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ScienceDirect
Estuarine, Coastal and Shelf Science 78 (2008) 685–693
ESTUARINE COASTAL AND SHELF SCIENCE
www.elsevier.com/locate/ecss

Controls on carbon cycling in two contrasting temperate zone estuaries: The Tyne and Tweed, UK

Jason M.E. Ahad [a,*], Johannes A.C. Barth [b], Raja S. Ganeshram [a], Robert G.M. Spencer [c,1], Günther Uher [c]

[a] School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JW, UK
[b] Center for Applied Geoscience (ZAG), University of Tübingen, D-72076 Tübingen, Germany
[c] School of Marine Science and Technology, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Received 4 October 2007; accepted 18 February 2008
Available online 23 February 2008

Abstract

In order to evaluate the respiration–photosynthesis dynamics in two contrasting North Sea estuaries, pH, temperature, alkalinity, chlorophyll-*a* (chl-*a*), and isotopic ratios of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and dissolved oxygen ($\delta^{18}O_{DO}$) were measured in the Tyne (July 2003) and Tweed (July 2003 and December 2003) estuaries. Using a concentration-dependent isotope mixing line, $\delta^{13}C_{DIC}$ values in the Tweed (July 2003) demonstrated mostly conservative behaviour across the estuary, reflecting mixing between riverine and marine sources, although some samples were slightly more ^{13}C-enriched than predicted $\delta^{13}C_{DIC}$ values. Low pCO_2 (less than 2 times atmospheric pressure) and ^{18}O-depleted $\delta^{18}O_{DO}$ signatures below equilibrium with the atmosphere provided further evidence for net autotrophy in the Tweed estuary in summer 2003. Conversely, in the Tyne during the summer and in the Tweed during the winter higher pCO_2 (up to 6.5 and 14.4 times atmospheric partial pressure in the Tweed and Tyne, respectively), slightly ^{13}C-depleted $\delta^{13}C_{DIC}$ and ^{18}O-enriched $\delta^{18}O_{DO}$ values indicated heterotrophy as the dominant process. The relatively large releases of CO_2 observed during these two estuarine surveys can be attributed to significant oxidation of terrigenous organic matter (OM). This study therefore demonstrates the usefulness of combined $\delta^{18}O_{DO}$ and $\delta^{13}C_{DIC}$ isotopes in examining the relationship between respiration–photosynthesis dynamics and the fate of terrestrially derived OM during estuarine mixing.

Keywords: carbon and oxygen isotopes; DIC; DO; heterotrophy; autotrophy; organic matter

1. Introduction

Estuaries are generally considered to be net heterotrophic systems and often act as sources of CO_2 to the Earth's atmosphere (Smith and Hollibaugh, 1993; Frankignoulle et al., 1998). In Europe alone, estimates of annual estuarine CO_2 emissions range between 30 and 60 million tons of carbon, which corresponds to 5–10% of the anthropogenic emissions from Western Europe (Frankignoulle et al., 1998). The magnitude of this flux depends mainly on the balance between uptake of photosynthetic CO_2 and its release via respiration. In turn, the relative intensity of these two processes depends on a wide variety of factors, including enhanced allochthonous input of labile organic matter, water residence time, sunlight availability, rates of community metabolism, temperature and nutrient load (Smith and Hollibaugh, 1993; Howland et al., 2000; Wang and Veizer, 2000; Abril et al., 2002; Ram et al., 2003). In addition, several studies have shown that seasonal variations can lead to estuaries shifting from net autotrophic to net heterotrophic functioning (Kemp et al., 1992; Smith and Hollibaugh, 1997; Howland et al., 2000; Ram et al., 2003).

Understanding the relative importance of respiration versus photosynthesis within an estuary can therefore provide

* Corresponding author. Present address: School of Geography and Earth Sciences, McMaster University, Hamilton, ON L8S 4K1, Canada.
E-mail address: ahadj@mcmaster.ca (J.M.E. Ahad).
[1] Present address: Department of Land, Air and Water Resources, University of California, Davis, CA 95616, USA.

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doi:10.1016/j.ecss.2008.02.006

a valuable insight into carbon cycling dynamics (i.e., production versus consumption) in these highly complex systems. Two parameters that can be used as natural labels to evaluate these processes include isotope ratios of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and dissolved oxygen ($\delta^{18}O_{DO}$). DIC concentrations in an estuarine environment are mainly controlled by

- the degree of mixing between marine and freshwater,
- atmospheric efflux,
- the relative intensities of photosynthetic and oxidative processes,
- carbonate and/or atmospheric CO_2 dissolution, and
- sediment re-suspension of organic matter and its subsequent turnover (Wang and Veizer, 2000; Abril et al., 2003, 2004).

