



## Spatial distributions of and diurnal variations in low molecular weight carbonyl compounds in coastal seawater, and the controlling factors



Kazuhiko Takeda<sup>a,\*</sup>, Shinya Katoh<sup>a</sup>, Yumi Mitsui<sup>a</sup>, Shinichi Nakano<sup>a</sup>,  
Nobutake Nakatani<sup>a,b</sup>, Hiroshi Sakugawa<sup>a</sup>

<sup>a</sup> Graduate School of Biosphere Science, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8521, Japan

<sup>b</sup> Department of Environmental and Symbiotic Sciences, Rakuno Gakuen University, 582 Bunkyo-dai-Midorimachi, Ebetsu, Hokkaido 069-8501, Japan

### HIGHLIGHTS

- Low molecular weight (LMW) carbonyl compounds in coastal seawater were determined.
- Photochemical productions of LMW carbonyl compounds in seawater were observed.
- LMW carbonyl compounds were largely consumed biologically.
- Photochemical degradation was relatively insignificant in the study area.

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### ABSTRACT

We studied the spatial distributions of and the diurnal variations in four low molecular weight (LMW) carbonyl compounds, formaldehyde, acetaldehyde, propionaldehyde, and glyoxal, in coastal seawater. The samples were taken from the coastal areas of Hiroshima Bay, the Iyo Nada, and the Bungo Channel, western Japan. The formaldehyde, acetaldehyde, and glyoxal concentrations were higher in the northern part of Hiroshima Bay than at offshore sampling points in the Iyo Nada and the Bungo Channel. These three compounds were found at much higher concentrations in the surface water than in deeper water layers in Hiroshima Bay. It is noteworthy that propionaldehyde was not detected in any of the seawater samples, the concentrations present being lower than the detection limit (1 nanomole per liter (nM)) of the high performance liquid chromatography (HPLC) system we used. Photochemical and biological experiments were performed in the laboratory to help understand the characteristic distributions and fates of the LMW carbonyl compounds. The primary process controlling their fate in the coastal environment appears to be their biological consumption. The direct photo degradation of propionaldehyde, initiated by ultraviolet (UV) absorption, was observed, although formaldehyde and acetaldehyde were not degraded by UV irradiation. Our results suggest that the degradation of the LMW carbonyl compounds by photochemically formed hydroxyl radicals is relatively insignificant in the study area. Atmospheric deposition is a possible source of soluble carbonyl compounds in coastal surface seawater, but it may not influence the carbonyl concentrations in offshore waters.

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### 1. Introduction

A large fraction of the dissolved organic matter (DOM) in the coastal environment pool is chromophoric dissolved organic matter (CDOM), which is one of the major light absorbing constituents of natural waters. Photochemical reactions of CDOM in aquatic environments are thought to play significant roles in the global carbon cycle, which includes the decomposition and remineralization of DOM. CDOM is photochemically broken down to generate a variety of products that influence various biogeochemical cycles in the aquatic environment and the atmosphere.

It has been reported that these photochemical reactions can lead to the formation of ammonium, amino acids (Aarnos et al., 2012; Bushaw et al., 1996), carbonyl sulfide (Andreae and Ferek, 1992), carbon monoxide (Ohta et al., 1999; Xie and Zafriou, 2009), and carbon dioxide (Johannessen and Miller, 2001; Wang et al., 2009; White et al., 2008). Low molecular weight (LMW) carbonyl compounds are also important products of the photochemical degradation of CDOM. (de Bruyn et al., 2011; Kieber et al., 1990; Zhou and Mopper, 1997).

