefins, alcohols, acids, ethers, esters, ketones, benzenes, amines, nitro-compounds, ring compounds, and organic compounds containing sulfur or phosphorus. They can also be classified into the 4 types of organic chemicals and contained different numbers of carbon elements. Most of these organics are less or non-biodegradable, which can be commonly detected in secondary effluent. However, to cover a broad range of carbon contents, several organic chemicals with a low carbon content, such as methyl alcohol, formic acid, and methylamine, were also added to the mixture. According to the different components and proportions of the pure organic substances shown in Table 1, six organic mixtures were obtained. These six organic mixtures were selected to determine the combustion heat and corresponding TOC concentration.

**Table 1** Components of organic mixtures

| Organic substance | Ratio of the organic substance (%) | | | | | |
|---|---|---|---|---|---|---|
| | Mixture 1 | Mixture 2 | Mixture 3 | Mixture 4 | Mixture 5 | Mixture 6 |
| *n*-Dodecane | | | 12.5 | 18.75 | 18.75 | |
| *n*-Hexadecane | | | | | | 12.5 |
| Nitromethane | 87.5 | | | | | |
| Methyl alcohol | | 93.75 | | | | |
| Dehydrated alcohol | | | 6.25 | 12.5 | 6.25 | |
| Formic acid | | 6.25 | | | | |
| Lactic acid | | | 18.75 | 18.75 | 18.75 | |
| 2-Propenoic acid | | | | | | 12.5 |
| Triethyl phosphate | | | 12.5 | 12.5 | 12.5 | 6.25 |
| Diethyl phthalate | | | | | | 12.5 |
| 2-Ethoxyethanol | | | 6.25 | 6.25 | 6.25 | 6.25 |
| Cyclohexanone | | | 6.25 | 6.25 | 6.25 | 6.25 |
| Methylamine | 12.5 | | | | | |
| Formamide | | | 25 | | | |
| *N*, *N*-Dimethyl formamide | | | | 18.75 | 6.25 | 6.25 |
| Triethanolamine | | | | | | 6.25 |
| Aniline | | | | | 18.75 | 18.75 |
| Morpholine | | | | | | 6.25 |
| Dimethyl sulfoxide | | | 12.5 | 6.25 | 6.25 | 6.25 |

## Experiments

### *Combustion heat measurement*

The combustion heats of the samples were measured using an RBC－II type rotating-bomb calorimeter (Yang et al. 2002). The calorimeter was calibrated with benzoic acid of 99.999 % purity, which has a standard heat of combustion of −26,434 J/g at 298.15 K. The experimental procedures were nearly the same as those outlined by Yang et al. (2002). The initial temperature and oxygen pressure of the combustion reaction were regulated to 298.15 ± 0.01 K and 2.5 MPa, respectively. A digital indicator for the temperature measurement was used to ensure better precision and accuracy during the experiment. The calibrated experimental result for the energy equivalent of the calorimeter (W) was 18,604.99 ± 8.14 J/ K with a precision of $4.38 \times 10^{-4}$. The samples' combustion heats were determined using the calorimeter, which had been calibrated with benzoic acid. Each sample was placed into a capsule with a combustion energy of 46,627.59 J/g at 298.15 K. The determination method was the same as that for calibrating the calorimeter with benzoic acid. The combustion heats of the samples were measured by six experiments. The values were calculated using Eq. (1):

$$-\Delta Q = \frac{W\Delta T\text{-Gb-5.983c-qm}}{m} \qquad (1)$$

where ΔQ denotes the combustion heat of samples (J/g), W is the energy equivalent of the RBC－II type rotatingbomb calorimeter (J/K), ΔT is the calibrate value of the temperature rise (K), G is the combustion enthalpy of Ni-Cr wire for ignition (0.9 J/cm), b is the length of the actual Ni-Cr wire consumed (cm), 5.983 is the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of 0.1000 mol/L solution of NaOH (J/mL), c is the volume of 0.1000 mol/L solution of NaOH consumed (mL), q is the combustion energy of the capsule (46,627.59 J/g), and m is the mass of the sample (g).

