# **RELEASING RATE OF DISSOLVED ORGANIC MATTER FROM SEDIMENT**

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#### ABSTRACT

The specific releasing rates of organic matter from stationary phase to dissolved organic matter for three sediments, obtained from Keelung River and Cherng-Ching Lake, were determined by using a leaching method during a 126 day course. It is assumed that the releasing rate of dissolved organic matter (DOM) form stationary organic matter is equivalent to the decomposition rate of the stationary organic matter, which obeys first-order kinetic. The average value of specific releasing rate constant (k<sub>f</sub>) of every duplicate sediment samples was found ranging from  $4.40 \times 10^{-4} \text{ yr}^{-1}$  to  $8.11 \times 10^{-4} \text{ yr}^{-1}$ . The narrow range of k<sub>f</sub> value for sediments is within a factor of less than 2. Among those selected properties of organic matter, such as total organic matter content, extractable organic matter content and elemental composition of humic acid, higher (N + O) / C of humic acid seems contributing to higher DOM releasing rate. It is postulated that (N + O) / C of humic acid, which contributes to the hydrophilicity of natural organic matter, may be a possible parameter for predicting k<sub>f</sub> value for other sediments. However, it should be further confirmed with more samples.

#### **INTRODUCTION**

Soils and sediments are major reservoirs of inorganic and organic carbon in the nature. Litter or newly added organic matter is labile and easily degraded. Therefore, it is expected that large amount of CO<sub>2</sub> and dissolved organic matter (DOM) are produced in a short period of time [1]. However, the pool of aged and humified natural organic matter (NOM) has long term environmental effects for its extremely large size and continuous slow conversion to CO<sub>2</sub> and DOM. Since the evolving rate of CO<sub>2</sub>, a green-house gas, from the organic reservoirs to the atmosphere has become an important environmental issue, numerous experiments were conducted to estimate the releasing rate of intermediate organic compounds and the final products, including CO and methane, from the decomposition of litter and plant residues [1-2].

The organic constituents in sediments and soils can be divided into two phases, the stationary phase and the dissolved phase. The DOM in pore fluid or bulk fluid can behave as both a pollutant itself that contributes to the oxygen demand of groundwater or

Attempts have been made to establish quantitative description of NOM decomposition, DOM production and adsorption/desorption on soils. Ligand exchange between carboxyl/hydroxyl

river waters and as a pollutant carrier that facilitates the movement of pollutants. The migration of aldrin, DDT and its daughter compounds is enhanced by dissolved organic carbon, which is simulated with the three-phase model more accurate than with the twophase model [3]. The apparent aqueous solubility of selected PAHs increased when soil was leached with organic matrix solution [4]. Dissolved pentachlorophenol facilitates the release of soil organics and colloids, which enhances transport of contaminants through cosolvancy or colloidal transport [5]. Enhanced dissolution of mercuric sulfide by DOM, especially hydrophobic (humic and fulvic) acids, was found [6]. C / N ratio of soil organic matter (SOM) influences the bioavailability of organic carbon and also is an indicator of the degree of aging for the organic matter. More humified soil shows higher C / N and higher C / H ratio (aromatic fraction) of humic components, which was found among 40 soil samples [7].

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functional group of NOM and iron oxide surfaces dominates NOM adsorption/desorption on solid particle [8]. Since the sorption of hydrophilic DOM on mineral was suppressed by hydrophobic DOM under conditions of limited sorption sites, hydrophilic DOM may be the most mobile organic component in soil solution [9]. The decomposition rate of SOM was usually assumed to be linearly proportional to the total organic matter content, that is, following a first-order kinetics. For example, the decomposition of labelled ryegrass in the field for 10-year incubation followed first-order kinetics [10]. Several studies on the mineralization of carbon addition to soil indicated first-order kinetics, which were reviewed by Huggins et al. [11]. The decomposition rate constant for soil mixed with alfalfa was determined by measuring the decrease of carbon in soil that were kept bare for 15 years after the initial application. The decrease in amounts of carbon showed first-order type decomposition [12]. After an initial rush, the controlling step of the decomposition of resistant NOM to form DOM, which produces more vulnerable organic matter for biological activities, may also follow the first-order kinetics. Without any external source, the only source of DOM is the stationary organic phase in the sediments or soils. It is important to know the releasing rates between the stationary phase and the dissolved phase in soils and sediments in order to properly predict the concentration and the mass flux of DOM through the soil and sediment column. The object of this study is, therefore, to investigate the releasing rate of DOM from stationary organic matter of sediment by leaching method. Moreover, the possible effect of selected properties of organic matter, such as extractable organic matter content and elemental composition of humic acid, on the specific releasing rate constant is discussed.

