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Mixing behavior and bioavailability of dissolved organic matter in two contrasting subterranean estuaries as revealed by fluorescence spectroscopy and parallel factor analysis

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ABSTRACT

Groundwater discharge represents a potentially important source of dissolved organic matter (DOM) for the coastal ocean, but the mixing behavior and bioavailability of DOM in subterranean estuaries are poorly known. This study examined the concentration, chemical composition and bioavailability of DOM in two subterranean estuaries of southwest Taiwan with contrasting pollution degrees, using dissolved organic carbon (DOC) and excitation emission matrix fluorescence spectroscopy-parallel factor analysis. The DOC and fluorescent components were non-conservative and very dynamic in both subterranean estuaries. In the less-polluted Longquanwan (LQW) subterranean estuary, the levels of DOC and fluorescence components were generally low, and the humic-like fluorescent components received significant additions during mixing between freshwater and seawater. In the highly-polluted Sizihwan (SZW) subterranean estuary, the DOC and fluorescence intensities were high in the freshwater end but were subject to active additions and removals during estuarine mixing. The humification index (HIX) and the autochthonous index (BIX) were 1.0–13.4 and 0.73–1.01 for all groundwater samples. The HIX were elevated in the low-to-mid salinity zone of the LQW subterranean estuary in March and increased with salinity in the SZW subterranean estuary. The BIX decreased with salinity in both subterranean estuaries. These results suggested that subterranean estuaries are important zones where both the level and the chemical composition of groundwater DOM change notably. In addition, the DOC, fluorescent intensities, HIX and BIX in groundwater showed limited changes in microbial incubation experiments (≤20%) in 28 days, which suggested low bioavailability of groundwater DOM.

1. Introduction

Dissolved organic matter (DOM) plays critical roles in the biogeochemical cycles of nutrients, trace gases and toxic metals in aquatic environments (Benner, 2003). The chromophoric DOM (CDOM) is an important component in determining the aquatic optical properties (Coble, 2007). Therefore, it is crucial to study the source, chemical characteristics and transformation pathways of DOM in aquatic environments such as the coastal ocean. In addition to the well-known sources of coastal DOM such as river discharge and autochthonous production, groundwater discharge is a potentially important but usually overlooked source of DOM.

Many studies demonstrate the importance of groundwater discharge in delivering freshwater and nutrients into the coastal ocean (Moore, 1996, 1999; Zhang and Satake, 2003; Burnett et al., 2003, 2006; Moore et al., 2008; Peng et al., 2008). Nonetheless, much fewer studies focus on the groundwater discharge of DOM, limiting the assessment about the effects of groundwater DOM on the coastal ocean biogeochemistry and ecosystems. In particular, in the subterranean estuary where the fresh groundwater mixes with the intruding seawater, the water residence time is long and there may be active microbial transformations and strong solid–liquid partitions of organic matter (Moore, 1999). A few studies suggest

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that the estuarine behavior of DOM is affected by active addition and removal processes (Santos et al., 2008, 2009; Kim et al., 2012, 2013), but our knowledge about the dynamics of DOM in subterranean estuaries is still rather limited.

Fluorescence spectroscopy provides many valuable indicators for the level and chemical composition of DOM, and has been popularly used in a rapidly growing number of studies on DOM (and CDOM) in rivers, lakes and oceans (e.g., Stedmon and Markager, 2005; Huguet et al., 2009; Kowalczuk et al., 2009; Guo et al., 2011; Osburn et al., 2012; Yang et al., 2013a). However, only recently have a few studies applied fluorescence spectroscopy to study DOM dynamics in subterranean estuaries, and fluorescent DOM may show contrasting behaviors in different study areas (Kim et al., 2012, 2013). Clearly, more studies are needed to explore the mixing behavior of DOM and the associated biogeochemical processes in subterranean estuaries. In particular, little is known concerning the changes in the DOM quality in subterranean estuaries, which can be studied using the compositional proxies based on fluorescence spectroscopy, such as the humification index (HIX) and the autochthonous index (BIX) (Huguet et al., 2009; Yang et al., 2012). In addition, the bioavailability of groundwater DOM is very important in affecting its biogeochemical roles in the coastal ocean, which is also largely unknown. Therefore, this study aimed to examine the mixing behavior and bioavailability of DOM in two contrasting subterranean estuaries, using dissolved organic carbon (DOC) and fluorescence excitation emission matrix-parallel factor analysis (EEM-PARAFAC).

2. Materials and methods

Taiwan Island is a subtropical island to the west of the Pacific Ocean. The mean annual rainfall is as high as ~2500 mm, with ~68% being concentrated during May–October which results in contrasting wet and dry seasons. The average population density is up to 639 persons km^{-2} and the fluvial discharge of terrestrial materials is highly disturbed in the western part of the island (e.g., Yang et al., 2013a). Two small contrasting subterranean estuaries below sandy beaches in Kaohsiung City were investigated in this study. One is located in the Longquanwan Bay (the LQW subterranean estuary) where the groundwater originates from the penetrating water in the adjacent Shoushan mountainous area and is relatively intact, although there may be limited pollution from some swimmers there. The other is located in the Sizihwan Bay (the SZW subterranean estuary, highly polluted) where the sewage from the adjacent National Yat-sen University flows over the beach into the sea and penetrates into the subterranean zone. The groundwater in both subterranean estuaries generally has higher nutrient levels than the overlying seawater (Chen et al., 2005).