### *TOC analysis*

TOC analyses of samples were executed according to the thermal catalytic oxidation principle using a Shimatzu TOC－VCPH analyzer. The organic chemicals and organic mixtures were diluted 10,000 times in pure water before TOC analysis was performed.

### *Calculation methods*

The organic components in the mixtures contain the elements of carbon, hydrogen, oxygen, nitrogen, and sulfur, so a general molecular formula of $C_xH_yO_zN_tS_m$ can be utilized to represent all of the organic substances. Considering a state where each organic substance is completely decomposed into the simplest form of inorganic substances by chemical oxidation, forming $CO_2$ (g), $H_2O$ (l), $N_2$ (g), and $SO_2$ (g), the chemical reaction for its complete oxidation can be written in a general equation as follows:

$$C_xH_yO_zN_tS_m + (x + y/4 + m - z/2)O_2 \rightarrow xCO_2 + y/2H_2O + t/2N_2 + mSO_2 \qquad (2)$$

The standard molar enthalpy change of reaction ΔrH0 (kJ/mol) for Eq. (2) can be calculated (Atkins and de Paula 2002) as:

$$\Delta_r H^0 = \sum v_{prod} \Delta_f H^0_{prod} - \sum v_{react} \Delta_f H^0_{react} \qquad (3)$$

where $v_{prod}$ and $v_{react}$ are the stoichiometric coefficients of each product and reactant from Eq. (2), respectively; $\Delta f\ H^0_{prod}$ and $\Delta f\ H^0_{reac}$t are the standard molar enthalpy of formation for each product and each reactant from the thermodynamic data base (Atkins and de Paula 2002) (kJ/mol).

Therefore, the theoretical reaction heat values $\Delta rH^0$ of the individual organic chemicals can be calculated with Eq. (3) using the stoichiometric coefficients for the reactants and products from Eq. (2) and the standard molar enthalpy of formation for each reactant and product derived from the thermodynamic database. Regarding the interaction between chemicals to be ignored, the theoretical reaction heat of six organic mixtures can be obtained by different proportions of the individual organic substances and their related $\Delta rH^0$. Therefore, the theoretical reaction heat of organic mixtures $\Delta rH^0_m$ (kJ/L) can be calculated as:

$$\Delta_r H^0_m = \sum_{i=1}^{16} r_i \cdot \frac{\Delta_r H^0_i}{Mi} \cdot \rho_i \qquad (4)$$

where $r_i$ is the ratio of organic substance i in the mixture as shown in Table 1,$\Delta rH^0_i$ is the standard molar enthalpy change of reaction for organic substance i (kJ/mol), $M_i$ is the molecular mass of organic substance i (g/mol), and $\rho_i$ is the density of organic substance i (g/L).

## Results and discussion

### Combustion heats and organic contents of individual organic chemicals and organic mixtures

Based on the experimental data of combustion heat, the corresponding combustion heat for the five individual organic chemicals ($\Delta Q_i$) and for the six organic mixtures ($\Delta Q_m$) were calculated according to Eq. (1) as well as the corresponding density of the organic substances. The results of the measured combustion heat were regarded as the measured $\Delta rH^0$. The mean results of the combustion heat for n-dodecane, triethylamine, morpholine, isopropyl alcohol, and methyl alcohol were 34,694.2, 29,267.1, 29,363.3, 25,418.7, and 16,977.3 kJ/L, respectively. The corresponding relative standard deviations were 0.14, 0.13, 0.09, 0.12, and 0.13 %, respectively. For the organic mixtures, the mean results for the combustion heat for mixtures 1 to 6 were 17,542.7, 21,892.5, 31,398.4, 36,880.7, 38,447.3 and 43,703.7 kJ/L, respectively. The corresponding relative standard deviations were 0.17, 0.17, 0.12, 0.12 0.13, and 0.11 %, respectively.

