

*Tesis Doctoral en Oceanografía Costera, 2017*

**UNIVERSIDAD AUTÓNOMA DE BAJA CALIFORNIA**

FACULTAD DE CIENCIAS MARINAS  
INSTITUTO DE INVESTIGACIONES OCEANOLÓGICAS



**DINÁMICA DE FLUJOS DE CARBONO EN BAHÍA SAN  
QUINTÍN DURANTE CICLOS ESTACIONALES  
ANÓMALOS DE SURGENCIAS COSTERAS**

TESIS

QUE PARA CUBRIR PARCIALMENTE LOS REQUISITOS NECESARIOS PARA OBTENER EL GRADO DE

**DOCTOR EN CIENCIAS EN OCEANOGRAFÍA COSTERA**

PRESENTA

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**UNIVERSIDAD AUTÓNOMA DE BAJA CALIFORNIA**

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POSGRADO EN OCEANOGRAFÍA COSTERA



**Dinámica de flujos de carbono en Bahía San Quintín durante  
ciclos estacionales anómalos de surgencias costeras**


TESIS

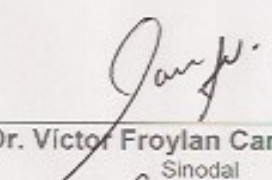
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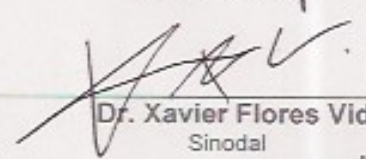
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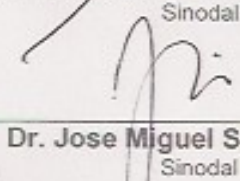
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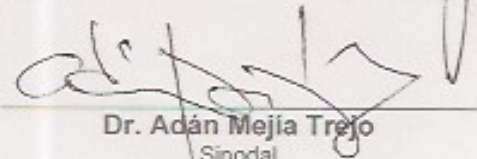
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# 1. INTRODUCCIÓN

El carbono, como elemento, tiene propiedades únicas que lo convierten en un importante componente para la vida, los flujos de energía y la regulación del clima del planeta (Carlson et al. 2001). El sistema de transformaciones químicas y biológicas ligadas a distintos compuestos orgánicos e inorgánicos que contienen carbono se denomina: *Ciclo del Carbono*.

## *1.1. Dinámica del sistema de CO<sub>2</sub> en el medio marino*

Entre los distintos reservorios de carbono en la Tierra, el océano se considera el principal depósito activo de carbono a escala global, con 37 veces más carbono que la atmósfera y 23 veces más que la biota terrestre y los suelos (Takahashi et al. 2002). Los stocks de carbono en estos depósitos se mantienen balanceados por procesos geológicos a grandes escalas temporales. Sin embargo, procesos biogeoquímicos a escalas de tiempo mucho menores conducen a la redistribución de estos reservorios entre los componentes activos del sistema (Carlson et al. 2001). El conocimiento del balance neto de carbono entre la atmósfera y el océano, así como de la biogeoquímica oceánica, ha cambiado profundamente durante las últimas décadas y, en la actualidad, se conocen solo de una forma aproximada (e.g., Borges, 2005; Álvarez-Borrego, 2007; Gruber, 2011; Chen et al. 2013).

Los océanos en su conjunto, actúan regulando el clima de la Tierra mediante un continuo intercambio de calor y gases de efecto de invernadero con la atmósfera. No obstante, el dióxido de carbono (CO<sub>2</sub>) es el que más interés y preocupación genera hoy en día, debido a que este gas es el principal responsable del fenómeno del cambio climático de nuestro planeta hacia un calentamiento global (IPCC, 2007). Antes de la era del hombre, las fluctuaciones naturales del CO<sub>2</sub> en la atmósfera oscilaron de 180 a 280 ppm (Bala, 2013). Sin embargo, en la actualidad, el incremento acelerado de los aportes de CO<sub>2</sub> atmosférico desde el comienzo de la revolución industrial (~1850) ha causado el desbalance en el ciclo global del carbono, exacerbando las variaciones naturales a escala global con valores superiores a 400 ppm (Bala, 2013).

A diferencia de otros gases atmosféricos, el CO<sub>2</sub> reacciona con el agua de mar dando lugar a cuatro especies distintas de carbono: el gas en solución o dióxido de carbono

acuoso ( $\text{CO}_{2(\text{ac})}$ ) y los tres productos de las reacciones de hidratación que son el ácido carbónico ( $\text{H}_2\text{CO}_3$ ), el bicarbonato ( $\text{HCO}_3^-$ ) y el carbonato ( $\text{CO}_3^{2-}$ ). La especie de carbono más abundante en el medio marino es el ión  $\text{HCO}_3^-$  (~ 90%), que junto con los iones  $\text{CO}_3^{2-}$ , constituyen el 99% del carbono inorgánico presente en el océano (Dickson et al. 2007). El 1% restante lo conforman las especies de  $\text{CO}_{2(\text{ac})}$  y  $\text{H}_2\text{CO}_3$ , que se suelen considerar como una única especie hipotética,  $\text{CO}_2^*_{(\text{ac})}$ . Las reacciones ácido-base que controlan la formación y distribución de las especies del carbono inorgánico en el agua de mar se describen a partir de las siguientes reacciones y sus respectivas constantes de equilibrio:



Las concentraciones de las distintas especies químicas no se pueden medir de forma directa, sino que se necesita del estudio experimental de variables asociadas. El *carbono inorgánico disuelto* (CID) es uno de ellos y representa la suma de las distintas especies químicas antes mencionadas. Este parámetro, junto con la *alcalinidad total* (AT), el *pH*, la *presión parcial de  $\text{CO}_2$*  ( $p\text{CO}_2$ ), y el conjunto de especies químicas del carbono en el medio marino se denomina **Sistema de  $\text{CO}_2$**  (o sistema de carbonatos). El estudio termodinámico del sistema del carbonatos en el agua de mar permite establecer la distribución de especies en el equilibrio y predecir sus cambios en función de la temperatura, la presión y la composición química de la disolución (Dickson et al. 2007). Para caracterizar el sistema del  $\text{CO}_2$  en el océano son necesarios al menos dos de estos cuatro parámetros, ya que funciona como un sistema acoplado cuyas variables se retroalimentan unas a otras. El carbono inorgánico disuelto y la alcalinidad total son cantidades conservadoras con respecto a la mezcla de masas de agua y los cambios en temperatura y presión, por lo que a menudo se utilizan para el estudio de modelos del ciclo de carbono en el océano (Wolf-Gladrow et al., 2007).

La alcalinidad total, se define como el número de moles de iones de hidrógeno equivalentes a la cantidad de especiesceptoras de protones en un kilogramo de muestra de agua de mar (Dickson et al. 1981; Dickson et al. 2007). Los equilibrios ácido-base implicados en el sistema de carbono ocurren en el medio marino junto con otras

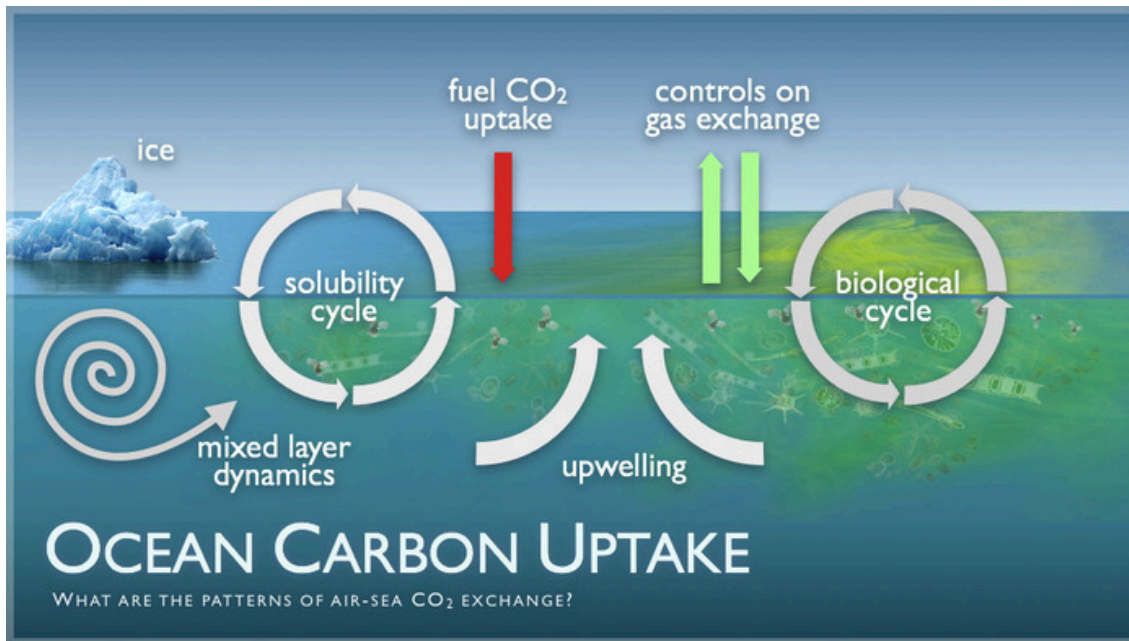
reacciones ácido-base que pueden afectar el valor de AT (Wolf-Gladrow et al. 2007). Por ello, es necesario establecer una cierta condición protónica que permita definir los niveles cero de protones para cada uno de los sistemas ácido-base. Dickson (1981) propuso un valor arbitrario de  $K=10^{-4.5}$ , de forma que aquellos ácidos cuyas constantes de disociación son mayores que este valor se consideran donadores de protones con respecto al punto de equivalencia y, por el contrario, aquellas bases conjugadas de ácidos con constantes de disociación menores o iguales a este, actúan como aceptores de protones. Teniendo en cuenta este criterio, si se consideran los principales equilibrios ácido-base presentes en el océano, AT se puede formular como:

$$\begin{aligned}
 TA = & [HCO_3^-] + 2 \cdot [CO_3^{2-}] + [B(OH)_4^-] + [HPO_4^{2-}] + \\
 & + 2 \cdot [PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + 2 \cdot [S^{2-}] + \\
 & + [OH^-] - [HSO_4^-] - [HF] - [H_3PO_4] - [H^+]
 \end{aligned} \tag{4}$$

Los corchetes representan las concentraciones totales de las distintas especies en solución, siendo  $[H^+]$  la concentración de protones libres.

Entre los principales procesos físicos y biogeoquímicos que modifican el sistema de  $CO_2$  se encuentran: cambios de temperatura, cambios de salinidad, procesos de producción y respiración de la materia orgánica, precipitación/disolución de carbonatos o el intercambio gaseoso entre la atmosfera y el agua de mar (Emerson y Hedges, 2009; Fassbender et al. 2011). Por lo tanto, es importante conocer la dinámica de estos parámetros en el medio marino para así poder inferir en los procesos involucrados y vislumbrar la capacidad del océano y los ecosistemas costeros en absorber y secuestrar las emisiones antropogénicas del  $CO_2$ , que modulan el impacto de este gas invernadero en el cambio climático global.

La captura del  $CO_2$  atmosférico en el medio marino, se encuentra mediada principalmente por la bomba biológica y la circulación oceánica (bomba física o de solubilidad) (Broecker y Peng, 1992; Raven y Falkowski, 1999) (Fig. 1), reduciendo en torno al 30% de las concentraciones atmosféricas de este gas invernadero (Feely et al. 2004). Estos mecanismos hacen que el intercambio de  $CO_2$  con la atmósfera no se dé uniformemente a lo largo del océano y los ecosistemas costeros, existiendo gran variabilidad espacial y temporal.



**Figura 1.** Diagrama conceptual de los principales mecanismos que modulan el intercambio de CO<sub>2</sub> entre la atmósfera y el océano (tomado de <http://www.pmel.noaa.gov>).

En particular, las zonas costeras son regiones muy dinámicas y altamente vulnerables al impacto de éstos estresores (i.e., el aumento del CO<sub>2</sub> antropogénico y las crecientes temperaturas), alterando substancialmente la química del carbono en el medio marino y, en consecuencia, los ciclos biogeoquímicos, los organismos marinos y los ecosistemas, así como el servicio que ellos proporcionan (Kemp y Testa, 2011; Gruber, 2011). No obstante, en la actualidad, sigue existiendo gran incertidumbre sobre cuáles son los principales factores que contribuyen a estos cambios y el papel de los sistemas costeros en el ciclo global del carbono, debido a la propia heterogeneidad que presentan estas regiones. En este contexto, la importancia de entender los procesos básicos que controlan la dinámica biogeoquímica del sistema de carbono a distintas escalas temporales y espaciales, es esencial para mejorar la capacidad de predecir escenarios futuros en el clima terrestre y su efecto sobre los ecosistemas marinos.

### ***1.2. El papel de las zonas costeras en el sistema de carbono***

Los sistemas costeros son zonas de transición entre tierra y mar abierto, que incluyen las plataformas continentales y numerosos ecosistemas internos como deltas, estuarios,

barreras coralinas, lagunas, manglares y bahías. La superficie total de la zona costera ( $26 \times 10^6 \text{ km}^2$ ) comprende el 7% de la superficie del océano ( $360 \times 10^6 \text{ km}^2$ ), albergando entre el 10% y el 30% de la producción primaria marina mundial. Estas zonas reciben importantes aportes externos de nutrientes y materia en suspensión de diferentes orígenes (85% de carbono orgánico y el 45% de carbono inorgánico) que accede a los océanos, actuando con frecuencia como potenciales amortiguadores entre la tierra y el océano (Gattuso et al. 1998).

La elevada productividad primaria y la intensa regeneración bentónica como consecuencia de dichos aportes externos, modulan la intensificación de los flujos de intercambio de carbono entre la atmósfera y la columna de agua y, entre la columna de agua y el sedimento, siendo estos flujos (en proporción) comparables al océano abierto (Hansell y Carlson, 2001; Duarte et al. 2005). Estas diferencias con respecto al océano abierto, hacen que las zonas costeras se constituyan como una parte diferenciada dentro del ciclo biogeoquímico del carbono, jugando un papel fundamental en el destino del  $\text{CO}_2$  antropogénico como promotores en el mantenimiento del sumidero oceánico para el  $\text{CO}_2$  atmosférico (Duarte et al. 2005). Sin embargo, sigue existiendo gran controversia en la literatura para su integración en el ciclo global del carbono, puesto que la diversidad geográfica y ecológica de estos ambientes costeros son factores importantes que influyen en el control del estatus metabólico del ecosistema global (Borges, 2005; Borges et al. 2005).

La tendencia en el metabolismo neto de un ecosistema (Producción Neta del Ecosistema, NEP con siglas en inglés) como autotrófico o heterotrófico neto (exportador o importador de material disuelto y/o particulado, respectivamente), representa el efecto de los procesos físicos y biológicos, así como las transformaciones químicas que contribuyen al balance de carbono en los ecosistemas acuáticos costeros (Testa et al. 2013). Los ciclos de carbono orgánico e inorgánico en estos entornos naturales, están íntimamente ligados a través de la producción primaria y la remineralización de la materia orgánica. Por tanto, el metabolismo del ecosistema integra los componentes pelágicos y bentónicos de estos ambientes, proporcionando información muy útil del funcionamiento y los intercambios entre éstos y los sistemas adyacentes (McGlathery et al. 2001). La estimación del balance metabólico puede ayudar a entender de forma más completada la dinámica del  $\text{CO}_2$  en estas regiones e identificar su papel como fuente o sumidero, de especial interés en el conocimiento del

ciclo biogeoquímico del carbono costero.