In the troposphere, LMW carbonyl compounds are important trace gases produced by oxidation process of anthropogenic and biogenic volatile organic compounds (Carlier et al., 1986). They are also emitted directly by the fossil fuels and biomass combustion. Due to their high solubility, LMW carbonyl compounds in the atmosphere are easily

\* Corresponding author. Tel.: +81 82 424 6506; fax: +81 82 424 0758.  
E-mail address: [takedaq@hiroshima-u.ac.jp](mailto:takedaq@hiroshima-u.ac.jp) (K. Takeda).

dissolved in rain, cloud water and dew, and they deposit directly on the ground and the sea surface as wet deposition. Their concentrations are higher in rain than in surface water by a couple of orders of magnitude, or more. Therefore, wet deposition of LMW carbonyl compounds is one of the important sources for surface water. LMW carbonyl compounds are exchanged directly between the surface water phase and the atmosphere (Kieber et al., 1990; Zhou and Mopper, 1990). Many attempts have been made to determine the apparent partition coefficients for LMW carbonyl compounds so that the air–sea exchange and their behavior in biogeochemical cycles can be modeled (Allou et al., 2011; Seyfioglu and Odabasi, 2006, 2007; Zhou and Mopper, 1990). The LMW carbonyl compounds in surface water are biologically labile, and they are consumed quickly by microorganisms (de Bruyn et al., 2013; Kieber et al., 1989). On the other hand, the production of LMW carbonyl compounds by biota has been reported (Dixon et al., 2013).

Hiroshima Bay, in the western part of the Seto Inland Sea, is typical of the Japanese enclosed coastal sea areas. The Ohta River, which is the biggest river flowing into the Hiroshima Bay, flows through Hiroshima City into the northern part of Hiroshima Bay. Hiroshima City is the capital of Hiroshima Prefecture with population of around 1.2 million people. The Iyo Nada and the Bungo Channel are the main channels connecting Hiroshima Bay with the Pacific Ocean. The river supplies riverine DOM, which is one of the important constituent of CDOM in the coastal environment (Kowalczyk et al., 2003; Mannino and Harvey, 2000; Nakaguchi et al., 2005; Vodacek et al., 1997). In this river–inshore–coastal–open ocean area, a CDOM concentration gradient could play a significant role in the photochemical activity and the photochemical production of LMW carbonyl compounds. Although the specific processes involving LMW carbonyl compounds such as photochemical production/degradation, and biological fates and air–sea exchange are relatively well known from previous studies, information about their distribution in enclosed coastal sea areas with large river input is limited.

In this paper, we present a study of the vertical and horizontal distributions of the LMW carbonyl compounds formaldehyde, acetaldehyde, propionaldehyde, and glyoxal in coastal seawater. The spatial distribution of LMW carbonyl compounds was determined in the coastal area from the Ohta River to the Pacific Ocean. Their diurnal changes in seawater were also determined. The LMW carbonyl compounds were analyzed using a high performance liquid chromatograph (HPLC) method developed previously, which has enough sensitivity to determine LMW carbonyl compounds at low nanomolar range (Takeda et al., 2006). Photochemical experiments and biological degradation tests were performed in the laboratory in order to explain their role in characteristic distributions and fates of the LMW carbonyl compounds. The results are discussed in relation to factors determining concentration levels of the LMW carbonyl compounds.

## 2. Experimental

### 2.1. Sampling sites

Seawater samples were collected during two cruises to the western Seto Inland Sea on 9–13 May, 2005 and 30 September–1 October 2005 by R/V Toyoshio Maru, which belongs to Hiroshima University. The sampling sites are shown in Fig. 1. Hiroshima Bay, which is a typical part of the Japanese enclosed coastal sea, is about 30 km from east to west and 50 km from north to south, with a total area of about 1000 km<sup>2</sup> and an average depth of 34 m. The Iyo Nada and the Bungo Channel are the main channels connecting Hiroshima Bay with the Pacific Ocean. In the cruise of May 2005, seawater samples were collected at 5 stations in Hiroshima Bay (ST-0: 34 20.5N, 132 25.0E, ST-1: 34 18.0N, 132 23.0E, ST-2: 34 11.0N, 132 21.0E, ST-3: 34 05.0N, 132 21.0E, ST-4: 33 59.0N, 132 23.0E) on 11 May 2005, and 3 stations in Iyo Nada and the Bungo Channel (ST-11: 33 42.0N, 132 15.0E, ST-12: 33 30 .0N, 132 00.0E, ST-21: 33 20.0N, 132 00.0E) on 12 May 2005. In the