### Comparison of combustion heat values with theoretical reaction heat values

Using Eq. (2) and Eq. (3), the theoretical reaction heat values of n-dodecane, triethylamine, morpholine, isopropyl alcohol, and methyl alcohol were calculated to be 7901.7, 4377.1, 2673.6, 2006.9, and 725.7 kJ/mol, respectively, according to their molecular structures and oxidation reactions. By plotting the measured and theoretical $\Delta rH^0$ versus theoretical organic carbon (ThOC), Fig. 2 shows the relationship between the theoretical and measured $\Delta rH^0$. Also shown in Fig. 2, the measured $\Delta rH^0$ (i.e., $\Delta Q_i$) and theoretical $\Delta rH^0$ for the five individual organic chemicals with different structures are well concentrated along the bisection line. This indicated an almost equal-value relationship between $\Delta Q_i$ and the theoretical $\Delta rH^0$, so it is feasible to substitute the theoretical reaction heat with the measured combustion heats for pure organic chemicals.

Referring to the six organic mixtures listed in Table 1, the theoretical $\Delta rH^0$ for each organic component can be calculated in the same manner as that of the pure organic chemicals. Then, based on the theoretical $\Delta rH^0$ of each organic component and Eq. (4), the value of $\Delta rH^0{}_m$ (kJ/L) can be calculated. Table 2 shows the difference between the experimental combustion heats and theoretical reaction heats of the six organic mixtures. The value of the experimental combustion heat is larger than that of the theoretical reaction heat, and except for mixture 5, the difference ($-\Delta Q_m$) and ($-\Delta rH^0{}_m$) increased when the TOC concentration was also increased.

Table 2 shows that there are certain differences between the measured combustion heat and theoretical reaction heat calculated for each mixture. A possible reason for this difference may be the non-covalent interactions between different organic chemicals in the mixture that cannot be accounted for in the theoretical calculation. There should be two types of non-covalent interactions, one as the weak hydrophobic force (van der Waals, π − π, CH − π) and hydrogen bonds, and another as the electrostatic linkages due to charge transfer, ion exchange, or ligand exchange (Mazzei and Piccolo 2015). Leenheer and Croué (2003) discovered that molecular structures can be formed by hydrogen bonding, nonpolar interactions, and polyvalent cation interactions. Gadad et al. (2007) reported that interactions between DOM and aromatic compounds are controlled by both π − π interactions and hydrophobic interactions. Therefore, a variety of molecular interactions, such as hydrophobic interactions, π − π interactions, hydrogen bonding, and van der Waals interactions, have been suggested to occur in organic compounds (Wang and Zhang 2014). For organic mixtures, one or more of the above-mentioned molecular interactions could form between different organic compounds, thus affecting the reactivity of organic compounds and increasing the energy requirement for organic mixture destruction. A more detailed comparison of the actual combustion heat and theoretical reaction heat for the mixtures will be given in "Estimating the additional dissociation energies between chemical molecules in the organic mixture".

**Table 2** Measured TOC, experimental combustion heat ($-\Delta Q_m$), and theoretical reaction heat $\left(-\Delta_r H_m^0\right)$ of 6 organic mixtures

| Organic substances | Measured TOC, g/L | Experimental combustion heat, kJ/L | Theoretical reaction heat, kJ/L | Difference between ($-\Delta Q_m$) and ($-\Delta_r H_m{}^0$), kJ/L |
|---|---|---|---|---|
| Mixture 1 | 228.2 | 17,542.70 ± 29.87 | 14,408.07 | 3104.1–3164.5 |
| Mixture 2 | 305.0 | 21,892.49 ± 36.98 | 17,195.54 | 4660.0–4733.9 |
| Mixture 3 | 455.4 | 31,398.35 ± 38.05 | 23,450.69 | 7909.6–7985.7 |
| Mixture 4 | 510.9 | 36,880.66 ± 42.99 | 26,472.71 | 10,365.0–10,450.9 |
| Mixture 5 | 570.1 | 38,447.31 ± 48.86 | 28,824.23 | 9574.2–9671.9 |
| Mixture 6 | 649.7 | 43,703.67 ± 47.99 | 30,571.80 | 13,083.9–13,179.9 |