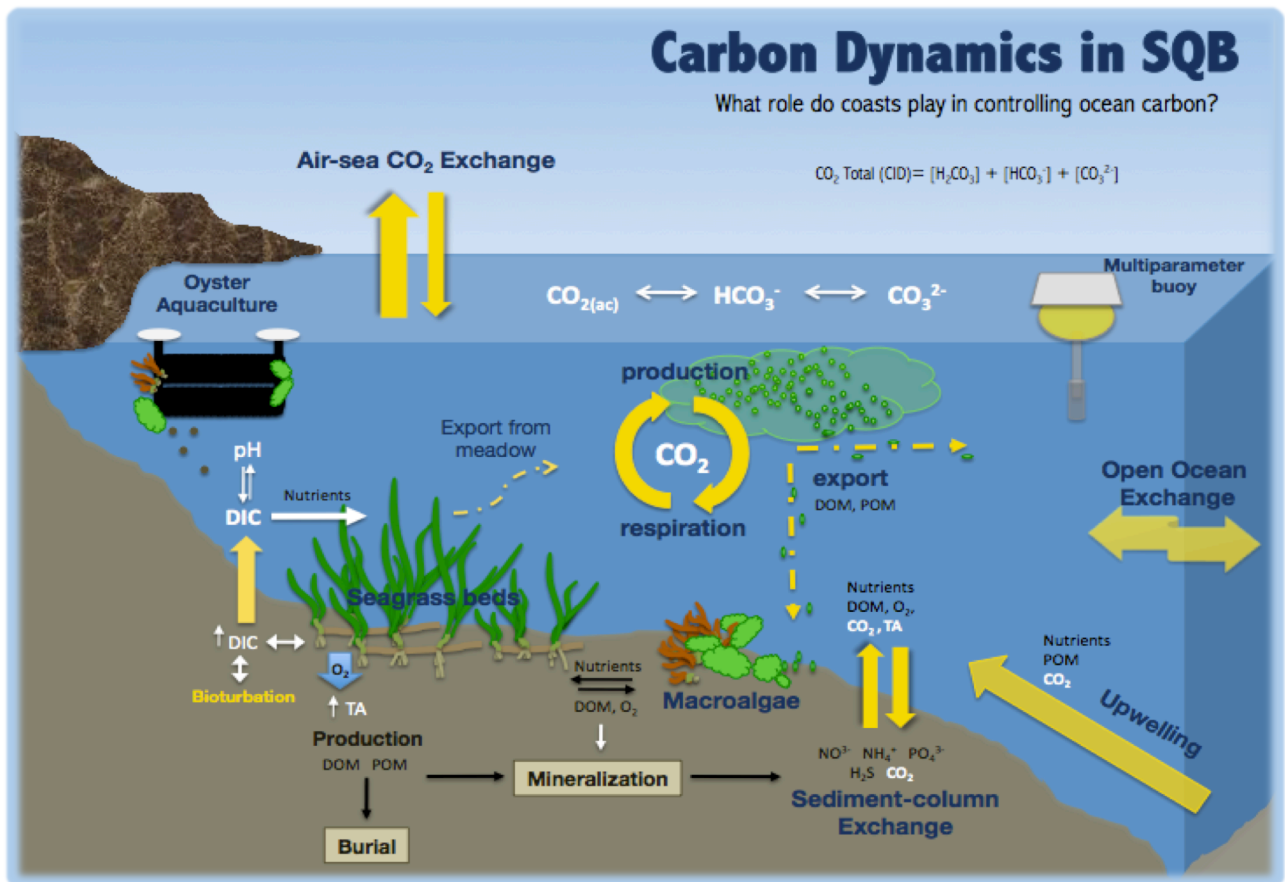
Sin embargo, en muchos casos, las zonas costeras no se tienen en cuenta en el computo global del carbono oceánico y son pocos los estudios que reconocen la contribución de estos ambientes a los flujos de carbono y su interacción con las zonas oceánicas adyacentes (e.g., Smith y Hollibaugh, 1993; Camacho-Ibar et al. 2003; Koné et al. 2009; Chen y Borges, 2009).

### ***1.3. Caso de estudio: Bahía San Quintín, una laguna hipersalina con presencia de pastos marinos y eventos de surgencia***

Bahía San Quintín es una laguna costera hipersalina de clima tipo mediterráneo, localizada en el Océano Pacífico (30° 30'N, 116°W), en la parte noroccidental de la península de Baja California, México, dentro del sistema de surgencias de la Corriente de California. En las últimas décadas, este sistema costero ha sido foco de estudio de los patrones de dependencia de los procesos físicos y biogeoquímicos entre el sistema y el océano contiguo (e.g., Lara-Lara y Álvarez-Borrego, 1980; Camacho-Ibar et al. 2003; Álvarez-Borrego, 2004; Hernández-Ayón et al. 2004). En menor medida, pocos estudios se han enfocado en dilucidar los flujos de intercambio de CO<sub>2</sub> entre los sistemas adyacentes y la laguna costera, así como entre los ambientes de la propia laguna (e.g., Ibarra-Obando et al. 2004; Hernández-Ayón et al. 2007; Ribas-Ribas et al. 2011). Distintos autores han reportado la caracterización de la alta productividad del sistema y el marcado comportamiento heterotrófico de la bahía (e.g., Ibarra-Obando et al., 2007; Camacho-Ibar et al., 2007; Zertuche-González et al., 2009). Sin embargo, Ribas-Ribas et al. (2011), mencionan la autotrofia neta del sistema durante la época de surgencias intensas, así como el doble comportamiento de la laguna como fuente y sumidero de carbono, proponiendo que este comportamiento es consecuencia de la producción primaria sujeta a extensas praderas de *Zostera marina*. No obstante, la mayoría de éstos estudios no abarcan escalas de tiempo suficientemente grandes para poder establecer patrones temporales locales de los flujos de CO<sub>2</sub> y del estatus metabólico del ecosistema de esta laguna.

Este trabajo tuvo como propósito estimar los flujos de intercambio de CO<sub>2</sub> aire-agua, así como la producción neta del ecosistema y el metabolismo bentónico de Bahía San Quintín, una laguna costera sometida a periódicos eventos de surgencias y a la presencia de extensas praderas de pastos marinos (*Zostera marina*), que juegan un papel

importante en la regulación de los procesos biogeoquímicos dentro del sistema y en su intercambio con el océano adyacente (Fig. 2). Cabe esperar, que las variaciones estacionales en las condiciones oceánicas se vean reflejadas en los procesos biogeoquímicos dentro de la laguna costera (Ribas-Ribas et al. 2011), por lo que el esfuerzo de la tesis se dirigió a generar datos que integraran los principales procesos que controlan la dinámica biogeoquímica del sistema de carbono a distintas escalas temporales y espaciales, con la finalidad de conocer los patrones temporales y los factores determinantes involucrados en el control del sistema de carbono en este complejo e invaluable ecosistema. Finalmente, dada la necesidad dentro de la comunidad científica de entender con mayor certeza cómo opera el océano costero y sus ambientes marinos en un mundo cambiante actual y futuro, se discuten las principales características observadas en Bahía San Quintín en las distintas condiciones de estudio.



**Figura 2.** Diagrama conceptual de los principales mecanismos y componentes del sistema que modulan la dinámica del carbono en Bahía San Quintín (modificado de <http://www.pmel.noaa.gov>).

## JUSTIFICACIÓN

La incertidumbre de la respuesta de los ecosistemas marinos y los ciclos biogeoquímicos de los elementos a las proyecciones de cambio global en un océano cambiante, hace relevante mejorar nuestra comprensión en el funcionamiento de estos sistemas, así como generar información que pueda ser utilizada para llegar a establecer patrones globales del papel de las zonas costeras, como fuente o sumidero, en el ciclo global del carbono. Del mismo modo, la generación de estudios específicos y sistemáticos que integren la variabilidad espacial y temporal de la dinámica de los flujos de carbono en los ambientes marinos costeros de México, sigue siendo una necesidad y un tema por resolver en la actualidad, debido a la escasez de datos disponibles para estas costas. Siendo Bahía San Quintín una de las lagunas costeras más estudiadas del litoral en el pacífico mexicano, aún se conoce muy poco sobre la respuesta de dicho ecosistema a las variaciones estacionales de la química del carbono en el agua de mar y los sedimentos, así como la influencia de los procesos físicos y biológicos que condicionan los patrones espaciotemporales del sistema de carbono en este hábitat dominado por macrófitos marinos e influenciado por surgencias costeras. Es por esto que realizar estudios para evaluar la dinámica del sistema de CO<sub>2</sub> en este tipo de ambientes, contribuye potencialmente a dilucidar algunos de los interrogantes actuales en el conocimiento de las zonas costeras y el ciclo global del carbono.

## OBJETIVOS GENERALES

- ☑ Examinar la variabilidad espacial y temporal de los parámetros del sistema de carbono en Bahía de San Quintín, una laguna costera hipersalina dominada por eventos de surgencias costeras y pastos marinos en la región sur de la Corriente de California.
  
- ☑ Estimar, por primera vez en una sistema costero de México, los cambios estacionales e interanuales de los flujos de intercambio de CO<sub>2</sub> entre la atmósfera y el medio marino e identificar los principales factores y procesos que los controlan.
  
- ☑ Discutir el papel de las condiciones del océano adyacente y los procesos internos, así como el papel del metabolismo bentónico, en el control de la biogeoquímica del carbono y el estatus trófico del sistema.

# HIPÓTESIS

La condición oceanográfica regional, la variación estacional de los patrones de viento (condición de la surgencia costera) y los procesos biogeoquímicos internos de la bahía, así como su intercambio con el océano adyacente, promueven cambios estacionales en el sistema de carbono y en el estatus metabólico del ecosistema global (NEP), entre periodos autotróficos y heterotróficos netos en épocas de surgencias, mientras que se mantiene su heterotrofia neta en épocas de no surgencia a lo largo del año.

Debido a que Bahía San Quintín está localizada al sur del sistema de surgencias costeras de la Corriente de California, la bahía presentará un comportamiento como fuente de carbono a lo largo del año, siendo éste sustentado por las surgencias costeras y el metabolismo bentónico del sistema.

## ESTRUCTURA DE LA TESIS



**Capítulo I.** Variaciones en el flujo de CO<sub>2</sub> aire-agua y la producción neta del ecosistema en una laguna costera de Baja California durante la condición de anomalía cálida del Pacífico Norte.

**Capítulo II.** Dinámica del carbono costero en un océano costero cambiante: Bahía San Quintín, un caso de estudio en la región sur del sistema de surgencias de la Corriente de California.

**Capítulo III.** El papel del sedimento en el control biogeoquímico del sistema de carbono en Bahía San Quintín.

## CAPÍTULO I

### Variaciones en el flujo de CO<sub>2</sub> aire-agua y la producción neta del ecosistema en una laguna costera de Baja California durante la condición de anomalía cálida del Pacífico Norte

#### OBJETIVO PARTICULAR

1. Examinar la variabilidad espacial y temporal de los parámetros del sistema de carbono en Bahía San Quintín a lo largo de un ciclo anual, con la finalidad de estimar los cambios estacionales de los flujos de intercambio de CO<sub>2</sub> aire-agua y del estatus metabólico del sistema durante la anomalía cálida del Pacífico Norte en 2014, e identificar los principales factores y procesos que los controlan.

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#### RESUMEN

El presente estudio examina la variabilidad temporal de los flujos de CO<sub>2</sub> aire-agua (FCO<sub>2</sub>) y la química del carbono del agua de mar en una laguna costera de Baja California durante una anomalía excepcionalmente cálida que se desarrolló en las costas del Pacífico Noreste durante 2014. Esta condición oceanográfica se pudo observar en Bahía San Quintín, alcanzando una anomalía máxima de 2 °C en la temperatura superficial del agua de mar para septiembre de 2014. La laguna se comportó como una fuente neta de CO<sub>2</sub> a la atmósfera en 2014 ( $3.3 \pm 4.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) con los flujos positivos más altos observados principalmente en los meses de verano ( $9.0 \pm 5.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ). La producción neta del ecosistema cambió estacionalmente entre condiciones de heterotrofia y autotrofia neta a lo largo del período de estudio, con un promedio anual de  $2.2 \pm 7.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , lo que indicó que Bahía San Quintín fue un sistema

autotrófico neto en 2014. Este patrón de variación estacional en el balance de carbono del sistema parece estar vinculado al ciclo de vida de las comunidades bentónicas dominantes, que juegan un papel importante en el metabolismo de todo el ecosistema. Bajo la entrada limitada de fuentes externas, junto con un aumento en las temperaturas del agua de mar, los flujos de carbono bentónicos y de nutrientes reciclados juegan un papel importante para sostener los procesos biogeoquímicos en la columna de agua dentro del sistema. Dado que la actividad de la surgencia costera puede influir en la magnitud de los FCO<sub>2</sub>, los resultados indican claramente que Bahía San Quintín es una fuente neta de carbono a la atmósfera independientemente de las condiciones oceánicas adyacentes. El estudio arroja luz sobre la dinámica del carbono y sus implicaciones metabólicas en este ambiente costero bajo una anomalía cálida regional, aportando información potencialmente relevante en vista del probable escenario futuro de cambio climático global.

**Palabras clave:** Flujos de CO<sub>2</sub> aire-agua; Surgencia costera; Metabolismo del ecosistema; Baja California; Condición cálida anómala del Pacífico Norte

# Air–Water CO<sub>2</sub> Fluxes and Net Ecosystem Production Changes in a Baja California Coastal Lagoon During the Anomalous North Pacific Warm Condition

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**Abstract** The present study examines the temporal variability of air–water CO<sub>2</sub> fluxes (FCO<sub>2</sub>) and seawater carbonate chemistry in a Baja California coastal lagoon during an exceptionally warm anomaly that was developed in Northeast Pacific coasts during 2014. This oceanographic condition led to a summer-like season (weak upwelling condition) during the study period, which reached a maximum surface temperature anomaly of 2 °C in September 2014. San Quintín Bay acts as a source of CO<sub>2</sub> to the atmosphere in 2014 ( $3.3 \pm 4.8$  mmol C m<sup>-2</sup> day<sup>-1</sup>) with the higher positive fluxes mainly observed in summer months ( $9.0 \pm 5.3$  mmol C m<sup>-2</sup> day<sup>-1</sup>). Net ecosystem production (NEP) switched seasonally between net heterotrophy and net autotrophy during the study period, with an annual average of  $2.2 \pm 7.1$  mmol C m<sup>-2</sup> day<sup>-1</sup>, which indicates that San Quintín Bay was a net autotrophic system during the atypical warm oceanographic condition in 2014. This pattern of seasonal variations in the carbon balance at San Quintín Bay appears to be linked to the

life cycle of benthic communities, which play an important role in the whole-ecosystem metabolism. Under the limited input from external sources coupled with an increase in seawater temperatures, the recycled benthic carbon and nutrient fluxes play a major role to sustain water-column processes within the bay. Since the upwelling condition may influence the magnitude of the air–water CO<sub>2</sub> fluxes, our results clearly indicated that San Quintín Bay is a net source of carbon to the atmosphere regardless of the adjacent oceanic conditions. Our study sheds light on the carbon dynamics and its metabolic implications in a shallow coastal ecosystem under a regional warm anomaly and contributes potentially relevant information in view of the likely future scenario of global climate change.

