



Contents lists available at ScienceDirect

## Marine Pollution Bulletin

journal homepage: [www.elsevier.com/locate/marpolbul](http://www.elsevier.com/locate/marpolbul)

## Characterization and source identification of organic matter in view of land uses and heavy rainfall in the Lake Shihwa, Korea

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## ARTICLE INFO

## Keywords:

Lake Shihwa  
Organic matter  
Stable isotope ratio  
Synchronous fluorescence spectra  
Multiple sources

## ABSTRACT

The characteristics and sources of organic matter in water of the Lake Shihwa, which receives inputs from rural, urban, and industrial areas, were evaluated by examining the biodegradable organic carbon concentration, fluorescence spectra, and carbon and nitrogen isotope ratios, especially during rainy season and dry season. The organic matter transported from rural areas was of refractory nature, while that of industrial origin decomposed rapidly. As compared to the dry season, the organic matter in the rainy season was characterized by a reduced labile fraction. During the dry season, the autochthonous organic matter dominated in the lake, however, the contributions of allochthonous organic sources by industrial and rural areas significantly increased at rainy season. This investigation revealed that the transport of organic matter of anthropogenic origin to the Lake Shihwa was mainly influenced by heavy rainfall. Moreover, each anthropogenic source could differently influence the occurrence of organic matter in water of the Lake Shihwa.

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### 1. Introduction

Incremental increase of anthropogenic activities in coastal areas, such as industrialization, urbanization, and agriculture practices, have resulted in enhanced input of nutrient and organic matter into aquatic systems (Boyes and Elliott, 2006; Carpenter et al., 1998), which in turn reduces water quality and ecosystem health (Smith and Schindler, 2009). The dispersal of anthropogenic inputs depends on the nature and origin of organic sources, and their preservation potential during transport, mineralization, and degradation (Gao et al., 2008; Owen and Lee, 2004). Anthropogenic inputs influence the quality and quantity of organic matter, and may also alter the biogeochemical cycling of organic matter and nutrients; moreover they also impact organic matter decomposition, which is important for recycling of nutrients and chemical elements (Cebrian and Lartigue, 2004; Takeda and Abe, 2001). Therefore, understanding the nature and the origin of organic matter could provide valuable information regarding the anthropogenic pressures in an aquatic ecosystem.

Among the various techniques available, the fluorescence techniques have been popularly used as predictors for the characterization of organic matter as they are rapid, non-destructive, and

sensitive (Hur et al., 2008; Reynolds, 2003; Reynolds and Ahmad, 1997). As compared with the conventional excitation or emission modes, the synchronous fluorescence spectra specially offer additional information regarding the structural signatures of organic matter (Pullin and Cabaniss, 1995; Senesi, 1990). On the other hand, stable isotope techniques are useful for distinguishing the origin of organic matter by using the characteristics that has distinct value between sources (Cloern et al., 2002; Grey et al., 2001). Terrestrial organic matter generally shows a depleted  $\delta^{13}\text{C}$  value as compared to organic matter of marine origin (Fry and Sherr, 1984). In addition, in several aquatic systems, high  $\delta^{15}\text{N}$  value of DIN due to anthropogenic nitrogen inputs from sewage have been reported (Savage and Elmgren, 2004; Schubert et al., 2013). Yet other studies reported that the low  $\delta^{15}\text{N}$  value of seston derived from wastes can influence on the interpretation of food webs (DeBruyn and Rasmussen, 2002; Van Dover et al., 1992). Certain researches used a combined approach, comprising isotope and fluorescence technique, in characterization of organic matter and identification of their sources (Nguyen and Hur, 2011; Retamal et al., 2007).

Artificial Lake Shihwa (surface area 43.8 km<sup>2</sup>, drainage basin 476.5 km<sup>2</sup>), an salt water lake of South Korea created in 1994, is typically under enormous anthropogenic pressure due to cumulative inputs from various sources (Hong et al., 2010; Li et al., 2004; Moon et al., 2012; Ra et al., 2011). Since the construction of sea

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dikes along this artificial lake, there has been a continuous inflow of organic matter from various sources (including inflow from rural, urban, and industrial regions), which has resulted in marked deterioration of its water quality. In order to restore the water quality of the lake, a total pollutant load management system (TPLMS) was launched in July 2013. Source identification could contribute to a better understanding regarding the increased anthropogenic inputs from the land areas to coastal areas. Thus, evaluation of the major sources contributing towards the organic matter in the Lake Shihwa, was undertaken in this investigation.

