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Fluxes of dissolved inorganic carbon in three estuarine systems of the Cantabrian Sea (north of Spain)

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Abstract

The diffusive and in situ fluxes of dissolved inorganic carbon (DIC) and total alkalinity (TA) have been measured and an estimation has been made of the water–atmosphere fluxes of CO_2 in three estuarine systems of the Cantabrian Sea during the spring of 1998. Each of these systems undergoes a different anthropogenic influence. The diffusive fluxes of dissolved inorganic carbon and total alkalinity obtained present values ranging between 0.54–2.65 and 0.0–2.4 mmol m^{-2} day^{-1}, respectively. These ranges are in agreement with those of other coastal systems. The in situ fluxes are high and extremely variable (35–284 mmol TA m^{-2} day^{-1}, 43–554 mmol DIC m^{-2} day^{-1} and 22–261 mmol dissolved oxygen (DO) m^{-2} day^{-1}), because the systems studied are very heterogeneous. The values of the ratio of the in situ fluxes of TA and DIC show on average that the rate of dissolution of $CaCO_3$ is 0.37 times that of organic carbon oxidation. Equally, the interval of variation of the relationship between the benthic fluxes of inorganic carbon and oxygen (F_{DIC}/F_{DO}) is very wide (0.3–13.9), which demonstrates the different contributions made by the processes of aerobic and anaerobic degradation of the organic matter, as well as by the dissolution–precipitation of $CaCO_3$. The water–atmosphere fluxes of CO_2 present a clear dependence on the salinity. The brackish water of these systems (salinity<20), where maximum fluxes of 989 mmol m^{-2} day^{-1} have been estimated, act as a source of CO_2 to the atmosphere. The more saline zones of the estuary (salinity>30) act as a sink of CO_2, with fluxes between −5 and −10 mmol m^{-2} day^{-1}.

Keywords: Dissolved inorganic carbon; Benthic fluxes; Dissolved oxygen; Alkalinity; Cantabrian estuaries; Carbonate dissolution; Water–atmosphere CO_2 fluxes

1. Introduction

Estuaries receive inorganic nutrients and organic matter from the land and represent important systems where terrestrial nutrients and organic matter are processed before entering the ocean. These systems

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are extremely dynamic, and usually characterised by strong physicochemical gradients, enhanced biological activity, and intense sedimentation and resuspension.

The supplies of carbon by estuaries present considerable seasonal variations (Gattuso et al., 1998) and depend on diverse factors, such as the flow rate and the section of the river, and the quantity of carbon dissolved in their waters. The origin of this carbon is principally the basin of the river itself, the atmosphere, and the continents. Continents provide carbon to their rivers from the chemical erosion of rocks, which is facilitated by reaction with the atmospheric CO_2. Chemical weathering and the subsequent export of inorganic carbon from soils to rivers account for significant amounts of terrestrially sequestered atmospheric CO_2 (Raymond and Cole, 2003). In fact, it has been estimated that, currently, the rate of sedimentation in coastal zones is probably twice that of the preindustrial era due to increased continental erosion resulting from deforestation and the changes that agricultural practices have undergone (Wollast, 1991). Raymond and Cole (2003) have estimated that cultivated land has riverine alkalinity concentrations that are five to six times higher than noncultivated land cover, for the upper Mississippi and Ohio basins, respectively.

A large part of the organic carbon deposited as sediment in estuaries is degraded by various metabolic routes, giving rise to significant benthic fluxes of inorganic carbon (Forja and Gómez-Parra, 1998). This inorganic carbon entering the estuaries can be transported by various means; a part will be exported to nearby marine zones, some will be emitted to the atmosphere in the form of CO_2, and part will remain in the water column, and in the sediment. The flux and/or residence of the inorganic carbon in each of these compartments will depend on the characteristics of each estuary, as well as on the season of the year and time of day when the study is carried out. For example, in the estuary of the Scheldt (North Sea), approximately 60% of the respiratory CO_2 is released to the atmosphere, 26% is transferred to the sediment and only 14% remains in the water column (Gattuso et al., 1998). The fluxes, sources, and mechanisms of CO_2 transport and transformation are among the most important current issues in marine and freshwater geochemistry (Cai and Wang, 1998).

The benthic fluxes of inorganic carbon are the result of a balance between the release of inorganic carbon to pore waters through the oxidation of organic carbon by the various aerobic and anaerobic mechanisms and the dissolution–precipitation of calcium carbonate. Until a few years ago, the contribution of the dissolution of $CaCO_3$ in the benthic flux of inorganic carbon was not considered significant. However, over the past decade, many researchers have come to attribute a large part of the benthic flux of inorganic carbon to processes of dissolution of $CaCO_3$ (Jahnke and Jahnke, 2000; Mucci et al., 2000; Cermelj et al., 2001).

In several studies, it has been proved that estuaries present a certain oversaturation of CO_2 with respect to the atmosphere, with partial pressures that vary between 500 and 9500 μatm. (Raymond et al., 1997; Frankignoulle et al., 1998). This extreme variability of CO_2 is significantly greater in space and time than is typically observed in open ocean environments. It has been found that CO_2 can present considerable spatial and temporal variations within the same estuary (Frankignoulle et al., 1998; Abril et al., 2000), due to the hydrodynamic and geomorphological complexity of these littoral zones. On this point, Frankignoulle et al. (1998) observed that the more fluvial part of the Scheldt estuary can act as a source of CO_2 to the atmosphere, while the more saline part, where primary production is usually very intense due to the availability of nutrients, can behave like a sink for atmospheric CO_2.

In this paper, we examine results of in situ benthic fluxes of inorganic carbon and dissolved oxygen (DO), diffusive inorganic carbon fluxes and pore water analyses, from three estuarine systems located in the north of Spain. Each of these systems undergoes a different anthropogenic influence; the estuary most affected by human activity is the Saja–Besaya estuary, followed by the Asón and the Urdaibai estuaries. It has been demonstrated how in these systems the dissolution of calcium carbonate makes an important contribution to benthic fluxes of inorganic carbon. To complete the characterisation of the vertical fluxes of inorganic carbon in the zones studied, an estimate has been made of the water–atmosphere fluxes of CO_2.