**Keywords** Air–water CO<sub>2</sub> fluxes · Coastal upwelling · Ecosystem metabolism · Anomalous North Pacific warm condition · Baja California

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## Introduction

The global ocean is a key component of the Earth's carbon reservoir, absorbing  $\sim 1.8 \text{ Pg C year}^{-1}$  of the  $\text{CO}_2$  emitted into the atmosphere (Doney et al. 2009). Generally, global climatology analyses of carbon fluxes do not consider the coastal ocean ( $\sim 7\%$  of total oceanic surface area) (e.g., Sabine et al. 2004; Takahashi et al. 2009). However, coastal waters are important biogeochemically active areas for the global carbon cycle and carbon sink, accounting for approximately 20% of total ocean  $\text{CO}_2$  fluxes (Gypens et al. 2011; Bauer et al. 2013). Although coastal systems play a significant role in biogeochemical dynamics, large uncertainties remain on how these systems affect the ocean and global carbon budgets. Recent summaries of global air–water  $\text{CO}_2$  fluxes ( $\text{FCO}_2$ ) for continental shelves and estuaries estimated that the former act as a net global carbon sink ( $\sim 0.40 \text{ Pg C year}^{-1}$ ), while inner estuaries, mangrove forests, and salt marshes are a carbon source ( $\sim 0.10 \text{ Pg C year}^{-1}$ ) to the atmosphere (Borges 2005; Chen and Borges 2009; Chen et al. 2013). In many cases,  $\text{FCO}_2$  estimates are poorly represented due to the strong spatial and temporal heterogeneity of coastal ecosystems. The inorganic carbon exchange is influenced by a range of processes that include, for example, biological productivity, upwelling, calcium carbonate precipitation and dissolution, organic matter respiration, organic and inorganic carbon inputs from rivers, etc.; hence, the quantification of lateral and vertical  $\text{CO}_2$  fluxes is key for determining how these affect the oceanic carbon cycle (Bauer et al. 2013). Specific studies and a better understanding of carbon dynamics are needed in coastal marine systems worldwide, given the current lack of information on  $\text{FCO}_2$  for these systems. The Pacific coast of the Baja California peninsula, Mexico, is one of these areas of interest where the contribution of coastal carbon fluxes to the global synthesis of  $\text{FCO}_2$  is little known. Currently, reports related to the coastal carbonate system (dissolved inorganic carbon (DIC), total alkalinity (TA), pH,  $p\text{CO}_2$ ) and  $\text{FCO}_2$  are scarce (e.g. Hernández-Ayón et al. 2007a, b; Feely et al. 2008; Ribas-Ribas et al. 2011; Reimer et al. 2013; Muñoz-Anderson et al. 2015).

The western coastal ecosystems of the Baja California region are located at the southern limit of the California Current System (CCS), influenced by northerly wind-driven coastal upwelling events most of the year (Macías et al. 2012). Coastal upwelling carries dense, cold,  $\text{CO}_2$ - and nutrient-rich waters to the sea surface near the shore, supporting the high biological activity in this area (Lachkar and Gruber 2013). The peak of the upwelling season occurs during spring and summer, where subarctic waters and subtropical waters in the CCS off Baja California can variably contribute along the year (Durazo 2009). The seasonality of upwelling conditions and its anomalies in the Northwest Pacific coast are influenced primarily by coastal winds, large-scale winds, and offshore and remote ocean conditions (García-Reyes and Largier

2012). Moreover, variations in upwelling conditions at the seasonal-to-interannual timescale in the CCS are linked to the variability in biogeochemical dynamics and biological components in coastal ocean ecosystems (Checkley and Barth 2009).

This study was conducted during an anomalous warm oceanographic condition called “The Blob” that occurred since late 2013 until at least late 2015 across the North Pacific basin (Hartmann 2014; Bond et al. 2015). Areas of the North Pacific have been as much as  $5\text{ }^\circ\text{C}$  warmer than average, affecting regional weather and climate patterns ([http://sccoos.org/projects/anomalies\\_workshop/](http://sccoos.org/projects/anomalies_workshop/)). The impact of these regional climate variations and changing environmental conditions in terms of trophic status and metabolic consequences in coastal ecosystems is poorly understood (Testa et al. 2013). In order to better understand the effects of the 2014 oceanographic condition on the coastal carbon dynamics and ecosystem metabolism, we focused the present work on two main goals: first, to examine the spatial and temporal variability of seawater carbonate chemistry in San Quintín Bay, a Baja California Mediterranean-climate coastal lagoon and, second, to estimate, for the first time for this site, the seasonal changes of  $\text{FCO}_2$  and net ecosystem production (NEP), identifying the key underlying factors and processes. We discuss the role of primary producers and environmental conditions on the system's trophic status and summarize the key implications of this anomalous condition on carbon dynamics and ecosystem metabolism in San Quintín Bay.

## Material and Methods

### Study Area

San Quintín Bay ( $30^\circ 30' \text{ N}$ ,  $116^\circ \text{ W}$ ) is a hypersaline coastal lagoon linked to the CCS, subject to frequent upwelling events, mainly in spring and summer, that supply the coastal lagoon with nutrients, phytoplankton, and DIC via tidal exchange (Ribas-Ribas et al. 2011). The lagoon is a well-mixed y-shaped system with only one connection to the ocean, covering an area of approximately  $42 \text{ km}^2$  with an average depth of 2 m. The seagrass *Zostera marina* is the main primary producer in San Quintín Bay, forming large meadows that cover approximately 40% of the bay surface (Ward et al. 2004). Nevertheless, significant seasonal macroalgal blooms occurring within the bay can also be observed (Zertuche-González et al. 2009), as well as large phytoplankton biomass during the upwelling season. The latter constitutes the most important external source of organic matter into the system (Camacho-Ibar et al. 2003).

## Field Sampling and Analytical Methods

The role of San Quintín Bay as a carbon source or sink in 2014 was investigated by setting a network of ten fixed stations across the bay's three biogeochemically distinct sections (Camacho-Ibar et al. 2003): the mouth (Mouth) (stations 1–3); the western arm, known as Bahía Falsa (BFa) (stations 4–7); and the eastern arm, known as Bahía San Quintín (bSQ) (stations 8–10) (Fig. 1). At each station, discrete water samples were collected monthly from November 2013 to November 2014 for carbonate system analyses. Seawater samples were stored in 500-mL borosilicate bottles and preserved with 100  $\mu\text{L}$  saturated mercuric chloride ( $\text{HgCl}_2$ ). Bottles were sealed with Apiezon grease to prevent evaporation and contact with the atmosphere. DIC was measured following the coulometric method described by Johnson et al. (1987). Prior to the analysis, accuracy and precision were assessed using Certified Reference Material (CRM) for DIC provided by Dr. Andrew Dickson from the Scripps Institution of Oceanography (Dickson et al. 2003). The reference material gave an average difference of 4  $\mu\text{mol kg}^{-1}$  relative to the certified maximum value, with a measurement error of 0.2 %. TA was measured with the potentiometric method described

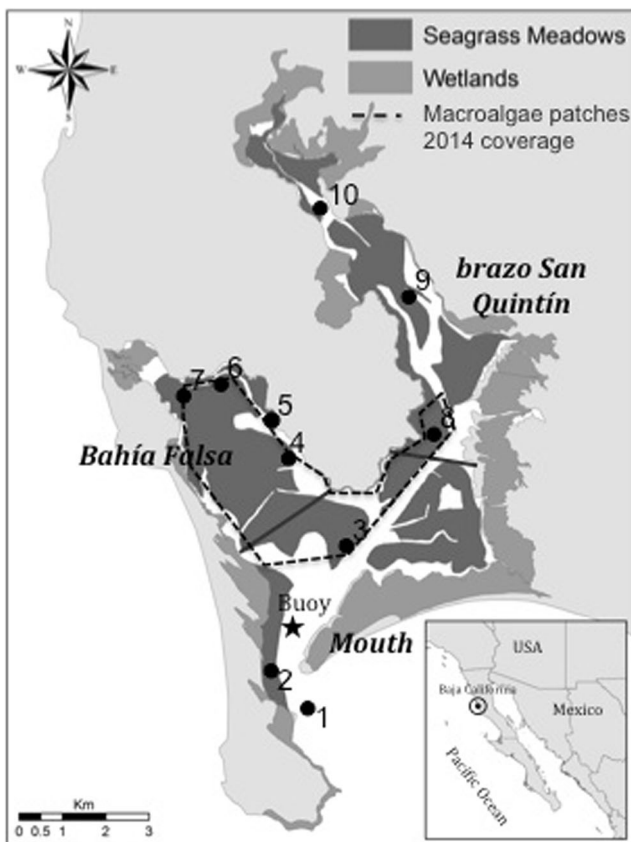
by Hernández-Ayón et al. (1999). Reference standard materials were used for the measurements, and the differences relative to the certified value were lower than 5  $\mu\text{mol kg}^{-1}$ , with a measurement error of 0.2 %.

Given that San Quintín Bay is a hypersaline coastal lagoon where evaporation processes in the innermost parts of the system are often very important, DIC and TA values were normalized for salinity (normalized dissolved inorganic carbon (NDIC) and normalized total alkalinity (NTA), respectively) using the corresponding salinity for each sampling month from station 1 (oceanic signal). The average salinity during the study period at the outer part of the mouth was  $33.64 \pm 0.30$ . Monthly sampling was conducted only during high tide in order to eliminate variations due to tidal condition.

In situ pH (seawater scale) and  $p\text{CO}_2$  were calculated with the CO2Sys.xls program developed by Lewis and Wallace (1998), using the pair DIC-TA and the dissociation constants proposed by Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). The precision of pH and  $p\text{CO}_2$  was  $\pm 0.01$  pH units and  $\pm 20$   $\mu\text{atm}$  ( $\pm\text{SE}$ ,  $n = 100$ ), respectively. Surface seawater temperature (SST) and salinity were determined using a handheld multiparameter probe (YSI Pro Plus, USA) at the time of seawater sampling. The probe was calibrated prior to each field trip following the manufacturer's recommendations.

Additionally, data from a time series were obtained from a buoy equipped with a multiparameter sonde (YSI 6920V2–2) anchored at the mouth of the bay (asterisk in Fig. 1). Observations were recorded at 15-min intervals for SST, pH (National Bureau of Standards (NBS) scale), and dissolved oxygen saturation (%DO) from February to December 2014 during the sampling period. These data were used to determine the following: (1) high-frequency physicochemical characteristics of ocean–bay seawater exchange and (2) the potential intrusion into the bay of water originated from coastal upwelling. The sonde was calibrated every 2 months during the sampling period following the manufacturer's recommendations. The optical dissolved oxygen probe was calibrated using the “one-point saturated air” method with a measured precision of  $\pm 1$  %, and the pH probe was calibrated against an NBS buffer with an error of  $\pm 0.01$  pH units. The water residence time ( $\tau$ ) was calculated with a one-box model, as described by Camacho-Ibar et al. (2003) for San Quintín Bay.

In order to observe the local effects of upwelling conditions on eelgrass primary production, aboveground biomass of *Z. marina* ( $\text{g dry weight (DW) m}^{-2}$ ) was estimated each month throughout the sampling period in different eelgrass meadows corresponding to four study sites (stations 2, 4, 7, and 8) across San Quintín Bay. Plants were randomly collected by scuba diving using a 40-cm-diameter PVC corer ( $n = 3$ ) and transported in separate plastic bags to the laboratory. DW of eelgrass aboveground biomass was evaluated after drying the samples at 60 °C to constant weight.



**Fig. 1** San Quintín Bay with its different areas: mouth of the bay (Mouth), Bahía Falsa (BFa) and Bahía San Quintín (bSQ). Numbers indicate sampling stations in 2014, and the black star indicates the location of the oceanographic buoy

The monthly anomalies of the coastal upwelling index (UIA) during the sampling period for the nearest Pacific Ocean Station (30° N; 119° W) at San Quintín Bay were obtained from the National Oceanic and Atmospheric Administration (NOAA) (NOAA/NMFS Pacific Fisheries Environmental Laboratory), available online at <http://upwell.pfeg.noaa.gov>. The monthly offshore temperature-standardized anomalies during the study period were calculated from satellite images derived from MODIS-Aqua data (region: 116° W–115° W, 30° N–30° N) obtained from the National Aeronautics and Space Administration (NASA) and available online at <http://gdata1.sci.gsfc.nasa.gov>.

### Biological and Temperature Control in $p\text{CO}_2$ Calculations

Seawater  $p\text{CO}_2$  is affected by seasonal changes in temperature, physical processes (horizontal and vertical mixing), and biological processes (primary production, respiration, and calcium carbonate dissolution and precipitation) that influence total seawater  $\text{CO}_2$  concentrations in coastal systems (Takahashi et al. 2002; Barron et al. 2006). In order to remove the temperature effect from the observed  $p\text{CO}_2$  ( $p\text{CO}_{2\text{ obs}}$ ), the  $p\text{CO}_{2\text{ obs}}$  values were normalized to 20.1 °C ( $p\text{CO}_2 T_{\text{mean}}$ ), which was the mean annual area-averaged seawater temperature ( $T_{\text{mean}}$ ) measured in the San Quintín Bay system during the study period according to the method of Takahashi et al. (2002):

$$p\text{CO}_2 T_{\text{mean}} = p\text{CO}_{2\text{ obs}} * \exp[0.0423(T_{\text{mean}} - T_{\text{obs}})] \quad (1)$$

where  $p\text{CO}_{2\text{ obs}}$  is the observed  $p\text{CO}_2$  at in situ temperature and  $T_{\text{obs}}$  is the in situ mean monthly area-averaged seawater temperature measured in degrees Celsius. Changes in this parameter are indicative of variations in total  $\text{CO}_2$  due to the combined influence of horizontal mixing, vertical mixing, and biological processes, assuming that water temperature remains constant at 20.1 °C. Since San Quintín Bay is considered a well-mixed system, we assumed that the changes observed would result mostly from biological effects. The effect of biological factors on surface water  $p\text{CO}_2$  is represented in a given area by the seasonal amplitude of  $p\text{CO}_2$  values normalized to the mean annual temperature ( $p\text{CO}_2 T_{\text{mean}}$ ), computed using the previous equation:

$$(\Delta p\text{CO}_2)_{\text{bio}} = (p\text{CO}_2 T_{\text{mean}})_{\text{max}} - (p\text{CO}_2 T_{\text{mean}})_{\text{min}} \quad (2)$$

On the other hand, the effect of temperature on  $p\text{CO}_2$  was calculated as proposed by Takahashi et al. (2002):

$$p\text{CO}_2 T_{\text{obs}} = p\text{CO}_2 T_{\text{mean}} * \exp[0.0423(T_{\text{obs}} - T_{\text{mean}})] \quad (3)$$

where  $p\text{CO}_2 T_{\text{obs}}$  is the mean annual area-averaged observed  $p\text{CO}_2$  at in situ mean area-averaged seawater temperature for

each month during the sampling period and  $p\text{CO}_{2\text{ mean}}$  is the mean annual area-averaged observed  $p\text{CO}_2$  (531  $\mu\text{atm}$ ).