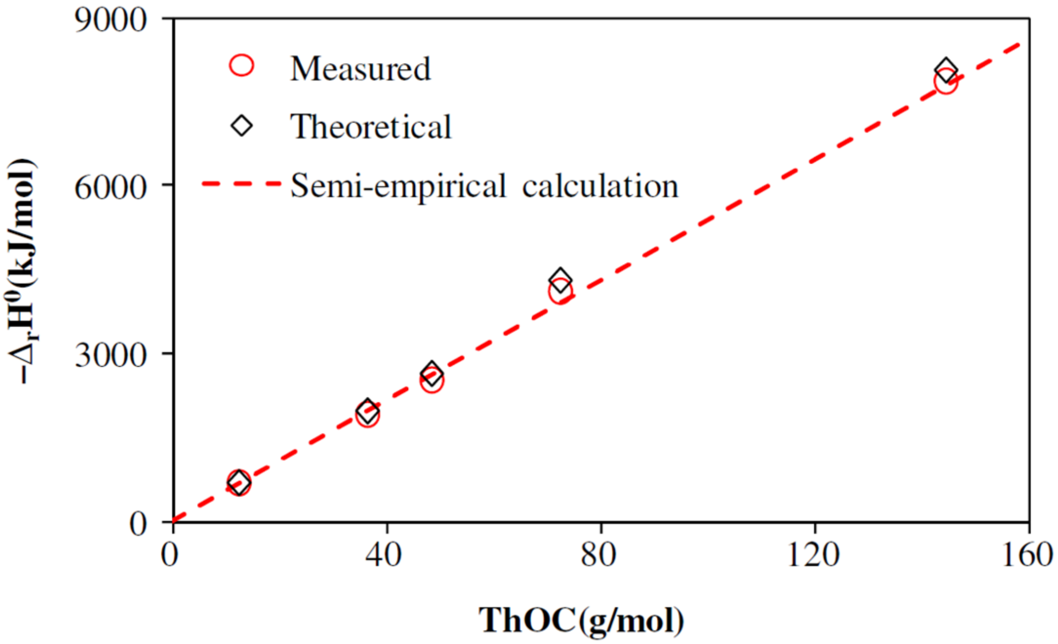


**Fig. 2** Relationship between theoretical and measured combustion heats of 5 organic chemicals

### Thermodynamic entropy calculated based on combustion heat

In this study, the chemical equation of oxidation for each organic substance is the same as the equation of combustion, so the heat of chemical oxidation is equal to the heat of combustion. The thermodynamic entropy can be evaluated using a combustion heat (ΔQ) analysis.

Based on the semi-empirical calculation of ΔSc, as shown in our previous study (Luo et al., 2012), the semi-empirical equation for the reaction heat $\Delta rH^0_{se}$ (kJ/L) of organic compounds produces $-\Delta rH^0_{se}$ = k'/TOC = 54.0TOC. For the theoretical methodology shown in Eq. (4), the organic components and proportions of the organic mixtures were needed for the calculation of reaction heat. However, for the semi-empirical methodology, the reaction heat of organic mixtures can be calculated by TOC values. Figure 3 shows the relationship between the measured combustion heats ($-\Delta Q_i$) and semi-empirical equation of reaction heat ($-\Delta rH^0_{se}$) for five individual organic chemicals. In Fig. 3, the values of $-\Delta Q_i$ are well concentrated along the dotted line of $-\Delta rH^0_{se}$ = 54.0TOC. Due to the limitations of the combustion heat and TOC analyses, it is impossible to measure the entire organic substances collection to build the semi-empirical equation. Although five organic chemicals represent a limited selection, they contained all of the basic organic elements and different structures and were selected from within the same range of ThOC. Thus, the semi-empirical equation of reaction heat is suitable for the individual organic chemicals. It is demonstrated that the ΔSc calculation can successfully be applied to the individual organic compounds.