Groundwater samples were collected from the LQW subterranean estuary on 27 March and 20 June 2013, and from the SZW subterranean estuary on 29 March and 21 June 2013 (Fig. 1). A wide range of salinity was covered, to examine the changes in the level and character of DOM during the mixing of freshwater and seawater. Groundwater was sampled with a 50-cm steel tube, one end of which was connected with a glass syringe through Teflon pipes and a stainless steel triple valve. The groundwater sampling depth was 50 cm, except for six sites in the LQW subterranean estuary in March when the beach depth was <50 cm and groundwater was sampled from the bottom of the beach (at 17–42 cm). The sampler was rinsed with several liters of Milli-Q water in the laboratory and with each sample three times in the field. Samples were also collected from the adjacent surface seawater in both bays, using pre-combusted (500 °C, 4 h) glass bottles. All samples were either filtered in the field or transferred into pre-combusted glass bottles, stored on ice and in the dark and filtered in the laboratory

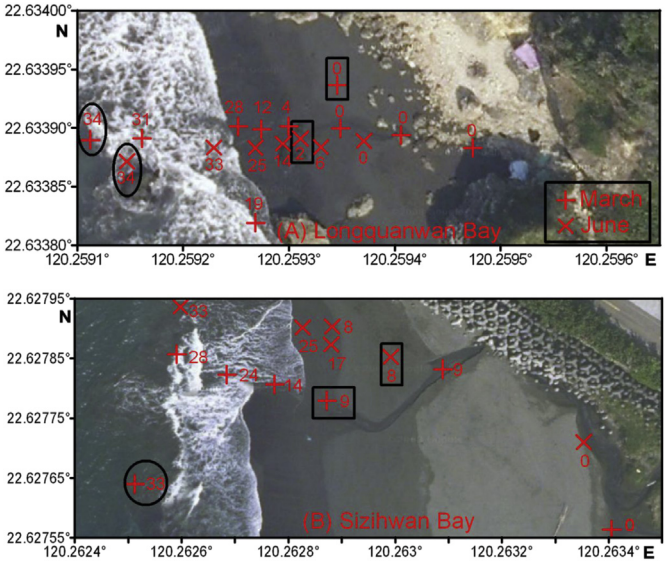

Fig. 1. Spatial distribution of salinity in the subterranean estuaries of LQW and SZW Bays, with groundwater samples for incubation in rectangular borders and surface seawater samples in circled borders.

on the same day. The samples were filtered through pre-combusted 0.7 μm GF/F filters and the filtrates stored in the cold (4 °C) and dark for fluorescence measurements within 1–2 days. The filtrates had $HgCl_2$ added and were stored in the cold and dark before the measurement of DOC concentration, for quantifying the DOM level. Salinity was measured with a handheld YSI EC300 Salinity Meter, while temperature and dissolved oxygen (DO) content were measured using a Hach HQ30d Flexi Portable DO Meter in the field.

Groundwater for microbial incubation was sampled from the inter-tidal zone of both subterranean estuaries. The adjacent surface seawater of the LQW Bay was also sampled for incubation. In March, water samples were initially filtered through pre-combusted 0.3 μm GF-75 filters to remove the majority of microbial biomass. The filtrate had microbial inocula collected at the same station added at a volume/volume ratio of 9/1. Microbial inocula were prepared by filtering the original water samples through pre-combusted 2.7 μm GF/D filters (Fellman et al., 2010). At the start of the experiment and after incubation for 28 days at 25 °C in the dark, the solution was re-filtered for DOC and fluorescence measurements. In June, water samples were filtered through pre-combusted 0.7 μm GF/F filters and were incubated for 28 days. The GF/F filtrates contained the majority of bacteria, and further addition of microbial inocula was not needed. The incubation methods in March and in June were slightly different, to make the results more reliable (i.e., independent of methodology) and more comparable with previous studies that typically used only one of the different incubation methods (e.g., Fellman et al., 2010; Vonk et al., 2013). All incubations were carried out in four duplicates and the mean variation coefficients were 11% for DOC and 2.7% for fluorescence intensities.

Fluorescence EEM spectra were measured using a Cary Eclipse fluorescence spectrophotometer by scanning emission spectra from 280 to 600 nm (every 2 nm) at excitation of 240–400 nm (every 5 nm). The scan rate was 1200 nm min^{-1} under the ratio mode. Samples with high absorbance were diluted with Milli-Q water to a point where $A(350)$ was <0.02 at 1 cm path length so as to minimize inner filter effects (Moran et al., 2000). Sample EEM spectra were Raman calibrated and had a Milli-Q water blank value scanned on the same day subtracted (Lawaetz and Stedmon, 2009). A total of 74 EEMs were modeled using PARAFAC in MATLAB 7.5 and