The resulting values indicate the distribution of  $p\text{CO}_2$  that would be expected only from temperature changes if a parcel of water having the mean  $p\text{CO}_2$  of 538  $\mu\text{atm}$  is subjected to seasonal temperature changes under isochemical conditions. The changes related to temperature were estimated as follows:

$$(\Delta p\text{CO}_2)_{\text{temp}} = (p\text{CO}_2 T_{\text{obs}})_{\text{max}} - (p\text{CO}_2 T_{\text{obs}})_{\text{min}} \quad (4)$$

The importance of temperature ( $T$ ) relative to biological parameters ( $B$ ) can be expressed in terms of the following ratio (Takahashi et al. 2002):

$$T/B = (\Delta p\text{CO}_2)_{\text{temp}} / (\Delta p\text{CO}_2)_{\text{bio}} \quad (5)$$

### Air–Water $\text{CO}_2$ Flux Estimates

Air–water  $\text{CO}_2$  fluxes were calculated according to  $\text{FCO}_2 = k\alpha(\Delta p\text{CO}_2)$ , where  $k$  is the  $\text{CO}_2$  transfer velocity,  $\alpha$  is the  $\text{CO}_2$  solubility coefficient in seawater (Weiss 1974), and  $\Delta p\text{CO}_2$  is the difference between the partial pressures of  $\text{CO}_2$  in water and air ( $\Delta p\text{CO}_2 = p\text{CO}_{2\text{ water}} - p\text{CO}_{2\text{ air}}$ ). The  $p\text{CO}_{2\text{ air}}$  used to estimate  $\Delta p\text{CO}_2$  was the monthly atmospheric data at the Pacific Ocean Station (POCN30) (30.0° N; 135.00° W), available from NOAA ([http://www.esrl.noaa.gov/gmd/dv/site/site\\_table2.html](http://www.esrl.noaa.gov/gmd/dv/site/site_table2.html)), ranging from 397 to 399  $\mu\text{atm}$  during the sampling period (November 2013 to November 2014). The parameter  $k$  was computed using the parameterization proposed by Ho et al. (2006) as a function of short-term steady wind velocities:  $k = 0.266u_{10}^2 (600/\text{Sc})^{1/2}$ , where “ $u_{10}$ ” is the wind velocity at a height of 10 m, and “ $\text{Sc}$ ” is the Schmidt number (Wanninkhof 1992). Monthly wind velocity ( $W$ ) was obtained from a weather station located in San Quintín Bay.

Positive  $\text{FCO}_2$  values indicate gas fluxes from water to the atmosphere, while negative values indicate fluxes from the atmosphere to water. Since the calculation of  $p\text{CO}_{2\text{ water}}$  involved a standard error of  $\pm 20$   $\mu\text{atm}$ , the error associated with the  $\text{FCO}_2$  estimate is  $\pm 0.03$   $\text{mmol C m}^{-2} \text{ day}^{-1}$  when wind velocity error was 8 %.

### Whole-System Metabolism Calculation

The biogeochemical budget model according to Gordon et al. (1996) was used to estimate non-conservative DIC fluxes ( $\Delta\text{DIC}$ ). A one-box model was used for the San Quintín Bay system, following the procedure for nutrient budgets described by Camacho-Ibar et al. (2003). The whole-bay mean values (stations 2 to 10) and the outermost station (1) from the mouth of the bay were used like the bay and the ocean end members, respectively. Station 1 was the only with merely oceanic signal, since the stations 2 to 10 were located near

large eelgrass meadows and probably being more affected by biological processes. Net ecosystem production (NEP) (i.e., the difference between the gross primary production and the ecosystem respiration) was also computed from the non-conservative DIC fluxes to determine the system's apparent net biogeochemical performance for carbon. Since  $\Delta\text{DIC}$  values are attributed not only to the difference between production and respiration rates of organic matter ( $\Delta\text{DIC}_o$ ), but also to the net  $\text{CO}_2$  exchanges with the atmosphere ( $\Delta\text{DIC}_g$ ) and  $\text{CaCO}_3$  precipitation and dissolution ( $\Delta\text{DIC}_c$ ), NEP was estimated as follows (Gordon et al. 1996):

$$\Delta\text{DIC} = \Delta\text{DIC}_o + \Delta\text{DIC}_g + \Delta\text{DIC}_c \quad (6)$$

$$\text{NEP} = -\Delta\text{DIC}_o \quad (7)$$

Using the expressions 6 and 7, NEP is defined as follows:

$$\text{NEP} = -(\Delta\text{DIC} - \Delta\text{DIC}_g - \Delta\text{DIC}_c) \quad (8)$$

The contribution of  $\text{CaCO}_3$  precipitation and dissolution on NEP was assumed to be negligible ( $\Delta\text{DIC}_c = 0$ ) in the present study, considering the results and carbonate content in sediment samples observed by Ribas-Ribas et al. (2011) (ranging from 0 to 1.2 %) for San Quintín Bay. Otherwise to the best of our knowledge, no information on the magnitude of these processes is available for the bay.

### Statistical Analyses

Temporal and spatial differences in hydrological and biogeochemical characteristics were analyzed using a non-parametric Kruskal–Wallis test, because the assumptions regarding normality and homoscedasticity criteria were not met for the data even when log transformed. The significance of correlations between environmental data and estimated parameters was tested using a Spearman's correlation matrix. Statistical analyses were performed using the SIGMAPLOT 11 statistical package (Systat Software Inc., USA). The minimum significance level set for statistical difference was  $p < 0.05$ . Additionally, the combined uncertainties on the calculated non-conservative DIC fluxes were estimated by error propagation calculation.

## Results

### Seasonal Ocean–Bay Physicochemical Conditions

UIA in coastal waters off San Quintín Bay ranged between  $-70$  and  $5 \text{ m}^3 \text{ s}^{-1} \cdot (100 \text{ m})^{-1}$  with an annual mean value of  $-23 \pm 26 \text{ m}^3 \text{ s}^{-1} \cdot (100 \text{ m})^{-1}$  (Table 1). Maximum negative UIA anomalies were observed from May to October 2014 (Fig. 2c), consistent with maximum temperature anomalies observed off San Quintín Bay in 2014 (Fig. 2d). Although the sampling

period started under near-normal offshore SST (Fig. 2d), the SST anomaly exceeded  $0.5 \text{ }^\circ\text{C}$  from May to November, peaking in September 2014. This month was anomalously  $2 \text{ }^\circ\text{C}$  warmer versus the same month in the previous years observed in comparison with climatology data developed from July 2002 to May 2015. Temperature values at the mouth of the bay were higher than  $20 \text{ }^\circ\text{C}$  during summer and fall 2014 (Fig. 2a).

Seawater temperature in San Quintín Bay ranged between  $\sim 15.0$  and  $26.0 \text{ }^\circ\text{C}$  during the study period, with minimum mean temperatures at the mouth ( $16.7 \pm 1.7 \text{ }^\circ\text{C}$ ) during spring months. Seawater temperatures were more than  $4 \text{ }^\circ\text{C}$  lower at the mouth than at the head of both arms (Fig. 2a) and were higher toward the inner portion of bSQ in spring and summer. Salinity showed small seasonal differences, with an annual mean value of  $34.33 \pm 0.39$  (Table 1). The minimum mean salinity was  $33.35 \pm 0.17$  observed in the outer portion of the mouth in fall 2013, and the maximum mean salinity was  $35.52 \pm 0.98$  observed in the inner part of bSQ in spring 2014 (Fig. 2b). Similar to temperature, salinity increased from the mouth of the bay toward the heads of bSQ and BFa, with increases of up to 5 units (Fig. 2b).

The timing of the water exchange varied seasonally for San Quintín Bay throughout the study period (Table 1). The annual mean residence time was  $15 \pm 6$  days for 2014. The whole-system water exchange time estimated in this study was consistent with figures previously reported by Camacho-Ibar et al. (2003), with exchange rates of  $12 \pm 2$  and  $21 \pm 9$  days for summer and winter 2014, respectively. Wind velocity in San Quintín Bay revealed upwelling-favorable winds, with an annual mean of  $3.1 \pm 0.8 \text{ m s}^{-1}$  during the study period and peak values observed from April to August (Table 1).

Figure 3 shows the time series of SST, pH, and %DO obtained from the oceanographic buoy located at the mouth of the bay. Seawater temperature ranged from  $13$  to  $25 \text{ }^\circ\text{C}$ , fluctuating broadly from early spring to mid-fall and then decreasing toward the winter season. Temperatures were lowest in the spring, ranging from  $13$  to  $19 \text{ }^\circ\text{C}$  and increasing steadily to reach a peak in September (Fig. 3a). The range of pH and %DO data during 2014 was  $7.9$  to  $8.4$  and  $75$  to  $140 \%$ , respectively, with means of  $8.1$  and  $95 \%$ , respectively and maxima between May and June 2014 (Fig. 3b, c). Pulses of cold water ( $<15 \text{ }^\circ\text{C}$ ) were recorded in April, May, and early June, with occasional decreases in pH of up to  $\sim 0.2$  units and seawater %DO below  $80 \%$ , both of which suggest the input of water into the lagoon from an adjacent watershed with slightly different chemical properties.

### Seasonal and Spatial Distribution of the Carbonate System and $\text{CO}_2$ Fluxes

Figure 4a–d shows seasonal averages of DIC, TA, pH, and  $p\text{CO}_2$ . DIC, TA, pH, and  $p\text{CO}_2$  recorded in San Quintín Bay

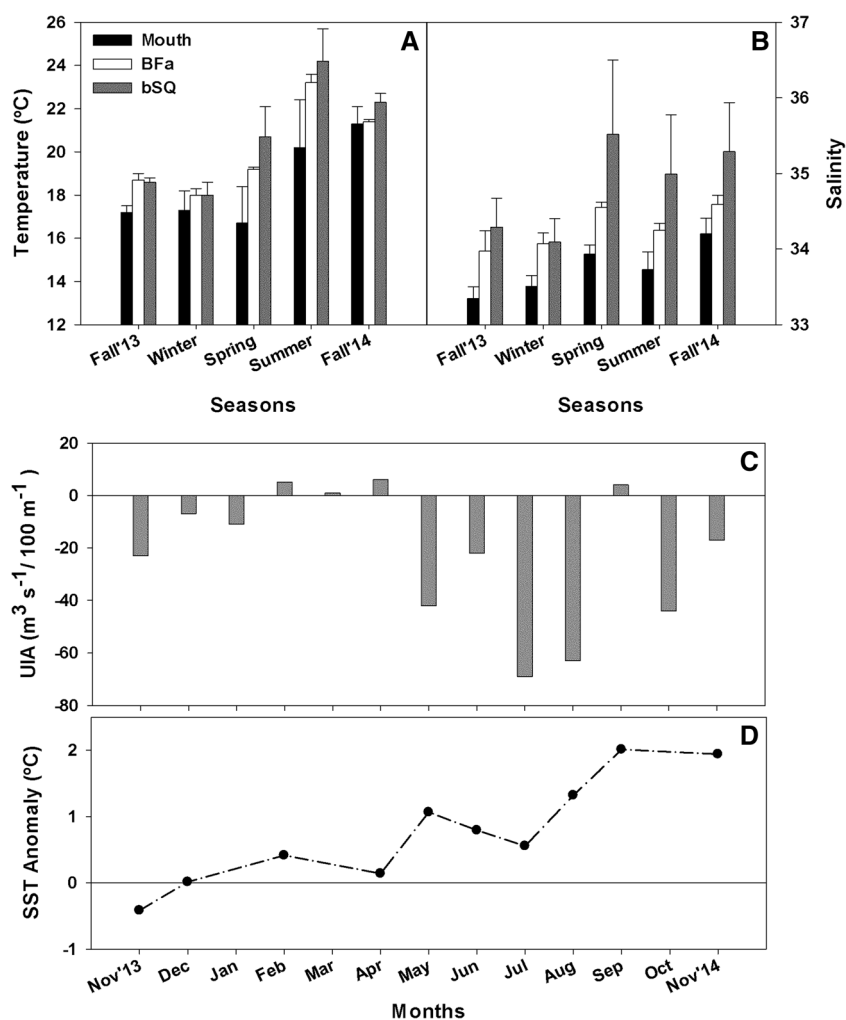
**Table 1** Summary of monthly hydrological observations for anomaly of upwelling index ( $\text{m}^3 \text{s}^{-1}/100 \text{m}^{-1}$ ), monthly wind speed ( $\text{m s}^{-1}$ ), residence time (days), seawater temperature ( $^{\circ}\text{C}$ ), and salinity at San Quintín Bay from November 2013 to November 2014

Date	Upwelling index anomaly ( $\text{m}^3 \text{s}^{-1}/100 \text{m}^{-1}$ )	Monthly wind speed ( $\text{m}^3 \text{s}^{-1}$ )	Residence time (days)	Temperature ( $^{\circ}\text{C}$ )	Salinity
November 2013	-23	1.8	23	18.2	33.88
December	-7	1.8	10	16.7	33.61
February	5	2.7	29	18.9	34.20
April	6	3.5	16	18.3	34.48
May	-42	3.6	16	19.5	34.83
June	-22	3.9	15	21.0	34.47
July	-69	3.8	11	21.7	34.15
August	-63	3.7	11	23.9	34.33
September	4	3.2	7	23.3	34.57
November 2014	-17	3.1	14	20.0	34.80
Annual mean ( $\pm\text{SE}$ )	-23 (9)	3.1 (0.3)	15 (2)	20.1 (0.3)	34.33 (0.07)

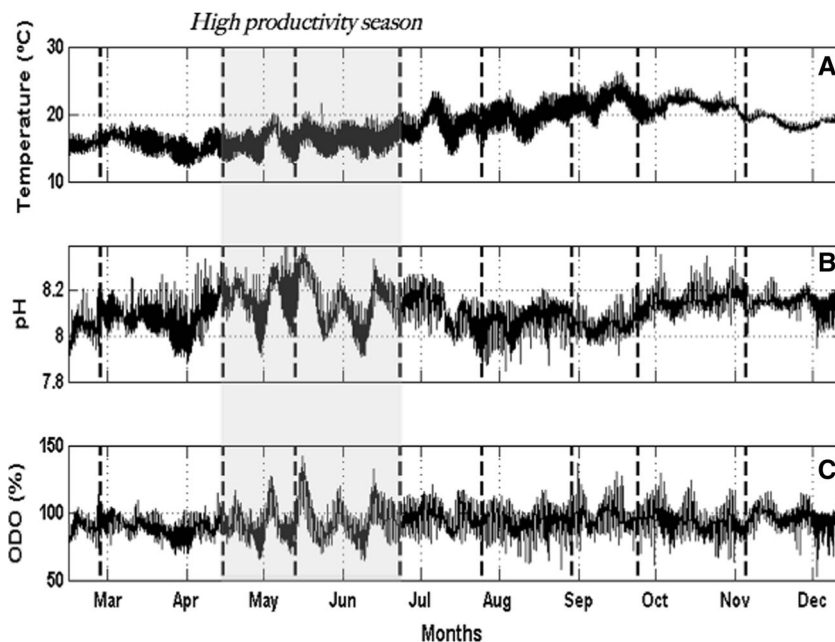
were in the range of 1930 to 2330  $\mu\text{mol kg}^{-1}$ , 2210 to 2650  $\mu\text{mol kg}^{-1}$ , 7.75 to 8.18, and 382 to 919  $\mu\text{atm}$ , respectively, with mean values of 2090  $\mu\text{mol kg}^{-1}$ , 2300  $\mu\text{mol kg}^{-1}$ , 7.95, and 538  $\mu\text{atm}$ , respectively. Throughout the study period, DIC and TA concentrations were lower at the mouth of the bay than at the heads of BFa and bSQ, except in spring, where

DIC values remained relatively similar along San Quintín Bay (Fig. 4a, b). Two contrasting environments were observed in the carbonate system parameters, mainly in spring (April–May) and summer (June–August) seasons, which showed significant differences ( $p < 0.05$ ). In spring, low DIC values ( $<2000 \mu\text{mol kg}^{-1}$ ) and low  $p\text{CO}_2$  values ( $<400 \mu\text{atm}$ ) were