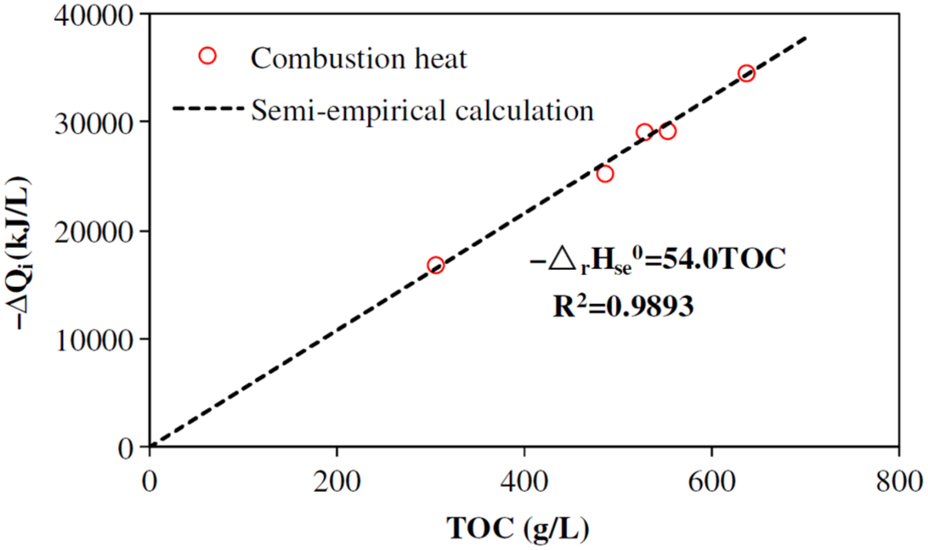


**Fig. 3** Relationship between measured combustion heats and semiempirical calculation of reaction heat for 5 individual organic chemicals

Figure 4 shows the relationship between the experimental combustion heat ($-\Delta Q_m$), theoretical reaction heat $-\Delta rH^{0}_{m}$, and semi-empirical reaction heat $-\Delta rH^{0}_{se}$ of the six organic mixtures. As illustrated in Figs. 3 and 4, it is evident that the combustion heat increases with the organic carbon content, regardless of the organic chemicals or organic mixtures. Moreover, a proportional relationships exists between $-\Delta Q_m$, as well as $-\Delta rH^{0}_{m}$, and the TOC concentration with a large proportionality coefficient of $-\Delta Q_m$ (Fig. 4). Although there is a small difference between $-\Delta rH^{0}$ m and the corresponding value of $-\Delta rH^{0}_{se}$, the values of $-\Delta rH^{0}_{m}$ were still well concentrated along the line of semi-empirical equation －ΔrH0se = 54.0TOC, as shown in Fig. 4. This indicated that the interaction between chemical molecules in the organic mixture could also be ignored in the ΔSc calculation.

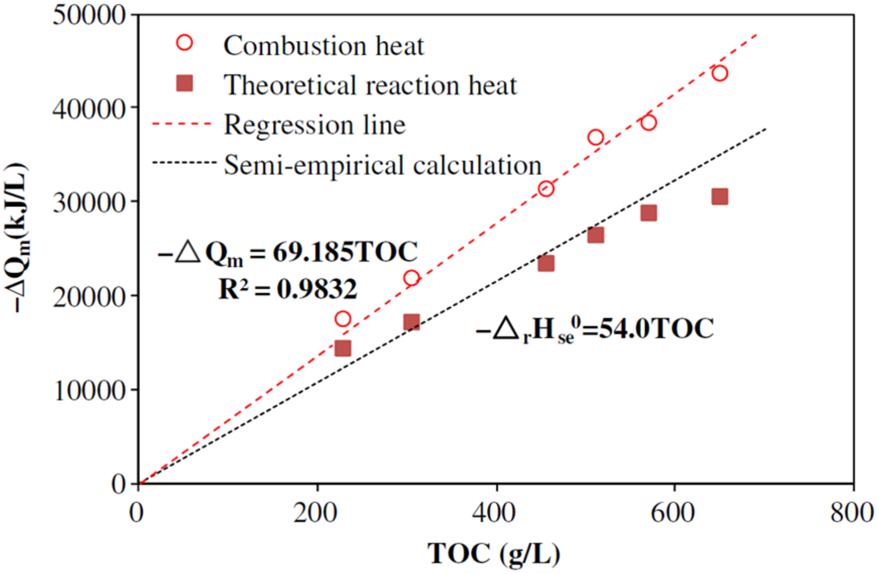


**Fig. 4** Relationship between experimental combustion heats, theoretical and semi-empirical reaction heats of 6 organic mixtures