cruise of September 2005, 5 stations in Hiroshima Bay (ST-0–ST-4) were sampled on 30 September 2005. On the cruise of May 2005, the vessel stayed at anchor for 48 h in ST-3 of Hiroshima Bay, and surface seawater was collected at 2-h or 3-h interval. For the photochemical experiment and biodegradation experiment, surface seawater of Hiroshima Bay was taken from the coast of Kurahashi Island located in the center of Hiroshima Bay (9 km east from ST-3) on 1 December 2005. Surface seawater samples were collected using a stainless steel kettle connected to a plastic rope. Seawater samples from deeper than 2 m were collected using Niskin sampling bottles. Sampling depth was estimated by length of wire of the Niskin sampling bottle under the sea.

River water samples were collected from the Ohta River. River water samples were collected at 2 sites; one was located in a suburban area of Hiroshima City about 16 km upper reaches from the river mouth, and the other was located in a rural area about 70 km upper reaches from the river mouth and about 30 km north-west far from the center of the Hiroshima City in a straight line. Samples were taken on 29 November 2005 using a stainless steel kettle connected to a plastic rope.

### 2.2. Reagents

Acetonitrile, methanol, and tetrahydrofuran, used in the HPLC mobile phases, were of HPLC grade. Deionized water was obtained from a Milli-Q Plus water purification system (Millipore, Tokyo, Japan) that was connected to a system containing Amberlite EG-5 ion exchange resin (Organo, Tokyo, Japan). Commercial distilled water of HPLC grade, purchased from Sigma-Aldrich Japan Co. (Tokyo, Japan), was used to prepare the reagents. 2,4-Dinitrophenylhydrazine (DNPH), purchased from Sigma-Aldrich Japan, was recrystallized twice from acetonitrile. The DNPH derivatization reagent was prepared and purified following a previous method (Takeda et al., 2006). A stock formaldehyde solution (10 millimole per liter (mM)) was made by diluting paraformaldehyde in commercial HPLC grade distilled water from a freshly opened bottle. Stock solutions of acetaldehyde, propionaldehyde, and glyoxal (10 mM) were also prepared in commercial HPLC grade distilled water. Serial standard solutions were prepared from 10 mM stock solutions in commercial HPLC-grade distilled water just prior to use.

### 2.3. Determination of LMW carbonyl compounds

The LMW carbonyl compounds were determined using a rapid and highly sensitive HPLC method based on DNPH derivatization with a simplified online preconcentration technique (Takeda et al., 2006). The expected carbonyl concentrations in seawater are in the low nanomolar range, and the method coupled with the online preconcentration technique had enough sensitivity for LMW carbonyl compounds.

To avoid the contamination of LMW carbonyl compounds, an unfiltered aliquot of each water sample was immediately, at the sampling site, transferred into a glass vial with the DNPH derivatization reagent. A 0.4 mL aliquot of the DNPH derivatization reagent was added to each 10 mL sample aliquot in an amber glass vial, and was capped tightly. The samples with the DNPH derivatization reagent were allowed to stand for at least 1 h, and a maximum of 8 h, at room temperature to form DNPH derivatives before being analyzed by HPLC (Mopper and Stahovec, 1986; Takeda et al., 2006).

A C-18 reverse phase column (RP-18GP; 5 µm particle size, 4.6 mm i.d., 150 mm long; Kanto Kagaku, Tokyo, Japan) was used for separation. A short C-18 reverse phase preconcentration column (RP-18GP; 5 µm particle size, 4.6 mm i.d., 5 mm long; Kanto Kagaku) was installed at the sample injection valve instead of a sample loop. A 2.5 mL aliquot of a derivatized sample solution was directly injected into the preconcentration column through the sample injection valve with a 2.5 mL gas-tight syringe, then 2.5 mL of 15% acetonitrile in water was passed through the preconcentration column to remove the excess unreacted DNPH. The seawater samples were analyzed by HPLC on the research vessel. The detection limits, estimated as three times the

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