**Fig. 2** Seasonal average values of **a** temperature ( $^{\circ}\text{C}$ ) and **b** salinity, for the three areas of San Quintín Bay; **c** monthly anomalies of the coastal upwelling index (UIA) ( $\text{m}^3 \text{s}^{-1}/100 \text{m}^{-1}$ ); and **d** monthly anomalies of the sea surface temperature (SST) during the study period



**Fig. 3** Temporal variability in **a** temperature (°C), **b** pH, and **c** dissolved oxygen saturation (%) from February to December in 2014 as recorded by the oceanographic buoy located in the mouth of San Quintín Bay. *Dashed lines* show discrete sampling dates during the study period

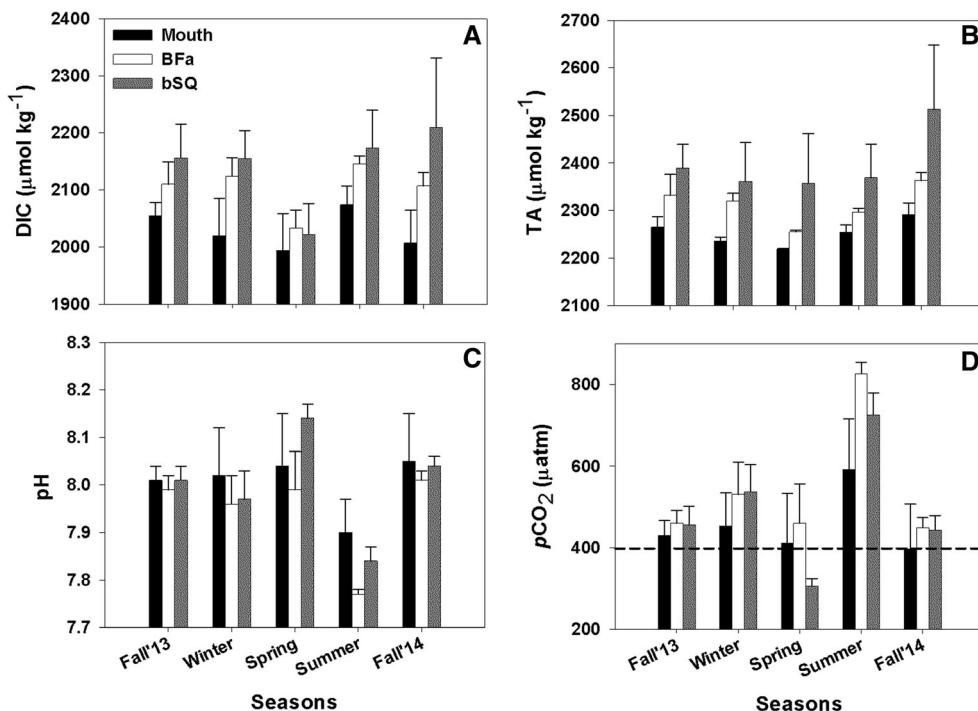


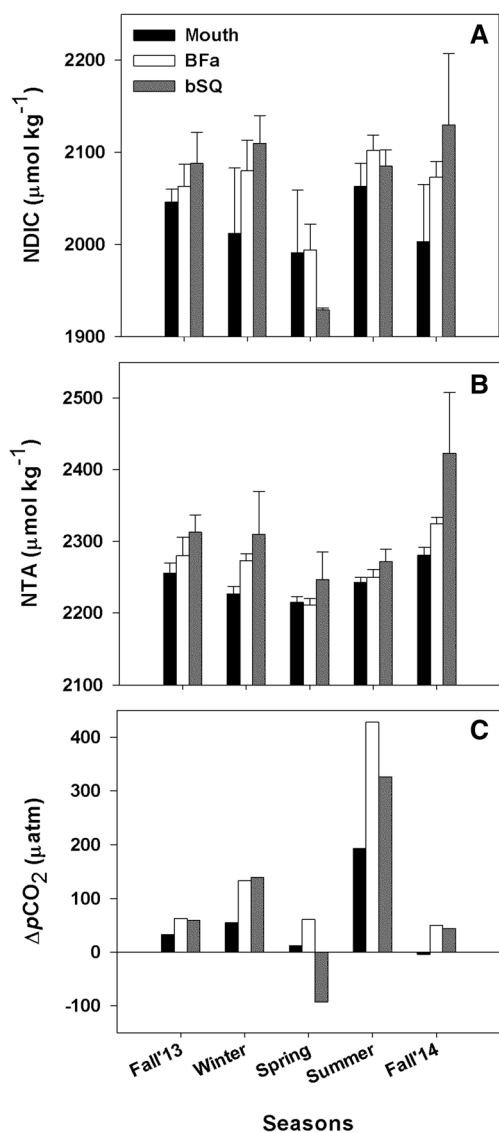
consistent with high pH values (>8.1). In contrast, high DIC values (>2100  $\mu\text{mol}\cdot\text{kg}^{-1}$ ) and high  $p\text{CO}_2$  values (>700  $\mu\text{atm}$ ) were consistent with low pH values (<7.9) during the summer (Fig. 4a, c, d). On the other hand, seasonality of TA distribution showed a lower variability than seasonal changes of DIC, with relatively homogeneous concentrations between seasons.

As expected, DIC and TA normalized by salinity had an evaporation effect greatest in the innermost parts of San Quintín Bay. Both NDIC and NTA concentrations showed an increase from the mouth of the bay toward the arms, except

in spring for NDIC, where a decrease was observed mainly at bSQ (Fig. 5a, b). These increasing concentrations were more notable in fall 2014 (>150  $\mu\text{mol}\cdot\text{kg}^{-1}$ ), coinciding with the highest seawater temperatures recorded during the sampling period. The  $p\text{CO}_2$  air–water gradient ( $\Delta p\text{CO}_2$ ) was positive for all seasons, except in spring at bSQ, where negative values were observed (Fig. 5c). Higher positive  $\Delta p\text{CO}_2$  values (>400  $\mu\text{atm}$ ) were recorded in summer both in BFa and, to a lesser extent, in bSQ (Fig. 5c). During the anomalously warm 2014,  $\text{FCO}_2$  in San Quintín Bay ranged approximately

**Fig. 4** Seasonal average  $\text{CO}_2$  system values for the three areas of San Quintín Bay during the study period: **a** dissolved inorganic carbon ( $\mu\text{mol}\cdot\text{kg}^{-1}$ ), **b** total alkalinity ( $\mu\text{mol}\cdot\text{kg}^{-1}$ ), **c**  $\text{pH}_{\text{sw}}$ , and **d** partial pressure of  $\text{CO}_2$  ( $\mu\text{atm}$ )





**Fig. 5** Seasonal average values of **a** normalized dissolved inorganic carbon ( $\mu\text{mol kg}^{-1}$ ), **b** normalized total alkalinity ( $\mu\text{mol kg}^{-1}$ ), and **c** delta partial pressure of  $\text{CO}_2$  ( $\mu\text{atm}$ ) for the three areas of San Quintín Bay during the study period

between  $-4.9$  and  $22.6 \text{ mmol C m}^{-2} \text{ day}^{-1}$ , with an annual mean of  $3.3 \pm 4.8 \text{ mmol C m}^{-2} \text{ day}^{-1}$  (Fig. 6a). Seasonal  $\text{FCO}_2$  averages were close to balance during the most of the year, except in summer months, when the  $\text{CO}_2$  exchange was higher (Fig. 6b). Overall, the whole system acted as a carbon source to the atmosphere, which peaked in July 2014 ( $15.1 \pm 6.9 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) (Table 2).

### Seasonal Variability of Eelgrass Biomass and Whole-System Metabolism

The eelgrass aboveground biomass varied seasonally between  $70$  and  $250 \text{ g DW m}^{-2}$  across the bay, with a peak in summer ( $238 \pm 13 \text{ g DW m}^{-2}$ ) and lower values in winter ( $81 \pm 8 \text{ g}$

$\text{DW m}^{-2}$ ) (Fig. 7). The eelgrass biomass production rapidly increased early in the upwelling season, followed by a marked decrease in late summer toward November 2014, with average values below the 2013 fall–winter. To note, our eelgrass biomass estimate represents an underestimate of total biomass, as the biomass of roots and rhizomes was not considered.

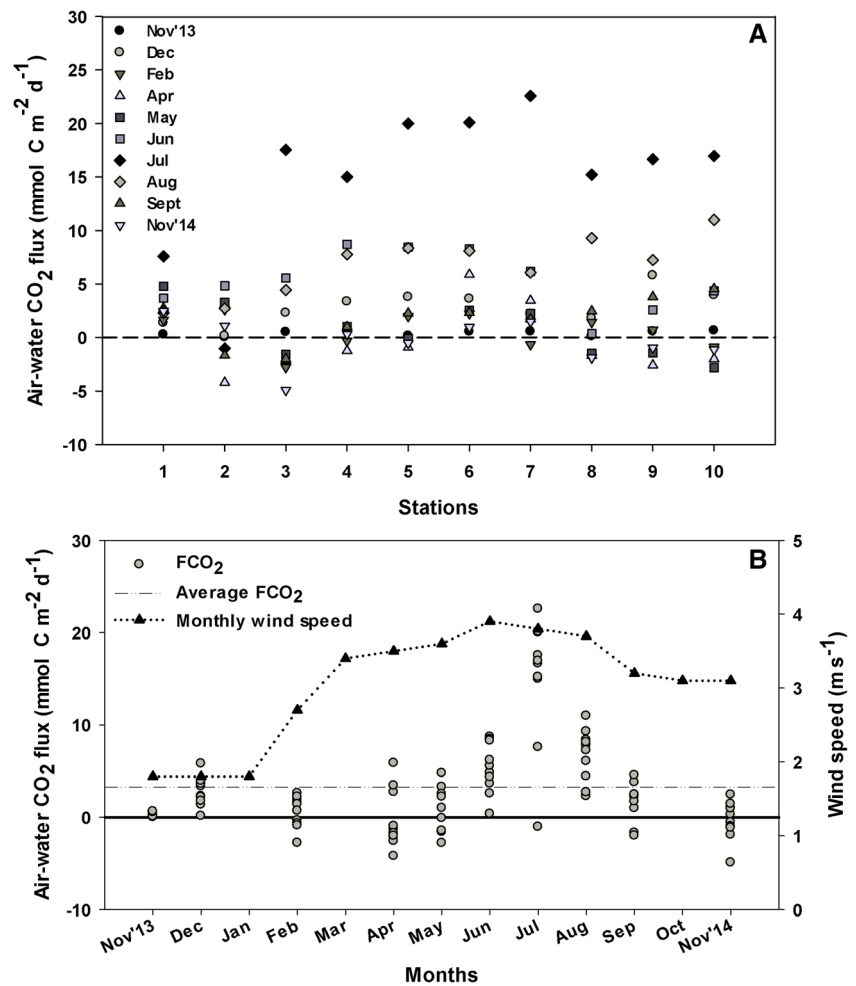
In general, NEP values switched between net heterotrophy and net autotrophy during the study period, with values close to balance toward the end of 2014 (Fig. 8). NEP ranged approximately between  $-10$  and  $15 \text{ mmol C m}^{-2} \text{ day}^{-1}$ , with negative values observed in December 2013 and July 2014 and positive values mainly during the upwelling season (April–June). Similar trend was observed for  $\Delta\text{DIC}$  distribution, with a maximum peak in July ( $\sim 19 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) and minimum values estimated in spring and early summer. The annual mean NEP and  $\Delta\text{DIC}$  estimates, with positive values ( $2.2 \pm 7.1 \text{ mmol C m}^{-2} \text{ day}^{-1}$  and  $1.1 \pm 9.8 \text{ mmol C m}^{-2} \text{ day}^{-1}$ , respectively), indicated that San Quintín Bay was a net autotrophic ecosystem during the study period (Table 2).

## Discussion

### Ocean–Bay Interactions and Biological Effects on Carbon Dynamics

The study period (November 2013 to November 2014) took place during the development of an unusual strongly positive temperature anomaly in the North Pacific Ocean, called The Blob, linked to a reduced cooling of the ocean during winter 2013–2014 (Hartmann 2014); this warm anomaly expanded and reached coastal waters in spring and summer 2014 (Bond et al. 2015). The anomalous oceanographic condition in 2014 markedly influenced the local dynamics of coastal waters off Baja California, where changes associated to the CCS wind patterns led to a drop in upwelling index values below average, as reflected by the monthly negative anomaly in the upwelling index (Fig. 2). These negative anomalous upwelling conditions occurred on shelf waters off San Quintín Bay, affecting the local ocean–bay interactions that largely influence and control biogeochemical processes within the system (Camacho-Ibar et al. 2003). The anomalous offshore SST condition was clearly observed in water adjacent to San Quintín Bay since May 2014, where the SST anomaly remained above  $0.5 \text{ }^\circ\text{C}$  and reached a peak of  $2 \text{ }^\circ\text{C}$  in mid-fall (Fig. 2d). The anomalous warm water was also observed in the surface temperature within the lagoon, both from discrete samples (Fig. 2a) and as recorded by the oceanographic buoy at the mouth of the bay (Fig. 3a). Considering that temperature is a suitable indicator of coastal upwelling waters flowing into San Quintín Bay ( $\sim 12 \text{ }^\circ\text{C}$ ) (Farfán and Álvarez-

**Fig. 6** Spatial (a) and temporal (b) variability of air–water CO<sub>2</sub> fluxes (mmol C m<sup>-2</sup> day<sup>-1</sup>) during the sampling period in San Quintín Bay. Triangles and the dashed black line represent monthly wind velocity (m s<sup>-1</sup>). The zero line represents the equilibrium value of CO<sub>2</sub> exchanges



Borrego 1983), no strong input of characteristic upwelling waters into the system was recorded during 2014.