For the six organic mixtures, Fig. 4 shows the proportional relationship between TOC and $-\Delta Q_m$. Using a correlative calculation, the linear proportional relationship appears as:

$$-\Delta Q_\mathrm{m} = k_m \cdot TOC \quad \left(R^2 = 0.9832\right) \qquad (5)$$

The highly correlative relationship between TOC and $-\Delta Q_m$ indicates that TOC can be used as a parameter for an approximate estimation of the $\Delta Q_m$ value. According to the Second Law of Thermodynamics (Atkins and de Paula 2002), the entropy change of a chemical reaction under constant temperature is the amount of heat change (ΔQ) divided by the absolute temperature (T). Thus, considering that the termination of organic decomposition is to the background level of $TOC_0$, the entropy increase of the organic decomposition via chemical oxidation due to secondary effluent discharge can be calculated as:

$$\Delta S_C^{\prime} = \frac{k_m \cdot \Delta \mathrm{TOC} \cdot V}{T} \qquad (6)$$

where $k_m$ = 69.185 kJ/g, ΔTOC is the reduced concentration of the total organic carbon from the secondary effluent ($g/m^3$), and V is the volume of the secondary effluent discharge ($m^3$).

The organic matter residual in the secondary effluent can be regarded as an organic mixture. Therefore, as long as the organic mass can be measured as TOC, Eq. (6) can be used to evaluate the impact of effluent discharge on the receiving water body in terms of ΔS'c. For example, wastewater treatment needs to be upgraded to reduce pollutant loading to the aquatic environment in China and other countries (Logar et al. 2014). Using Eq. (6), a reduction of TOC by 1 mg/L is equivalent to a reduction of ΔS'c by 232 J/K·m3 under the assumption of T = 298.15 K (25 °C). For a domestic wastewater treatment plant with a capacity of $1.0 \times 10^5$ $m^3$/day, when advanced treatment, such as carbon adsorption is applied, an additional TOC reduction of 4 to 5 mg/L can often be obtained (Wei et al. 2009). In this case, the net benefit can be evaluated as approximately $1.0 \times 10^5$ kJ/K, indicating a remarkable reduction of the impact on the receiving water body.

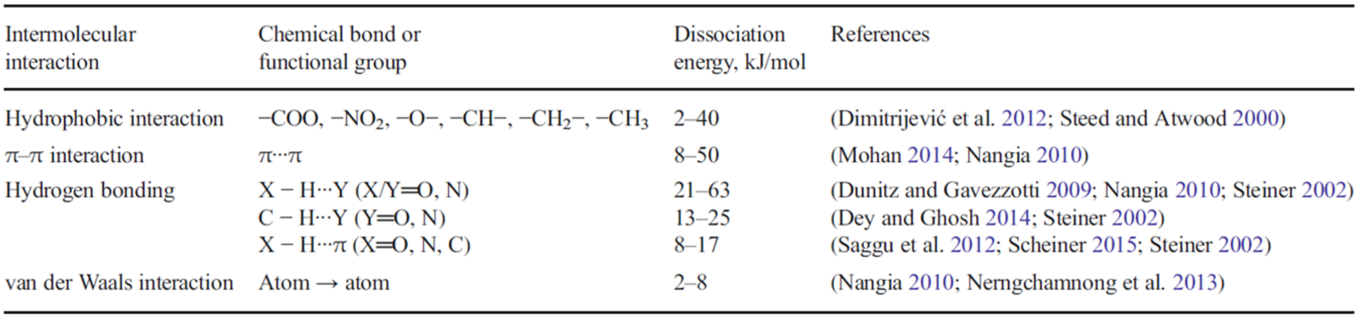
### Estimating the additional dissociation energies between chemical molecules in the organic mixture