The present study was conducted to: (i) characterize dissolved and particulate organic matter in water of the Lake Shihwa, and its surroundings creeks (rural, urban, and industrial areas), during the dry and rainy season, (ii) determine the sources of organic matter (autochthonous vs. allochthonous) and their contributions, using carbon and nitrogen isotopic compositions, and, (iii) identify the factors controlling the composition and sources of organic matter in the event of heavy rain.

## 2. Materials and methods

### 2.1. Sampling and in situ measurement

Sample collection was conducted by two sampling campaign carried out during 14–15 May (dry season), and, 5–7 September (rainy season) 2012, based on the amount of precipitation (Fig. S1 of Supplemental Materials (S)). Surface water were collected from the Lake Shihwa (S1–S9) and its surrounding creeks targeting potential sources of organic matter associated with land uses and activities (rural, urban, and industrial) (Fig. 1). Measurement of water temperature and salinity was conducted in site, using a calibrated multi-probe (YSI-650 MDS, YSI Incorporated, OH).

### 2.2. Analyses of total organic carbon and biodegradable organic carbon

The water sample was filtered using a pre-combusted (4 h at 450 °C) Whatman GF/F filter in order to separate dissolved and particulate fractions. The concentrations of dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) were measured with a TOC analyzer (TOC-V<sub>CPH</sub>, Shimadzu, Kyoto, Japan). The filter samples for determination of the particulate organic carbon (POC) were

acidified with 12 N hydrochloric acid fumes in order to remove inorganic carbon. The concentrations of POC and PN were determined using an elemental analyzer (Euro EA3028, EuroVector, Milan, Italy). The total organic carbon (TOC) was calculated as the sum of DOC and POC.

Determination of biodegradable total organic carbon (BTOC) was carried out using a method of Servais et al. (1995) with slight modifications (Hur, 2011; Nguyen and Hur, 2011; Park et al., 2010). Large zooplanktons were removed from bottles before incubation, using 100 µm mesh net, in order to avoid interference from grazing. Here, the samples were dark incubated at 20 °C for 4 weeks, with intermittent shaking, to prevent oxygen limitation. The concentrations of BTOC were calculated by subtracting the measured TOC of the incubated sample, from the initial TOC.

### 2.3. Characterization of dissolved organic matter

Synchronous fluorescence spectra of the DOM were estimated using a luminescence spectrometer (LS-55, Perkin–Elmer, Liantrisant, UK) with a constant offset ( $\Delta\lambda = 30$  nm), based on the protocol outlined by Hur et al. (2008, 2011). In this study, four regions were allocated to the integrated areas of the fluorescence intensities: protein-like fluorescence (PLF) at 250–300 nm, fulvic-like fluorescence (FLF) at 300–380 nm, humic-like fluorescence (HLF) at 380–420 nm, and terrestrial humic-like fluorescence (THLF) at 420–600 nm (Hur et al., 2011).

### 2.4. Analysis of chlorophyll-*a*

Pigments were extracted in acetone (90%) for 24 h in the dark at 4 °C; chlorophyll-*a* (Chl *a*) concentrations were determined spectrophotometrically (Jeffrey and Humphrey, 1975).

### 2.5. Analyses of carbon and nitrogen stable isotope ratios

The stable isotopic compositions of POC and PN were determined using Isotope Ratio Mass Spectrometer (Isoprime, GV Instruments, Manchester, UK). The analytical precisions (SD) were 0.05‰ and 0.1‰ for carbon and nitrogen, respectively; these were estimated by running standards analyzed along with the samples (IAEA standards CH6 and N1). Stable isotope ratios were calculated using the standard  $\delta$  notation:



Fig. 1. Map showing the Lake Shihwa and the inflow sources that discharge into the lake along with the sampling sites (S: Lake Shihwa; W and R: reed wetland and rural area; I: industrial area; and U: urban area).

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