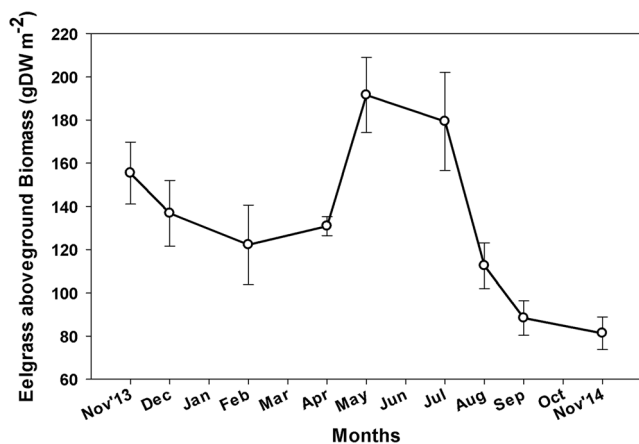
In San Quintín Bay, where the upwelling index is closely associated to wind patterns (Ribas-Ribas et al. 2011), upwelling conditions determine the net fluxes of nutrients between

the ocean and the lagoon, leading to strong changes in nutrient fluxes at the interannual, seasonal, and even single-upwelling-event timescales (Farfán and Álvarez-Borrego 1983; Camacho-Ibar et al. 2003; Hernández-Ayón et al. 2004). “Typical” nitrate concentrations under a “normal” upwelling

**Table 2** Values of observed *p*CO<sub>2</sub> (*p*CO<sub>2</sub> obs, μatm); temperature-normalized *p*CO<sub>2</sub> at 20.1 °C (*p*CO<sub>2</sub>@*T*<sub>mean</sub>); mean area-averaged *p*CO<sub>2</sub> at in situ temperature (*p*CO<sub>2</sub><sub>mean</sub>@*T*<sub>obs</sub>); and calculated values of non-

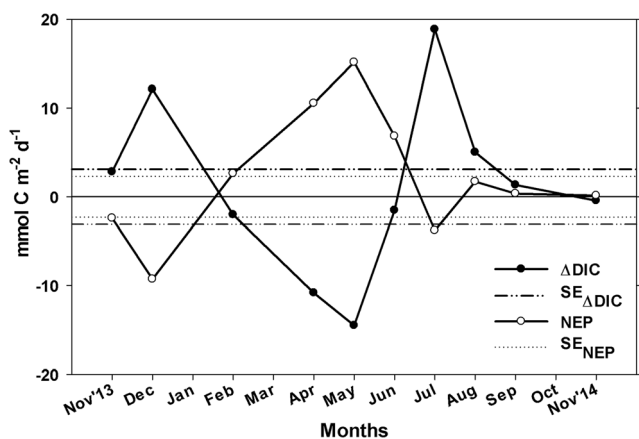
conservative DIC fluxes (ΔDIC, mmol m<sup>-2</sup> day<sup>-1</sup>), air–water CO<sub>2</sub> fluxes (FCO<sub>2</sub>, mmol m<sup>-2</sup> day<sup>-1</sup>), and net ecosystem production (NEP, mmol m<sup>-2</sup> day<sup>-1</sup>) in San Quintín Bay during the study period

	<i>p</i> CO <sub>2</sub> obs	<i>p</i> CO <sub>2</sub> @ <i>T</i> <sub>mean</sub>	<i>p</i> CO <sub>2</sub> <sub>mean</sub> @ <i>T</i> <sub>obs</sub>	ΔDIC (mmol m <sup>-2</sup> day <sup>-1</sup> )	FCO <sub>2</sub> (mmol m <sup>-2</sup> day <sup>-1</sup> )	NEP (mmol m <sup>-2</sup> day <sup>-1</sup> )
November 2013	456	502	478	2.80	0.39	-2.41
December	587	688	449	12.10	2.83	-9.27
February	443	474	492	-2.03	0.59	2.62
April	387	425	479	-10.83	-0.29	10.54
May	425	444	504	-14.50	0.64	15.14
June	656	643	537	-1.54	5.30	6.84
July	919	873	554	18.85	15.06	-3.79
August	646	559	608	5.02	6.72	1.70
September	482	417	608	1.33	1.68	0.35
November 2014	382	358	593	-0.45	-0.32	0.13



**Fig. 7** Seasonal average values of aboveground biomass (g DW m<sup>-2</sup>) of seagrass *Zostera marina* in San Quintín Bay during the study period

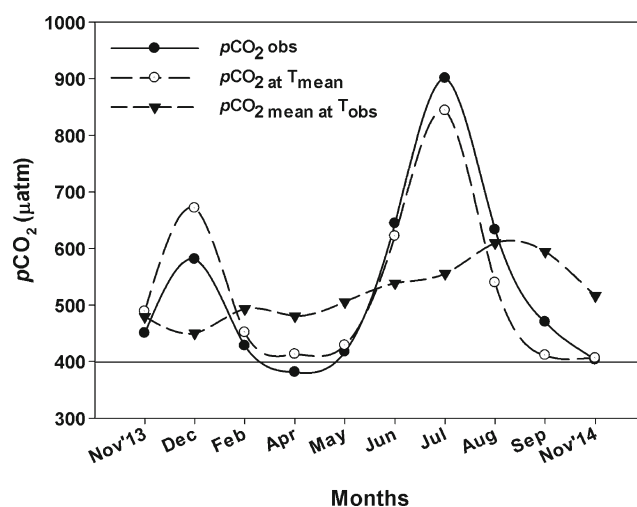
condition are in the range between 3 and ~13  $\mu\text{M}$  (Hernández-Ayón et al. 2007a, b). Camacho-Ibar et al. (2003) reported nitrate concentrations of ~0.5 to ~0.9  $\mu\text{M}$  in summer (weak upwelling), with a larger contribution of ammonium to the dissolved inorganic nitrogen (DIN) pool. On the other hand, Hernández-Ayón et al. (2004) described interannual fluctuations in nutrient dynamics in San Quintín Bay's western arm during and after the 1997–1998 El Niño event. These authors observed that in Bahía Falsa (BFa), ammonium acted as a nitrogen source to the ocean during warm conditions, with significant benthic ammonium pulses (18–45  $\mu\text{M}$ ), while nitrate concentrations were low (0.8–2.0  $\mu\text{M}$ ). In our study, nitrate concentrations (data not shown) were approximately  $0.6 \pm 0.4$  and  $0.4 \pm 0.4$   $\mu\text{M}$  on an annual basis and in spring–summer, respectively, similar to levels observed in San Quintín Bay in summer and warm El Niño conditions. These data suggest that the warm anomaly in 2014 maintained San Quintín Bay under a summer-like condition throughout the study period, characterized by weak upwelling events with



**Fig. 8** Non-conservative DIC fluxes ( $\Delta\text{DIC}$ ) using a one-box model and net ecosystem production (NEP) computed from DIC fluxes.  $\Delta\text{DIC}$  and NEP estimates indicate that San Quintín Bay switched between net heterotrophy (organic respiration) and net autotrophy (inorganic uptake), approaching a balance from November 2013 to 2014

higher seawater temperatures and depletion of incoming nutrients from adjacent shelf waters, relative to normal conditions. Under this scenario, nutrient recycling from sediments resulting from the decomposition of organic matter by in situ biota (via benthic fluxes) likely plays a key role as an autochthonous source of nitrogen and inorganic carbon for N-limited primary producer communities. The larger variations observed in pH and %DO from the buoy, particularly during the upwelling season (April–June), are consistent with this assumption, reflecting changes in biological production probably associated with a higher nutrient availability within the lagoon (Fig. 3b, c).

The distribution of carbon system parameters also reflects the importance of internal biogeochemical processes in San Quintín Bay in response to the anomalous oceanographic condition, as clearly seen in spring and summer (Fig. 4a–d). The internal supply of nutrients apparently linked to benthic fluxes during spring possibly stimulated a net autotrophy (i.e., primary production) that led to the decrease in DIC and  $p\text{CO}_2$ , with the consequent rise in pH (Fig. 4a, c). A notably NDIC decrease at the inner arms of the bay was observed in spring months (Fig. 5a), which can be attributed to degasification and carbon uptake by macrophyte photosynthesis, previously reported by Ribas-Ribas et al. (2011). Higher DIC and  $p\text{CO}_2$  coupled with lower pH during summer jointly suggest the predominance of a net heterotrophy (aerobic respiration), probably enhanced by the rise in water temperature and higher autochthonous organic matter levels produced previously. These results are consistent with the seasonality of  $p\text{CO}_2$  at in situ temperatures, similar to the temperature-normalized  $p\text{CO}_2$  (Fig. 9), and clearly indicate the dominance of biological processes on  $p\text{CO}_2$  in the whole system ( $T/B = 0.3$ ), which is typical of areas with marked seasonal changes in



**Fig. 9** Observed  $p\text{CO}_2$  ( $p\text{CO}_2$  obs, black circle line), temperature-normalized  $p\text{CO}_2$  at 20.1 °C ( $p\text{CO}_2@T_{\text{mean}}$ , white circle dashed line), and the mean area-averaged  $p\text{CO}_2$  at in situ temperature through the year ( $p\text{CO}_2_{\text{mean}}@T_{\text{obs}}$ , black triangle dashed line)

biological activity (Takahashi et al. 2002). Our findings suggest that despite the warm anomaly condition, temperature was not the driving force that controlled the  $p\text{CO}_2$  distribution in San Quintín Bay, with just a minor effect on the magnitude of air–water  $\text{CO}_2$  fluxes during the study period. However, temperature fluctuations may directly and indirectly affect net production and respiration rates in coastal ecosystems (e.g., decomposition rates, enzyme-catalyzed cell metabolism) (Testa et al. 2013). Therefore, the offshore anomalous SST condition observed in the lagoon could have directly influenced the magnitude of these biological activities.

The  $\text{CO}_2$  exchange estimated during 2014 resulted in  $\text{CO}_2$  sea–air outgassing mainly during the summer season, while the rest of the year was slight or close to balance (Table 2). Our findings are consistent with other studies in coastal ecosystems that showed overall annual air–water  $\text{CO}_2$  fluxes close to balance, with higher fluxes in summer (Chen and Borges 2009). The higher  $\text{CO}_2$  flux observed in our study during the upwelling season ( $\sim 5 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) was far lower than fluxes reported for San Quintín Bay during intense upwelling events ( $\sim 50 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) by Ribas-Ribas et al. (2011). The low DIC concentrations at the mouth of the bay ( $\sim 2000 \mu\text{mol kg}^{-1}$ ), similar to normal oceanic seawater values, in comparison with intense upwelling measurements ( $\sim 2150 \mu\text{mol kg}^{-1}$ , Ribas-Ribas et al. 2011), suggest the absence of upwelling waters largely influenced by offshore conditions. Given the previously mentioned data, we propose that the spatial and temporal variability in net sea–air  $\text{CO}_2$  fluxes estimated in San Quintín Bay during 2014 probably reflected the biogeochemical carbon transformations driven primarily by benthic ecosystems.

#### Carbon Balance and NEP Changes during 2014

The tendency in net ecosystem metabolism (system status) either toward export (net autotrophic) or import (net heterotrophic), as well as in dissolved and particulate matter, represents the net effect of physical and biological processes that contribute to organic carbon balance in coastal aquatic ecosystems (Testa et al. 2013). On an annual basis, the metabolic balance of Mediterranean-climate coastal lagoons located within the CCS upwelling system are considered as net heterotrophic systems, largely associated with the tidal exchange of adjacent shelf waters and coastal systems (Smith and Hollibaugh 1997; Camacho-Ibar et al. 2003; Delgadillo-Hinojosa et al. 2008). In San Quintín Bay, while most studies have reported a net heterotrophic status explained by the import of labile phytoplanktonic carbon which fuels ecosystem respiration (e.g. Hernández-Ayón et al. 2004; Ibarra-Obando et al. 2007), net autotrophic conditions have been observed during intense upwelling events (Ribas-Ribas et al. 2011). The NEP and carbon balance ( $\Delta\text{DIC}$ ) estimates reported here revealed an evident seasonality in the system's status, which

shifts from net heterotrophy in winter and summer to net autotrophy mainly during the upwelling season (Fig. 8). This trend is consistent with previous studies in San Quintín Bay (e.g., Camacho-Ibar et al. 2003; Ribas-Ribas et al. 2011) and is in general agreement with observations in many temperate estuaries and shallow coastal lagoons, where NEP peaks in spring influenced by annual light and temperature cycles (McGlathery et al. 2001; Testa et al. 2013).

Overall, NEP ranges in 2014 were narrower than those reported in earlier studies for this site (Camacho-Ibar et al. 2003; Hernández-Ayón et al. 2004; Ribas-Ribas et al. 2011). Net heterotrophy values estimated during our study were slightly lower to net whole-system estimates previously reported under normal conditions in San Quintín Bay ( $\sim 14 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) (Camacho-Ibar et al. 2003; Ibarra-Obando et al. 2004), while net autotrophy was between three and six times lower than values reported by Ribas-Ribas et al. (2011) during intense upwelling conditions. The higher net autotrophy reported by Ribas-Ribas et al. (2011) can be explained by the increased ecosystem productivity sensitive to external inorganic nutrient inputs and high  $\text{CO}_2$  concentrations from upwelled waters. In contrast, the temperature rise in 2014 probably favored respiration within the system (Hopkinson and Smith 2005), releasing inorganic carbon and nutrients that stimulated primary production. This production, in turn, yielded organic matter that fueled benthic respiration and internal supply of “recycled” nutrients for primary producer communities. Under this environment, the ecosystem status eventually approaches a balance condition (NEP = 0), where the periods of metabolic imbalance are influenced by the stimulated production or consumption of organic matter, as observed in Fig. 8. On an annual basis, contrary to what would be expected for San Quintín Bay, our positive NEP estimates suggest that primary production dominated the gross metabolism, apparently linked to the regional anomalous condition in 2014 (Table 2). This behavior could be explain due to the following: (1) limited external supply of organic material to account for an excess of respiration (net heterotrophy) over photosynthetic activity and (2) high benthic primary production rates (over respiration rates) fueled by carbon and nutrient release during remineralization within the system.

Benthic communities (i.e., seagrass beds, macroalgae, and benthic microalgae) are often highly productive components that dominate shallow marine ecosystems and play a key role in regulating the turnover rate of carbon and nutrients (McGlathery et al. 2007). San Quintín Bay is a coastal lagoon characterized by extensive eelgrass meadows that largely contribute to the metabolism of the benthic ecosystem, which is the key driver of the metabolic signal (70 %) (Ibarra-Obando et al. 2004). At low nutrient concentrations across the water column (summer-like condition), *Z. marina* is able to efficiently uptake sedimentary nutrient pools via underground

biomass to support its production rates (Sandoval-Gil et al. 2015). Positively increased NEP values coincided with the onset of the eelgrass growth season (Fig. 7) and are associated with seasonal variations in both water temperature and light levels on eelgrass leaves (Cabello-Pasini et al. 2003; Sandoval-Gil et al. 2015). Aboveground eelgrass biomass dropped markedly from July to November 2014; this produced relatively large inputs of residual organic matter available in the water column and local sediments, which stimulated heterotrophy (Testa et al. 2013). This biomass drop resulted in average values below those of the previous fall–winter, probably because of the anomalously warm environment condition (Fig. 7). Similar to seagrasses, the nutrient storage capacity of macroalgae supports high growth rates with low-to-moderate nutrient availability, which contribute organic matter inputs to fuel respiration processes (McGlathery et al. 2013). As expected, a positive  $\Delta$ DIC in mid-summer indicates that the system displayed high  $\text{CO}_2$  levels (Fig. 8), which led to a  $\text{CO}_2$  efflux from the decomposition of organic matter. Although both eelgrasses and macroalgae have been reported as important temporary carbon and DIN sinks at San Quintín Bay (Zertuche-González et al. 2009; Sandoval-Gil et al. 2015), organic matter bioavailability (i.e., labile biomass) drives the metabolic rates and nutrient budgets in coastal ecosystems (Testa et al. 2013). Considering that breakdown rates of macroalgal debris are generally higher (days–weeks) versus those of seagrass detritus (weeks–months) (McGlathery et al. 2013), macroalgae tissues would make a major potential source of DIC to sustain the  $\text{FCO}_2$  values observed in summer.

Based on the seasonal biomass records for the three most abundant macroalgae, i.e., *Ulva* sp., *Gracilaria* sp., and *Chondracanthus squarulosus* in San Quintín Bay in 2014 (Table 3), the organic matter derived from macroalgae biomass from April to August represented approximately 12, 72, and 100 %, respectively (136 t of carbon) (Pacheco-Ruiz, personal communication). Assuming that most

macroalgal detritus remained within the system, carbon fluxes associated with them would be sufficient to support respiration rates between 0.6 and 8.6  $\text{mmol C m}^{-2} \text{day}^{-1}$ —which could explain the peak  $\text{FCO}_2$  levels observed in mid-summer (Fig. 6b)—which contribute around to 45 % of the  $\text{CO}_2$  released into the water column (Fig. 8). The seasonal variation patterns in carbon balance in San Quintín Bay are seemingly linked, at least partially, to macroalgal communities that may temporarily stimulate the net heterotrophic metabolism of planktonic communities. However, other processes that occur both within sediments and at the water–sediment interface (e.g., microphytobenthos metabolism or anaerobic respiration) could be contributing factors on carbon dynamics in this coastal system as well (Ibarra-Obando et al. 2004).