For chemical mixtures, the reaction heat can be obtained either by semi-empirical calculation, − $-\Delta rH^0_{se}$=54.0TOC, or by measurement, $-\Delta Q_m$ = 69.185TOC, where themeasured value provides an approximately 28%increase in the heat required to decompose the same organic mass. Mixing chemicals with different and complex molecular structures leads to various intermolecular interactions. Because the interaction energy between different organic molecules in the mixture could not be accounted for in the semi-empirical calculation, it was inevitable to underestimate the chemical reaction heat (or energy). This energy, called additional dissociation energy due to intermolecular interactions between different organic compound molecules, may not be negligibly small, but instead may comprise a considerable part of the total energy.

As discussed in "Comparison of combustion heat values with theoretical reaction heat values", the intermolecular interactions could include hydrophobic interactions (HI), π − π interactions, hydrogen bonding (HB), and van der Waals interactions (vdW) between the different organic compounds. Hydrophobic interactions are a special class of interaction representing associations of nonpolar groups in polar solvents. Functional groups of hydrophobic interaction include alkyl groups, ester groups, nitro groups, and so on (Dimitrijević et al. 2012). Aromatic π – π interactions (sometimes called π – π stacking interactions) occur between aromatic rings, often in situations where one is relatively electron rich and one is electron poor (Steed and Atwood 2000). Hydrogen bonds have the general motif X − H···Y, where the X−H group is a proton donor and Y is a proton acceptor. Hydrogen bonds are highly directional non-covalent interactions with bond strength ranging from weak (5 – 16.7 kJ/mol) to moderate (16.7 – 62.7 kJ/mol) and even to strong (83 – 167 kJ/mol) (Steiner 2002). Moderate hydrogen bonds are generally formed by neutral donor and acceptor groups, such as –OH and −NH. In addition to intermolecular O−H···Y (Y═O, N) and N−H···Y hydrogen bonds, a variety of weak C−H···Y contacts could also be present (Dunitz and Gavezzotti 2009). Another type ofweak hydrogen bond in which π-systems play the role of acceptor, including O−H···π, N−H···π, C−H···π, and S−H···π interactions, are also important in chemical systems (Saggu et al. 2012).Van derWaals interactions are driven by induced electrical interactions between two or more atoms or molecules that are very close to each other. This is the weakest of all intermolecular attractions, with interaction energies in the range of 2 – 8 kJ/mol (Nangia 2010).

To have a good understanding of the molecular interactions present in mixtures, Table 3 shows the range of additional dissociation energies that can be attributed to each interaction. Using previously reported energy data, the possible interaction energies ignored by the semi-empirical equation were estimated using the most probable molecular interactions between different molecules of the six mixtures (Table 4). The six organic mixtures have different ranges of additional dissociation energy from the four possible intermolecular interactions. The percentage of additional dissociation energy to measured energy (combustion heat) was as follows: from 9.6 to 30.2 % for mixture 1, 11.8 to 32.3 % for mixture 2, 7.7 to 22.2 % for mixture 3, 6.7 to 19.4 % for mixture 4, 6.4 to 19.3 % for mixture 5, and 5.4 to 16.8 % for mixture 6. When more possible intermolecular interactions were used in the calculation, the additional dissociation energy accounted for a lower the percentage of the measured energy.

**Table 3** Estimation of additional dissociation energies due to intermolecular interactions



| Intermolecular interaction | Chemical bond or functional group | Dissociation energy, kJ/mol | References |
|---|---|---|---|
| Hydrophobic interaction | $-COO$, $-NO_2$, $-O-$, $-CH-$, $-CH_2-$, $-CH_3$ | 2–40 | (Dimitrijević et al. 2012; Steed and Atwood 2000) |
| π–π interaction | π···π | 8–50 | (Mohan 2014; Nangia 2010) |
| Hydrogen bonding | X − H···Y (X/Y═O, N) | 21–63 | (Dunitz and Gavezzotti 2009; Nangia 2010; Steiner 2002) |
|  | C − H···Y (Y═O, N) | 13–25 | (Dey and Ghosh 2014; Steiner 2002) |
|  | X − H···π (X═O, N, C) | 8–17 | (Saggu et al. 2012; Scheiner 2015; Steiner 2002) |
| van der Waals interaction | Atom → atom | 2–8 | (Nangia 2010; Nerngchamnong et al. 2013) |