### MATERIALS AND METHODS

#### **Sample Preparation**

Sediment samples were obtained beside the Dah-Jyr bridge (sediment 1) and the Cherng-Der bridge (sediment 2) over Keelung River in Taipei and from Cherng-ching Lake (sediment 3) in Kaohsiung. Keelung River has a catchment basin of about 500 km<sup>2</sup> and a total length of 86 km. This river receives domestic sewage from the urbanized area. Dah-Jyr bridge is located upper than Cherng-Der bridge along the river. Cherng-Ching Lake is a man-made water reservoir for receiving Kao-Ping river water and responsible for the water supply source for Kaohsiung city.

# **Leaching Experiment**

In order to remove the DOM originally accumulated in the sediments, about 150 grams of wet sample were washed with 200 ml distilled water three times and were filtered through filter membranes with pore



Fig. 1. The leaching apparatus for the sediment sample.

size of 0.45 µm (HV type, Millipore). Figure 1 shows the apparatus of leaching experiment. A filter funnel with a filter membrane of pore size  $0.45 \ \mu m$  (142 mm diameter) was connected to a leachate collecting flask. Water soaked sediment sample (at water holding capacity) with less than 3 mm in thickness was formed on the filter membrane, which was equipped in the filter funnel. The sample on the membrane was incubated under water saturate condition, and was leached with 20 ml milli-Q water every leaching run. It is assumed that the leaching water amount was sufficient to remove most DOM in the sample. The leaching water was recovered as leachate after several minutes. The time intervals between two leaching runs were shorter over early period in order to remove the residue original DOM as soon as possible and then were longer in order to obtain valid leachate sample with total organic carbon concentration higher than that of the instrument detection limit. Leachate was immediately analyzed for dissolved total organic carbon (TOC) content (TOC Analyzer, Model 700, O. I. Corporation). The instrument detection limit for TOC was 10 ng C/L. The conversion factor of organic carbon to organic matter was assumed to be 0.5 [13]. The residual organic matter content of the leached sample was calculated as the difference between the initial and the cumulative leached mass, i. e. the native organic matter depletion dynamics was tracking by measuring the TOC of the leachate. Evolved gasses from the leachate or samples were neglected. The initial organic matter content of soil and sediment was determined by the loss of weight under 550 ignition  $(OM_t)$  [13]. The blank (the same apparatus without sample) showed no significant atmospheric organic

carbon input and no interference from the filter membrane.

## **Sample Characterization**

Sample was subjected to sequential extraction to Table 1. The releasing rate constants and the properties of the investigated sediments.

	Sediment 1	Sediment 2	Sediment 3
$k_{f} (1/yr)^{(a)}$	7.52×10 <sup>-4</sup>	$4.85 \times 10^{-4}$	$7.41 \times 10^{-4}$
	$8.25 \times 10^{-4}$	3.94×10 <sup>-4</sup>	8.61×10 <sup>-4</sup>
Average $k_f (1/yr)$	$7.89 \times 10^{-4}$	$4.40 \times 10^{-4}$	$8.01 \times 10^{-4}$
$OM_t\%^{(b)}$	4.44	7.04	6.51
$OM_{ex} / OM_t\%$	8.80	8.81	29.8
$OM_w / OM_t \%$	6.15	5.24	29.4
Humic acid <sup>(c)</sup>			
H / C	0.12	0.12	0.12
O / C	0.431	0.299	1.39
N / C	0.175	0.067	0.090
(N + O) / C	0.506	0.367	1.48

Note: <sup>(a)</sup> The row shows the duplicate values.

<sup>(b)</sup> The ratio is on the basis of dry weight.

 $^{(c)}$ H / C, C / O and C / N are wt/wt ratio.

obtain the various fraction of organic matter [14]. First, sample was extracted by a Soxhlet extractor with 300 mL n-hexane for 48 hr. The extract was then subjected to filtering, concentrating, drying and weighing. The above procedure was repeated with 300 mL chloroform. The fractions extracted in this procedure represented the fraction of less hydrophilic organic matter. Secondly, sample was extracted with 100 mL 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7 (aq)</sub> in a shaker for 24 hr. The resulted extract was centrifuged for 5 minutes (2000 g) and filtered with a 0.45 µm membrane. This procedure was repeated with 100 mL 0.5 M NaOH(aq) and then with 100 mL D. I. water. The fractions extracted with aqueous solution and water were combined and defined as OM<sub>w</sub>, which represented the fraction of more hydrophilic organic matter. Total extractable organic matter content (OMex) is referred to the summation of the organic matter extracted with organic solvent, with aqueous solution and with water [14]. The nitrogen content for sediment samples was determined with the Macro-Kjeldahl method. Humic acid (HA) was extracted from sediment with alkaline [15] and then was freeze-dried prior to being used. The major element composition (C, H, N and O) of HA was determined by element analyzer (Perkin-Elmer 240 C).