The increased NTA coupled with higher NDIC concentrations, which were observed in the arms of the bay, mostly in winter and fall (Fig. 5), may reflect a major role of these sedimentary exchanges that affect directly or indirectly these quantities in shallow coastal areas (Thomas et al. 2009). Since carbon is added to seawater, as a consequence to sedimentary-improved regeneration of organic materials attributed to temperature and macrophyte production in San Quintín Bay, an increase in DIC could be expected for these seasons. On the other hand, accumulation of this organic matter supply has the potential to stimulate benthic, anaerobic degradation with a large enhancement of total alkalinity release from surface sediments (Thomas et al. 2009). In San Quintín Bay, benthic denitrification (remineralization of organic matter using nitrate as electron acceptor) represents a key sedimentary process coupled with benthic and water column nitrification (the aerobic oxidation of ammonium to nitrate) (Camacho-Ibar et al. 2003). This anaerobic process represents a loss of bioavailable water column nitrogen, reflecting low nitrate concentrations during summer and winter conditions (Camacho-Ibar et al. 2003). Moreover, since denitrification is an irreversible process (i.e., permanently remove reactive nitrogen from

**Table 3** Summary of average values of the contribution of macroalgal-derived detritus biomass to ecosystem pool ( $\text{tDW}\cdot\text{km}^{-2}$ ), residual carbon content ( $\text{g C km}^{-2}$ ), and inorganic carbon fluxes ( $\text{mmol C m}^{-2} \text{day}^{-1}$ ) in San Quintín Bay during 2014

	<i>Z. marina</i>	<i>Ulva</i> sp.	<i>Gracilaria</i> sp.	<i>Chondracanthus</i> sp.
Initial biomass ( $\text{tDW km}^{-2}$ )	191.6	162.7	152.8	7.6
Final biomass ( $\text{tDW km}^{-2}$ )	112.5	144.1	42.8	0.0
$\Delta$ biomass ( $\text{tDW km}^{-2}$ )	79.1	18.6	110.0	7.6
Carbon stock ( $\text{g C m}^{-2}$ )	30.1	6.0	41.8	2.9
Carbon flux <sup>a</sup> ( $\text{mmol C m}^{-2} \text{day}^{-1}$ )	10.9	1.2	8.6	0.6
Coverage area (%)	40	30	30	30
Carbon (%)	38	32	38	38

Calculations were based on coverage area, carbon content (%C), and biomass difference measurements between the spring maximum (April) and the summer minimum (August) biomass for each species. The carbon content for *Gracilaria* sp. reported by Atkinson et al. (1989) was used for red algae, while field carbon data values for *Ulva* sp. were used for San Quintín Bay (unpublished data)

<sup>a</sup> Inorganic carbon fluxes associated to macrophyte communities, assuming that most macrophyte detritus were remineralized within system

ecosystem), contributions of released ammonia by this anaerobic organic matter degradation constitute a net gain of the generated TA, which is of particular importance in shallow coastal areas (Thomas et al. 2009). This is evident, for example, in the observed values of TA in bSQ in fall 2014 (Fig. 5b), where the enhanced primary production from late winter until late summer stimulated anaerobic processes within the sediments, releasing large amounts of TA. Accordingly, the effect of DIC added by decaying biological activity is buffered by this increasing release of TA that prevented a strong pH decline and that maintained  $p\text{CO}_2$  values close to balance (Fig. 5c). As mentioned before, these results support the conclusion that benthic release of recycled carbon and nitrogen pools is probably fueled by biological activity in San Quintín Bay during the warm anomaly in 2014 and may explain the increased TA and DIC values observed at the water column toward the arms of the bay. Further processes that may enhance TA in coastal environments are the production of organic bases from microalgae or the dissolution of calcium carbonate. Early studies in San Quintín Bay have already reported the contribution of organic bases from microalgae to the titration alkalinity (Hernández-Ayón et al. 2007b; Ribas-Ribas et al. 2011). However, the calculated TA from pH (buoy data), salinity, and DIC measures suggests that TA values are not affected by organic alkalinity, with changes around  $\pm 7 \mu\text{mol kg}^{-1}$  from the mouth toward the arms of the bay. On the other hand, in benthic environments dominated by seagrass meadows,  $\text{CaCO}_3$  dynamics can also play an important role in carbon balance variations (Barron et al. 2006). Nevertheless, recent observations of the carbonate content in the sediments of San Quintín Bay by Ribas-Ribas et al. (2011) suggest that inorganic carbon precipitation or dissolution does not contribute significantly to internal DIC biogeochemical fluxes in this system. It can be concluded that benthic fluxes on surface sediments probably play a key regulatory role in the whole ecosystem through their storage and transformation capacity of organic matter and nutrients, which is favored by the anomalously warm environmental condition. So, a better understanding is needed about sedimentary processes and the role of benthic habitats to integrate the biogeochemical response of carbon dynamics in these environments to climate variations at a regional scale.

## Summary

The atypical oceanographic condition developed in the North Pacific during 2014 led to a negative anomaly of the upwelling index in coastal waters off Baja California, which markedly influenced the local dynamics within this region. As a result, we observed a continuous summer-like season (weak upwelling condition) in San Quintín Bay during the study period (November 2013 to 2014). Despite the warm anomaly,

temperature was not the key driver of the  $\text{CO}_2$  outgassing in this shallow system, largely influenced by the high seasonal variability in biological activity. San Quintín Bay acts as a source of  $\text{CO}_2$  to the atmosphere in 2014 ( $3.3 \pm 4.8 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) with the higher positive fluxes mainly observed in summer months ( $9.0 \pm 5.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ). The spatial and temporal variability estimated in net air–water  $\text{CO}_2$  fluxes during 2014 appears to reflect a “baseline signal” of biogeochemical carbon transformations driven by an ecosystem dominated by macrophytes. On an annual basis, San Quintín Bay was a net autotrophic system during the anomalous warming, with an annual average of  $2.2 \pm 7.1 \text{ mmol C m}^{-2} \text{ day}^{-1}$ . However, the net ecosystem status switched seasonally between net heterotrophy in winter and summer and net autotrophy during the upwelling season (April–June), apparently influenced by the life cycles of the dominant primary producers in response to annual light and temperature cycles.

The warm anomaly favored respiration rates that released inorganic carbon and dissolved nutrients, stimulating organic matter production that fueled benthic respiration and a local supply of recycled nutrients for N-limited primary producers. The seasonal biomass production of macroalgal communities was a potential source of  $\text{CO}_2$  during the study period and probably was the primary contributor to the net ecosystem metabolism in summer. Clearly, the data recorded in San Quintín Bay in 2014 suggest that macroalgal blooms are a potential local source of organic matter to fuel ecosystem respiration; hence, this factor should be taken into account in future investigations related to biogeochemical fluxes and ecosystem status in this shallow system. Eelgrass detritus contributed, to a lesser extent, to the summer net heterotrophy observed; however, in an annual cycle, the net production of *Z. marina* was a key contributor to the whole-ecosystem metabolism in San Quintín Bay. Since the upwelling condition may influence the magnitude of the air–water  $\text{CO}_2$  fluxes, our results clearly indicated that San Quintín Bay is a net source of carbon to the atmosphere regardless of the adjacent oceanic conditions. Our study sheds light on the relative importance of physical processes, biological communities, and environmental conditions in response to carbon dynamics and NEP in a shallow coastal ecosystem under a regional climate anomaly and provides potentially relevant information about global climate change scenarios in similar coastal systems.

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Dinámica de flujos de carbono durante ciclos estacionales anómalos de surgencias costeras en una laguna costera de la región sur del Sistema de la Corriente de California

## CAPÍTULO II

### Dinámica del carbono costero en un océano costero cambiante: Bahía San Quintín, un caso de estudio en la región sur del sistema de surgencias de la Corriente de California

#### OBJETIVO PARTICULAR

1. Caracterizar los patrones temporales de variación de los flujos de intercambio de CO<sub>2</sub> aire-agua y del estatus metabólico de Bahía San Quintín durante distintos ciclos estacionales atípicos de surgencias costeras, con la finalidad de describir las principales implicaciones de las anomalías climáticas estudiadas y la dinámica marina regional en el control de la biogeoquímica del ciclo del carbono costero en este ambiente.

\* **Trabajo en preparación (primer borrador):** Ávila-López *et al.* (2017). *Coastal carbon dynamic in a changing coastal ocean: San Quintín Bay, a study case in the southern California Current Upwelling System.*

#### RESUMEN

La comprensión de los patrones temporales en los procesos físicos y biogeoquímicos durante años anómalos es útil para determinar la sensibilidad de los ecosistemas a posibles escenarios futuros en las aguas costeras del mundo. Para describir el papel de las variaciones en la dinámica marina regional y su implicación en los cambios del sistema de carbono costero, se estudiaron, junto con el análisis de propiedades hidrográficas locales, las tendencias espaciotemporales en los flujos de intercambio de CO<sub>2</sub> aire-agua (FCO<sub>2</sub>) y la producción neta del ecosistema (NEP, siglas en inglés) en una laguna costera de Baja California. Climatológicamente, la actividad de las surgencias en las costas de Baja California durante los años estudiados (2002, 2004, 2005 y 2014), influenciados por diversos regímenes de cuenca como el enfriamiento del evento La Niña, el fuerte evento de aguas del subártico durante 2002-2006 y el

calentamiento superficial atípico provocado por la anomalía cálida del sur de California; fue inusual pero no sin precedentes dentro de su variabilidad natural. Se observó una fuerte y rápida respuesta ecosistémica en Bahía San Quintín durante los distintos eventos anómalos de surgencia estudiados, con variaciones estacionales e interanuales en FCO<sub>2</sub> y NEP principalmente influenciadas por la velocidad del viento, el origen de las aguas de surgencia y el régimen climático dominante. El estatus metabólico de la bahía osciló entre valores de -13 a 35 mmol C m<sup>-2</sup> d<sup>-1</sup>, indicando claramente un cambio estacional entre los procesos dominantes de producción (autotrofia neta) y respiración (heterotrofia neta) de materia orgánica, observados principalmente durante la temporada de máxima actividad de surgencias costeras y los meses de verano-otoño, respectivamente. Bahía San Quintín fue una fuente neta de carbono durante todas las estaciones de surgencias costeras estudiadas, con valores de 1.6 ± 1.2 a 12.2 ± 10.8 mmol C m<sup>-2</sup> d<sup>-1</sup> a lo largo del sistema, principalmente influenciado por la condición ambiental local. Aparentemente, la concentración de carbono inorgánico disuelto (DIC, siglas en inglés) en el agua advectada por surgencia podría ser una característica clave que contribuyó en gran medida a los patrones de distribución de carbono y a la respuesta del ecosistema en la bahía, que mostró cambios en la condición metabólica del ecosistema sensibles a la intensidad de la surgencia costera y a las condiciones de la oceanografía regional. La disminución de la velocidad del viento y, por consiguiente, la intensidad de la surgencia ante las proyecciones de calentamiento global, pueden afectar particularmente la distribución biogeoquímica del carbono en este sistema poco profundo.

**Palabras clave:** Flujos de CO<sub>2</sub> aire-agua; Surgencia costera; Metabolismo del ecosistema; Régimen climático; Sistema de la Corriente de California

### **Coastal carbon dynamic in a changing coastal ocean: San Quintín Bay, a study case in the southern California Current Upwelling System**

*Ávila-López et al., en preparación. Primer borrador.*

#### **ABSTRACT**

Understanding temporal patterns in physical and biogeochemical processes in anomalous years is useful in determining the sensitivity of ecosystems to possible future scenarios in coastal waters worldwide. We used spatiotemporal trends in air-water CO<sub>2</sub> fluxes (FCO<sub>2</sub>) and net ecosystem production (NEP) in a Baja California coastal lagoon, jointly with hydrographic properties in order to describe the role of regional shift in marine dynamics that involve change in coastal carbon dynamic. Climatologically, coastal upwelling activity off Baja California during the studied years in 2002, 2004, 2005 and 2014, associated with diverse basin-wide regimes like the cooling of La Niña event, the unusual strong subarctic event during 2002-2006 and the atypical surface warming triggered by the Southern California Warm Anomaly; were unusual but not unprecedented within its natural variability. Among altered seasonal cycles of coastal upwelling, we observed a rapid and strong ecosystem response in San Quintín Bay, with seasonal and interannual variation in FCO<sub>2</sub> and NEP mostly influenced by wind speed, upwelling source waters and climate regime. The metabolic balance in the bay clearly indicated an annual shift in dominant processes between organic matter production (net autotrophy) and respiration (net heterotrophy), mainly observed during the peak of the upwelling season and summer-fall, respectively, and ranged between -13 to 35 mmol C m<sup>-2</sup> d<sup>-1</sup>. San Quintín Bay acted as a carbon source during all studied coastal upwelling seasons, ranged between  $1.6 \pm 1.2$  to  $12.2 \pm 10.8$  mmol C m<sup>-2</sup> d<sup>-1</sup> along the system mainly influence by local environmental condition. Apparently dissolved inorganic carbon (DIC) concentration in upwelling-dominated coastal systems was a key feature that largely contributed to carbon distribution patterns within the bay and ecosystem

response, which showed change in ecosystem structure strongly sensitive to coastal upwelling intensity and regional condition. Decreased wind speed and, consequently, coastal upwelling intensity under warming projections, may particularly affect the biogeochemical carbon distribution in this shallow system.

**Keywords:** Air-water CO<sub>2</sub> fluxes, coastal upwelling, ecosystem metabolism, climate regime, California Current System.

## 1. INTRODUCTION

Coastal marine biogeochemistry and ecosystems are closely connected with the physical processes in the upper ocean. Both horizontal and vertical advection and mixing are among the most fundamental physical processes that control the variability of a wide range of physical, biogeochemical and biological properties (e.g., heat, nutrients, oxygen, dissolved carbon, plankton and fish egg) in coastal marine systems worldwide (e.g., Linacre et al. 2010; HESSING-LEWIS and HACKER, 2013; Chapa-Balcorta et al. 2015; Jacox et al. 2015). Nevertheless, how these transportations and budgets affect them are often not well understood, even under current climate conditions due to short period of data availability (García-Reyes et al. 2015). The steady increase in recent decades in the shift of anthropogenic CO<sub>2</sub> and heat from the atmosphere to the marine environment has led to a significant change in the physical and chemical ocean conditions (IPCC, 2013). In particular, coastal upwelling-dominated ecosystems, like the California Current System (CCS), are critical hotspots due to them presenting a strong coupling between atmospheric forcing, ocean circulation, biogeochemical cycling, and food web dynamics, which make them key areas of interest under current and future climate scenarios (Gruber 2011; García-Reyes et al. 2015).

In the coastal systems influenced by the CCS located along the northeastern Pacific Ocean, seasonal coastal upwelling events deliver tidally advected dense and cold waters with high CO<sub>2</sub> level to the nearshore (Checkley and Barth 2009). In these marine environments, upwelled waters are the most important external source of nutrients, organic and inorganic carbon that dominate the functioning and ecosystem structure of its coastal system habitats (e.g., Smith and Hollibaugh, 1997; Ribas-Ribas et al. 2011; HESSING-LEWIS and HACKER, 2013). Warming waters and climate-related changes to ocean dynamics could have significant effects on productivity, organism structure and the transportation of nutrient and organic matter that provide important connectivity across these coastal environments (Leising et al. 2015). Warm anomalies can also be associated to winds strength variability that can strongly influence benthic macrophyte production in seasonal and interannual scales in macrophyte-dominated coastal systems (Champenois and Borges 2012; HESSING-LEWIS and HACKER, 2013). Along the coast of California Current Ecosystems (CCE), different authors have already mentioned the evident impact of altered seasonal cycles in coastal upwelling, resulting in change of local coastal environments (e.g., Schwing et al. 2006; Barth et al. 2007; Ávila-López et

al. 2016). In spite of this, the effects of these changes on marine ecosystems and biogeochemistry of coastal upwelling systems are largely unclear (García-Reyes et al. 2015).