In a system where soil CO_2 is primarily derived from decomposition of C_3 plant organic matter ($\delta^{13}C$ ca. $-27‰$; Wang et al., 1998), the CO_2 produced has the same $\delta^{13}C_{DIC}$ value as the initial substrate as the carbon undergoes little or no fractionation during turnover. The partial diffusion of this CO_2 gas can then result in a ^{13}C-enrichment of up to $+4.4‰$ (Cerling et al., 1991). The dissolution of CO_2 and its subsequent reaction with the DIC pool at temperatures between 10 and 20 °C and pH between 7.0 and 9.0 results in a fractionation of about $+8‰$ (Wigley et al., 1978). Therefore, DIC in river water during baseflow conditions typically has $\delta^{13}C$ values ranging around $-15‰$ for systems dominated by silicate weathering. If carbonates are dissolved the $\delta^{13}C_{DIC}$ values are further enriched since most marine carbonates generally range around $0‰$ (Faure, 1986). $\delta^{13}C_{DIC}$ values around $0‰$ can also be expected in atmospherically equilibrated waters, since the isotopic composition of atmospheric CO_2 is around $-8‰$ and equilibration with aquatic DIC causes the above-mentioned fractionation of $+8‰$.

Photosynthesis and respiration can further alter DIC concentrations and its isotopic composition. Photosynthesis causes a ^{13}C-enrichment due to preferential removal of the lighter isotope during DIC (or CO_2) uptake whereby respiration causes a negative isotopic shift due to the oxidation of organic matter with a more negative $\delta^{13}C$ signature (Mook and Tan, 1991). This is particularly the case when more ^{13}C-depleted organic matter from C_3 (the most common plant species in terrestrial environments) is converted to DIC. The above shows that several factors can influence the isotopic composition of the DIC. Therefore, the isotopic composition of dissolved oxygen ($\delta^{18}O_{DO}$) becomes a highly useful tool to isolate the influence of photosynthesis versus respiration.

$\delta^{18}O_{DO}$ signatures have been employed in only a few studies to examine respiration–photosynthesis dynamics in aquatic systems (Quay et al., 1995; Wang and Veizer, 2000). The air–water equilibrium value for dissolved O_2 (DO) is $+24.5‰$. It is the result of a $+0.7‰$ shift during dissolution (Benson and Krause, 1984) from the atmospheric oxygen that has a universal value of $+23.8‰$ (Coplen et al., 2002). If photosynthesis dominates, DO becomes supersaturated and the resulting $\delta^{18}O_{DO}$ decreases to values less than $+24.5‰$, due to the production of isotopically lighter O_2. During aquatic photosynthesis the latter originates from the source water that is always more enriched in ^{16}O compared to the original atmospheric O_2 (Wang and Veizer, 2000). On the other hand, respiration leads to DO under-saturation, and the resulting $\delta^{18}O_{DO}$ becomes more positive than the air equilibrium value of $+24.5‰$ due to the preferential removal of ^{16}O from the dissolved oxygen pool (Kiddon et al., 1993; Wang and Veizer, 2000). The isotopic composition of $\delta^{18}O_{DO}$ is not influenced by carbonate or silicate weathering and generally moves into the opposite direction (compared to $\delta^{13}C_{DIC}$) when influenced by either photosynthesis or respiration. Since this isotope system also has a distinct value for atmospheric equilibration it provides a powerful tool combined with $\delta^{13}C_{DIC}$ to differentiate processes.

In this study we have measured pH, temperature, alkalinity, chlorophyll-*a* (chl-*a*), $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ in summer low-flow conditions (July 2003) in the Tyne and Tweed estuaries and winter high flow-conditions (December 2003) in the Tweed estuary. The objectives of this study were as follows:

- to outline the dominant processes of carbon cycling, and
- to understand the dominance of secondary photosynthetic and respiration processes that in turn control the emission or uptake of CO_2.

This setting is ideal to compare two contrasting estuaries in terms of anthropogenic influence under almost identical climatic conditions. While both rivers drain catchments containing large areas of peat moorland, the Tyne estuary is characterised by a high degree of urbanisation whereas agricultural activity is the dominant anthropogenic influence in the Tweed. To our knowledge it is also the first European study to apply combined stable isotopes of DIC and DO.

2. Materials and methods

2.1. Study sites

The River Tyne flows through the city of Newcastle and its suburbs with an approximate population of 1,100,000. It has a total drainage area of $\sim$2900 km^2 and an average freshwater flow of 48 m^3 s^{-1}. Its two main tributaries are the North Tyne, which receives humic-rich waters from blanket peat areas, and the South Tyne, which drains relatively pristine moorland. The geology in the upper Tyne basin consists of Carboniferous limestones and the Namurian Millstone Grit Series, which is characterised by thick, coarse and fine-grained sandstones, together with silt- and mudstones. The Lower and Middle Coal Measures, in which the dominant rock types are shales, mudstones and sandstones, underlie the lower Tyne basin. The maximum extent of the mesotidal Tyne estuary (Fig. 1) is $\sim$33 km and the freshwater residence time ranges between 5 and 20 days. Although industrial fluxes are in decline to the lower part of the estuary it continues to receive significant amounts of urban waste, particularly from the Howdon sewage