#### **Estimation of the Specific Transformation Rate Constant**

The decay rate of stationary organic matter is assumed to be proportional to its content of sediment. The releasing rate of DOM form stationary organic matter is assumed to be equivalent to the decomposition rate of the stationary organic matter, and can be expressed as equation (1).

$$\frac{dM_{d}}{dt} = \frac{dM_{s}}{dt} = -k_{f}M_{s}$$
(1)

where  $\frac{dM_d}{dt}$  is the DOM releasing rate,  $M_s$  is the

stationary organic content of sediment, t is the time variable, and  $k_f$  value is the specific transformation rate constant. The TOC of leachate was measured and was used to calculate the residual  $M_s$  of stationary phase. The slope of the plot of  $\ln M_s$  vs. time during the longer term is used to calculate  $k_f$  value because the residual original DOM, which might not be flushed away by the washing treatment, affects the curve during the early leaching period.

### RESULTS

#### **Properties of Sediment**

Table 1 shows the specific releasing rate constants and the properties of three investigated samples. The weight percentage of the total organic content for sediments 2 ( $OM_t$  %) is slightly higher than that for the others. However, both the ratio  $OM_{ex}$ /  $OM_t$  and  $OM_w$ /  $OM_t$  are diversified between three sediments. It implies that native organic matters have different origins. It is postulated that the extractable organic fraction of sediment 1 and sediment 2 may be more drastically flushing away by the running river. Therefore, the ratio of extractable fraction to the total organic mater is lower for both of sediment 1 and sediment 2 than that for sediment 3.

The lower H / C ratio of humic acid is attributed to the generation of methane and water during methanogenesis and dehydration involved in humification process [7]. However, the H/C ratio, indicating the aromaticity of humic acid, shows no difference between the three sediments (Table 1). It seems that the humic acids of the three sediments are in the similar stage of humification and H/C ratio of them may be a little significant factor in this study. On the other hand, the higher (O + N) / C ratio of himic acid indicates that humic acid is richer in hydrophilic functional groups like  $-CO_2H$ , - COH and  $-NO_2$ , which implies



Fig. 2. The ratio of leachate product to the organic matter of stationary phase.

a higher solubility of humic acid to water. (O + N) / C ratio of himic acid for Sediment 3 is higher than that for the other two sediments 2.9 to 4 times.

#### **Native Organic Matter Depletion Dynamics**

The accumulative leachate production ratio for the three sediments, obtained with the organic content of leachate divided by total organic content of each sediment, increases rapidly during the first ten days (Fig. 2). The initial stage for native organic matter depletion dynamics is attributed to the residual DOM remaining in samples after prewashing. There is no lag during the leaching course implies that native organic matter continues transforming into DOM. The following constant production rate reached steady rate, which obeyed first-order kinetic, and was adopted for estimating the specific releasing rate constant ( $k_f$ ).

#### The Specific Releasing Rate Constant (kr)

The estimated  $k_f$  value is shown in Table 1. The result for each sediment shows good duplicate. The average  $k_f$  value was found  $7.89 \times 10^{-4}$  yr<sup>-1</sup>,  $4.40 \times 10^{-4}$  yr<sup>-1</sup> and  $8.01 \times 10^{-4}$  yr<sup>-1</sup> for sediment 1, 2 and 3, respectively. The discrepancy of the  $k_f$  values between the three sediments was only up to a factor of 1.8.

#### DISCUSSION

The release of DOM is resulted from many chemical and biological processes supposedly include-

ing dissociation, fragmentation, depolymerization and solubilization. Evidences showed that the ratio of carbon fraction mineralized as  $CO_2$  relative to the amount of leached soluble organic carbon was ranging between 2.6 and 8, which depended on the conditions of flooding and freeze-thaw to the soils [16]. Compared with the residual SOM, the amount of gaseous products and DOM is small, which should have insignificant effect on the estimation for the residual SOM within the experimental period. At least, it has no striking effect on the  $k_f$  value estimates based on short-term experiments (Fig. 2).