**Table 4** Possible dissociation energies ignored by semiempirical calculation for chemical mixtures

| Organic mixture | Number of possible intermolecular interaction | | | | Additional dissociation energy | |
|---|---|---|---|---|---|---|
| | HI | π–π | HB | vdW | Estimation, kJ/L | Percent of the measured energy |
| 1 | 3 | 0 | 8 | 14 | 1692.9–5296.2 | 9.6 %–30.2 % |
| 2 | 1 | 0 | 6 | 11 | 2574.4–7064.4 | 11.8 %–32.3 % |
| 3 | 38 | 0 | 82 | 134 | 2417.7–6958.0 | 7.7 %–22.2 % |
| 4 | 40 | 0 | 86 | 140 | 2477.6–7170.6 | 6.7 %–19.4 % |
| 5 | 45 | 1 | 93 | 154 | 2453.2–7421.9 | 6.4 %–19.3 % |
| 6 | 68 | 2 | 131 | 224 | 2361.4–7329.2 | 5.4 %–16.8 % |

Additional dissociation energy was calculated as the sum of the energy from each intermolecular interaction. Inreality, energy from multiple interactions is often greater than the sum of the forces acting separately (positively cooperative) (Williams et al. 2004). The synergistic effects of noncovalent interactions are omnipresent in chemical and biological systems. Quiñonero et al. (2008) demonstrated that there is a certain interplay between π − π and X − H/π interactions (X═C, N, O) in complexes in which both interactions coexist. These synergistic effects are modest in magnitude for neutral molecules; nevertheless, their contribution to the total interaction energy is important. The interactions between different organic compounds and their synergistic effects in organic mixtures were ignored in the semi-empirical calculation of − $-\Delta rH^0_{se}$. As shown in Tables 2 and 4, in the theoretical calculations of reaction heat, the hydrophobic interactions, π − π interactions, hydrogen bonding, and van derWaals interactions (vdW) between different organic compounds were not accounted for mixtures 1 and 2. These interactions with their synergistic effects were also not accounted for in mixtures 3 to 6 in the theoretical calculations. The additional dissociation energy evaluated in Table 4 should have resulted in an increase in the combustion heat of the mixtures; therefore, $k_m$ = 69.185 kJ/g is the more suitable coefficient for entropy increase calculation in Eq. (6).

## Conclusions

Calculating thermodynamic entropy can assist in quantitatively evaluating the impact of organic discharge into a water environment. Here, the decomposition of excess organic carbon to the background level demands energy consumption, resulting in an entropy increase in the aquatic system. According to the thermodynamic principles, the energy required for the oxidation of organics is equivalent to their combustion heat. By employing a direct measurement of the combustion heat of typical organic compounds, the linear relationship between ΔSc and ΔTOC was experimentally verified, and the proportionality coefficient was determined to be the same as the semiempirical equation proposed in the authors' previous study. It can thus be concluded that for individual organic compounds of varied chemical structures, the energy required for their oxidation is mainly determined by the organic mass. Evaluating ΔSc is possible via TOC analysis of the discharged organic matter. However, the oxidation of organic mixtures may be a more complicated chemical process involving interactions between various functional groups of these organic components. This may inevitably bring about the consumption of additional dissociation energy, as indicated by the larger proportionality coefficient for mixtures in Eq. (6). The semi-empirical method significantly underestimated the dissociation energy of organic mixtures; thus, improvements are required for predictions under environmentally relevant conditions. Organic matter in secondary effluent can be considered to be an organic mixture, so the modified ΔSc – ΔTOC relationship for organic mixtures should be adopted to replace the previously proposed semi-empirical equation for calculating the entropy increase.

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