Among those properties for the investigated sediments, higher (N + O) / C of humic acid seems contributing to higher DOM releasing rate (Table 1). However, it should be further confirmed with more samples. In fact, the range of  $k_f$  value for the three sediments is surprisingly narrow, that is, within a factor of less than 2. In other words, it is possible to assign a fixed value to an estimate of  $k_f$  value for sediment with a bias even less than a factor of 2 without any knowledge of the properties of these natural solids.

For the sediments, the total NOM  $(OM_t \%)$  is the source for DOM, but its relative amount is less relevant to k<sub>f</sub> value than the extractable component  $(OM_{ex}/OM_t \%)$ . The contribution to  $k_f$  is more from the extractable component than from the total OM, which implies that extractability of OM could represent the potential of OM mobility. Among three extractable fractions, the one extracted with basic aqueous solution (OM<sub>w</sub>) especially shows close relationship with k<sub>f</sub>. It is suggested that OM<sub>w</sub> rather than the fractions extracted with organic solvents corresponds the most important part of the OM<sub>ex</sub>. It could be further postulated that the DOM is generated from the hydrophilic fraction of total OM rather than the hydrophobic fraction. Humic acid is also a part of the extractable component. It is expected that the characteristics of HA will have some relationships with the value of k<sub>f</sub>. From the viewpoint of hydrophilic functional groups as a whole, the element composition of oxygen and nitrogen should be considered together. There is no definite correlation could be found between OM humification situation and its mobility, which reveals again that the hydrophilic fraction corresponds the OM mobility as aforementioned.

Some related first-order decomposition rate constants of SOM found by other researchers are listed in Table 2. The results of several simulating events had been investigated. The reported decomposition rate constants in soils are generally larger than that of this study by a factor of about three orders of magnitude and that in oceanic sediments are close to that of this study. The differences between literature and this study are supposedly attributed to different soil history, treatment (aerobic or anaerobic, flooded or not) and plant residual addition. Moreover, oceanic sediments [17] are undisturbed and its condition is much similar to that of this study, which shows comparable decomposition rate to that of this study. It is also postulated that the difference of decomposition rate between soil and sediment may be

attributed to the texture.

Through the releasing rates of DOM from sediments obtained from this study, we may better estimate the source terms in the mass transport models concerning the migration of DOMs in the sediment bed. Moreover, it could be further utilized to estimate Table 2. The first-order decomposition rate constants of SOM reported by other researchers under various conditions.

Rate constant (1/yr)	Conditions	Reference
$1.96 \times 10^{-2}$ to $8.67 \times 10^{-2}$ for soluble OC <sup>(1)</sup>	Normal, flooding or freeze-thaw treatment	[16]
$6.08 \times 10^{-3}$ to $1.37 \times 10^{-1}$ for soluble OC <sup>(1)</sup>	Nonflooding or flooded treatment	[18]
$1.83 \times 10^{-2}$ to $1.42 \times 10^{-1}$ for total OC <sup>(2)</sup>	Soil was added with alfalfa initially and left bare for 15 yr	[12]
$3.2 \times 10^{-6}$ to $2.75 \times 10^{-5}$ for total OC in		[17]
oceanic sediments <sup>(2)</sup>		

Note: <sup>(1)</sup>The data were derived with the results of cumulative carbon during a short-term period. The assumption for the ratio of total organic carbon content to soil is 0.02 wt/wt.

<sup>(2)</sup>Cited from the references.

the sediment oxygen demand loaded to the overlaying water body. Future research is needed to expand the investigated sample population with more various types of sediments.

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# 底泥中溶解性有機質的釋出速率

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關鍵詞:底泥、溶解性有機質、淋洗、腐植酸、釋出速率

# 摘 要

本研究利用淋洗方法探討基隆河與澄清湖的底泥中,有機質由固定相轉換成溶解性有機質的比釋出速率,實驗期程為 126 天。假設溶解性有機質自固定相有機質中的釋出速率等於固定相有機質的分解速率,並屬一階動力。三種底泥二重複批次的平均比釋出速率常數值 $(k_f)$ 在 4.40 × 10<sup>-4</sup> yr<sup>-1</sup> 至 8.11 × 10<sup>-4</sup> yr<sup>-1</sup>之間,其差異範圍相當窄,僅在 2 倍之內。在有機質的特性中,諸如總有機質含量、可萃取性有機質含量以及腐植酸的元素分析等,腐植酸的(N + O) / C 似乎對  $k_f$  值有貢獻,推測可能是由 N 及 O 構成的天然有機質的親水性 官能基來源,此參數較有可能用以預測其他底泥樣品的溶解性有機質的釋出速率,但需以更多的底泥樣品實驗作更進一步的確認。