To further understand the regional dynamics and global change in marine-dominated habitats, we investigated temporal patterns in inorganic carbon dynamic and metabolic ecosystem status (net ecosystem production) during atypical upwelling events in a Baja California coastal lagoon located in the southern region of the CCS. These coastal environments are located in a key transitional area where the convergence of different water masses and the associated local dynamics play an important role for the functioning of the entire CCS (Durazo 2015). Coastal upwelling events are more frequent and intense in spring and early summer, when regional winds strengthened (Pérez-Brunious et al. 2007). Even so, northwesterly winds prevail during most of the year occurring coastal upwelling events year-round at the nearshore off BC that bring upwelled waters to coastal systems (Macías et al. 2012).

The study case, San Quintín Bay, is a macrophyte-dominated habitat that provides a range of relevant ecosystem functions and multiple local services of high economic and social value (e.g., Montes-Hugo and Álvarez-Borrego 2007; Jorguensen et al. 2010; Sandoval-Gil et al. 2016). Although coastal system like this are particularly important components of carbon transformation and burial (Bauer et al. 2013), their role in anthropogenic CO<sub>2</sub> emissions and the global carbon cycle is still poorly known. In this context, determining CO<sub>2</sub> exchanges through the air-water interface in coastal environments is critical to understanding regional carbon balance and its interaction with adjacent marine ecosystems, as well as the continued human pressures in costal zones and the global carbon balance (Doney 2010; Cai et al. 2011; Kuwae et al. 2016). In addition, estimating the net ecosystem metabolic status (i.e., the difference between the gross primary production and the ecosystem respiration) provides important insights into the function of coastal ocean ecosystems and biogeochemical processes (Testa et al. 2013), implying relevant issues in uncertainty of marine systems response to global change projections.

The aim of this work is exploring seasonal and interannual changes in air-water CO<sub>2</sub> fluxes (FCO<sub>2</sub>) and net ecosystem production (NEP) in an upwelled-dominated system during different scenarios of anomalous seasonal cycle of coastal upwelling events, to understand the implications of regional shifts in marine dynamics that involve marine

biogeochemical carbon changes and could provide novel measurements for researchers in the knowledge to coastal carbon dynamics in a global changing ocean. Firstly, our analysis is focused on the seasonal variability in coastal upwelling associated with interactions between upwelling source waters and climate regime. Secondly, we described main features in coastal upwelling seasons observed off San Quintín Bay and shed light on the potential influence in coastal carbon dynamic and ecosystem functioning and structure. Finally, regarding the future effects of global change, a hypothetic future environmental scenario for this coastal lagoon is integrally analyzed to highlighting the more relevant hydrographic and biogeochemical properties features observed.

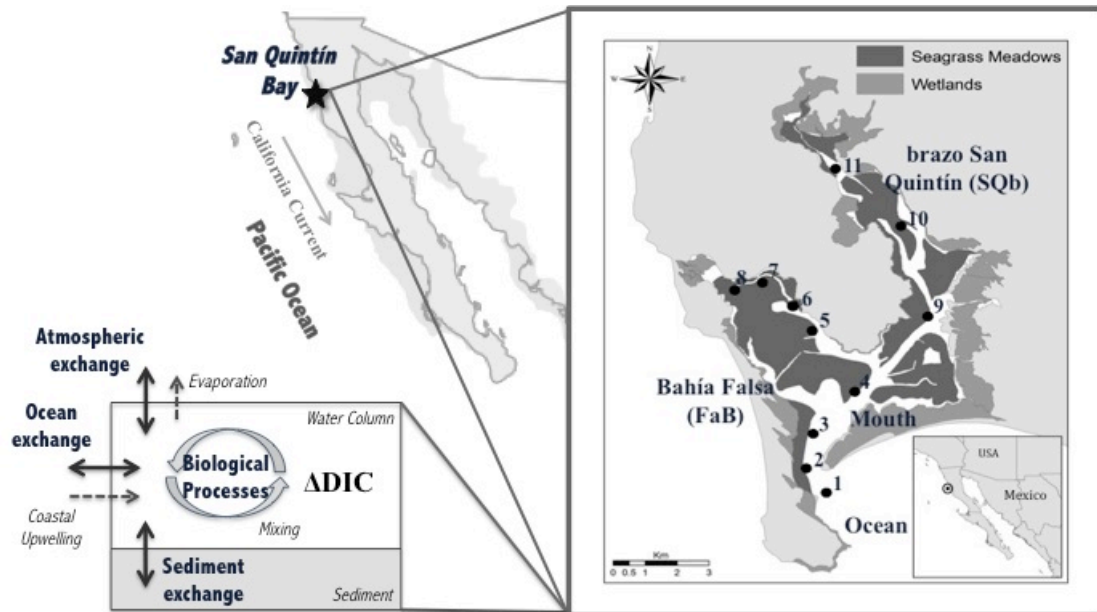
## 2. METHODS AND ANALYSIS

### *Site description*

San Quintín Bay is a hypersaline coastal lagoon located on the northwestern Pacific coast of Baja California within the CCS upwelling system (30° 30'N, 116°W) (Fig.1). It is a shallow well-mixed Y-shaped system with a single narrow connection to the ocean (mouth) and with two arms; the western arm, known as Bahía Falsa (BFa) and the eastern arm, known as Bahía San Quintín (bSQ). This embayment covers an area of approximately 42 km<sup>2</sup> with an average depth of 2 m where water exchange and circulation are mainly dominated by semidiurnal tidal flows (tidal amplitude of 2.4 m during spring tides). Temperature and salinity gradients increase from the bay mouth to the head of both arms like result of water residence time and evaporation processes (Camacho-Ibar et al., 2003). Frequent upwelling events, which intensify during spring and summer months (April to June), supplying by tidal exchange, new nutrients, phytoplankton and DIC to the inner of the coastal lagoon (Ribas-Ribas et al., 2011).

Physical processes mainly control the biogeochemical characteristics of the oceanic influence portion of the bay, while the inner region of both arms are dominated by biological processes (Hernández-Ayón et al., 2007) and benthic metabolism (Ibarra-Obando et al., 2004; Ávila-López et al., 2016). The seagrass *Zostera marina* is the dominant primary producer in San Quintín Bay (Ward et al. 2004), however it can also be observed significant seasonal macroalgal blooms (Zertuche-González et al. 2009) and an increase of phytoplankton biomass during the intense upwelling season located mainly in BFa (Camacho-Ibar et al. 2003). A large shellfish aquaculture, mainly the

Pacific oysters aquaculture (*Crassostrea gigas*), is an important economic activity in the western arm of this system, which is naturally sustained by upwelling events along the year (Emery et al. 2015).



**Fig. 1.** San Quintín Bay location with its different areas: mouth of the bay (Mouth), Bahía Falsa (BFa) and Bahía San Quintín (bSQ). Numbers indicate sampling stations along the system in studied years. The lower panel (left) shows the major fluxes and processes contributing to dissolved inorganic carbon (DIC) budget for this coastal lagoon.

### *Field sampling and water column measurements*

The role of San Quintín Bay as a carbon source or sink in different coastal upwelling conditions was investigated by setting a network of 11 fixed stations across the system (Fig.1). Spatial and temporal variations were examined comparing anomalous events in four years (2002, 2004, 2005 and 2014) during two marked upwelling seasons. The samples were carried out during both the upwelling season (US) (April to June) in 2002, 2004, 2005 and 2014; and the non-upwelling season (NUS) (August to November) in 2004 and 2014. At each station, discrete water samples were collected for carbonate system analyses. Seawater samples were stored in 500 mL borosilicate bottles and preserved with 100  $\mu$ L saturated mercuric chloride ( $\text{HgCl}_2$ ). Bottles were sealed with Apiezon grease to prevent evaporation and contact with the atmosphere. Dissolved inorganic carbon (DIC) was measured following the coulometric method described by Johnson et al. (1987), while total alkalinity (TA) was measured with the

potentiometric method described by Hernández-Ayón et al. (1999). Accuracy and precision were assessed prior to both the DIC and the TA analysis, using Certified Reference Material (CRM) for DIC provided by Dr. Andrew Dickson from Scripps Institution of Oceanography (Dickson et al. 2003). The reference material gave an average difference relative to the certified maximum value of  $4 \mu\text{mol kg}^{-1}$  of DIC (a measurement error of 0.2%) and  $5 \mu\text{mol kg}^{-1}$  of TA, with a measurement error of 0.2%. In order to remove evaporation signal, DIC values were normalized for salinity (NDIC) using the corresponding average salinity for each sampling period from the most oceanic signal (station 1) (Tabla 2). Partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) was calculated applying the pair DIC-TA measured, with a precision of  $p\text{CO}_2$  was  $\pm 5 \mu\text{atm}$ , using the CO2Sys.xls program developed by Lewis and Wallace (1998). The dissociation constants were the proposed by Mehrbach et al. (1973) as refitted by Dickson and Millero (1987).

At each station, surface water samples (20 mL) were collected to quantify nutrients concentrations ( $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ). The samples were filtered through GF/F fiberglass filters, collected in plastic tubes and frozen for subsequent nutrient analysis in the laboratory. Surface seawater temperature (SST) was determined with thermographs (HOBO, Onsetcomputers, USA) that were anchored at the mouth and at the heads of bSQ and BFa (stations 1, 11 and 7, respectively) (Fig.1) during 2002, 2004 and 2005; and using a handheld multiparameter probe (YSI Pro Plus, USA) at the time of seawater sampling during 2014. The salinity of the samples was determined using a salinometer (AUTOSAL Guildline) in 2002, 2004 and 2005; and with a handheld multiparameter probe (YSI Pro Plus, USA) at the time of seawater sampling during 2014. The multiparameter probe was calibrated prior to each field trip following the manufacturer's recommendations. Water column samples were conducted during high tide in order to eliminate variations due to tidal condition. The water residence time ( $\tau$ ) was calculated with a one-box model, as described by Camacho-Ibar et al. (2003) for San Quintín Bay.

In order to observe the characteristics of local oceanographic conditions in each sample period, the monthly upwelling index for coastal waters off San Quintín Bay ( $30^\circ\text{N}$   $119^\circ\text{W}$ , Pacific Ocean Station) was obtained from the National Oceanic and Atmospheric Administration (NOAA) (NOAA/NMFS Pacific Fisheries Environmental Laboratory), available online at <http://upwell.pfeg.noaa.gov>. The coastal upwelling

index greatly contributes to our understanding of physical-biological coupling in eastern boundary current systems (Schwing et al. 1996), and represents the offshore Ekman transport based on geostrophic wind stress data, which approximates the amount of water upwelled from the base of the Ekman layer. Since upwelling has a cumulative effect on ecosystem productivity and structure (Bograd et al. 2009), we also computed a cumulative upwelling index (CUI) based on integrating the mean daily upwelling indices at 30°N 119°W, that highlight the potential relevance in local impact. The climatological mean (1967-2015) CUI and an annual normalized CUI anomaly (CUIA) series was computed for the region off San Quintín Bay, following the procedure described by Schwing et al. (2006). Additionally, climatological means of potential temperature (°C) and salinity diagram for sampled years were obtained through the analysis of hydrographic data collected off the western coast of the Baja California (BC) peninsula (since 1997 to present) by the Mexican California Current Investigations (Investigaciones Mexicanas de la Corriente de California, IMECOCAL) program. Vertical distribution patterns were used to highlight the properties of regional water masses presented across the line 107 of the IMECOCAL sampling grid, located in coastal waters off San Quintín Bay.

### *Air-sea carbon flux calculations*

Air-sea carbon fluxes ( $FCO_2$ ) were estimated according to the following equation:

$$FCO_2 = k \alpha (\Delta pCO_2) \quad (1)$$

Where  $k$  is  $CO_2$  transfer velocity;  $\alpha$  is the  $CO_2$  solubility coefficient in seawater (Weiss 1974); and  $\Delta pCO_2$  is the difference between the partial pressure of  $CO_2$  in water and air ( $\Delta pCO_2 = pCO_{2water} - pCO_{2air}$ ).

The parameter  $k$  was computed using the parameterization proposed by Ho et al. (2006) as a function of short-term steady winds velocities:  $k=0.266u_{10}^2 (600/Sc)^{1/2}$ , where “ $u_{10}$ ” is the wind velocity at a height of 10 m, and “ $Sc$ ” is the Schmidt number. The  $pCO_{2air}$  value used was according to the study period in each sampling condition (Table 1), using the Pacific Ocean Station base data (POCN30) (30.0°N; 135.00°W), available from NOAA (NOAA-ESRL Cooperative Air Sampling Network) ([http://www.esrl.noaa.gov/gmd/dv/site/site\\_table2.html](http://www.esrl.noaa.gov/gmd/dv/site/site_table2.html)). Monthly wind velocity was obtained from a weather station located in San Quintín Bay.

Positive  $\text{FCO}_2$  values indicate gas fluxes from water to the atmosphere, while negative values indicate fluxes from the atmosphere to water. Since the calculation of  $\text{pCO}_{2\text{water}}$  involved a standard error of  $\pm 20 \mu\text{atm}$ , the error associated with the  $\text{FCO}_2$  estimate was  $\pm 0.03 \text{ mmol C m}^{-2} \text{ d}^{-1}$  when wind velocity was 8%.

### *Whole-system metabolism calculation*

In order to determine the system's apparent net biogeochemical performance for carbon, the biogeochemical budget model according to Gordon et al. (1996) was used to estimate non-conservative DIC fluxes ( $\Delta\text{DIC}$ ) in water column, following the one-box model procedure described in Camacho-Ibar et al. (2003) for San Quintín Bay. The whole-bay mean values (stations 3 to 10) and the outermost stations (1 and 2) from the mouth of the bay value were used like the bay and the ocean end-members, respectively. Net ecosystem production (NEP) was calculated from the estimate non-conservative DIC fluxes, however, since  $\Delta\text{DIC}$  values are attributed not only to the difference between production and respiration rates of organic matter, but also to net  $\text{CO}_2$  exchanges with the atmosphere ( $\Delta\text{DIC}_g$ ) and  $\text{CaCO}_3$  precipitation and dissolution ( $\Delta\text{DIC}_c$ ), NEP was estimated as follows:

$$\text{NEP} = -(\Delta\text{DIC} - \Delta\text{DIC}_g - \Delta\text{DIC}_c) \quad (2)$$

However, the contribution of  $\text{CaCO}_3$  precipitation and dissolution on NEP was assumed to be negligible ( $\Delta\text{DIC}_c = 0$ ) in the present study, based on results observed in carbonate sediment contents by Ribas- Ribas et al. (2011).

## **3. RESULTS**

The work presented here examines the primary physical and biogeochemical mechanisms controlling the air-sea  $\text{CO}_2$  fluxes and the net ecosystem metabolism in San Quintín Bay, an upwelling-dominated coastal lagoon off Baja California, México, for two different seasonal upwelling conditions: the upwelling season (US) (April-June) and the declined upwelling season (NUS) (August-November). Additionally, four years of altered seasonal cycle are highlighted for comparison: a) the end of the La Niña event in 2002; b) the strong subarctic regime of 2002-2006 in 2004; c) the delayed coastal upwelling in 2005; and d) the warming anomaly in 2014.

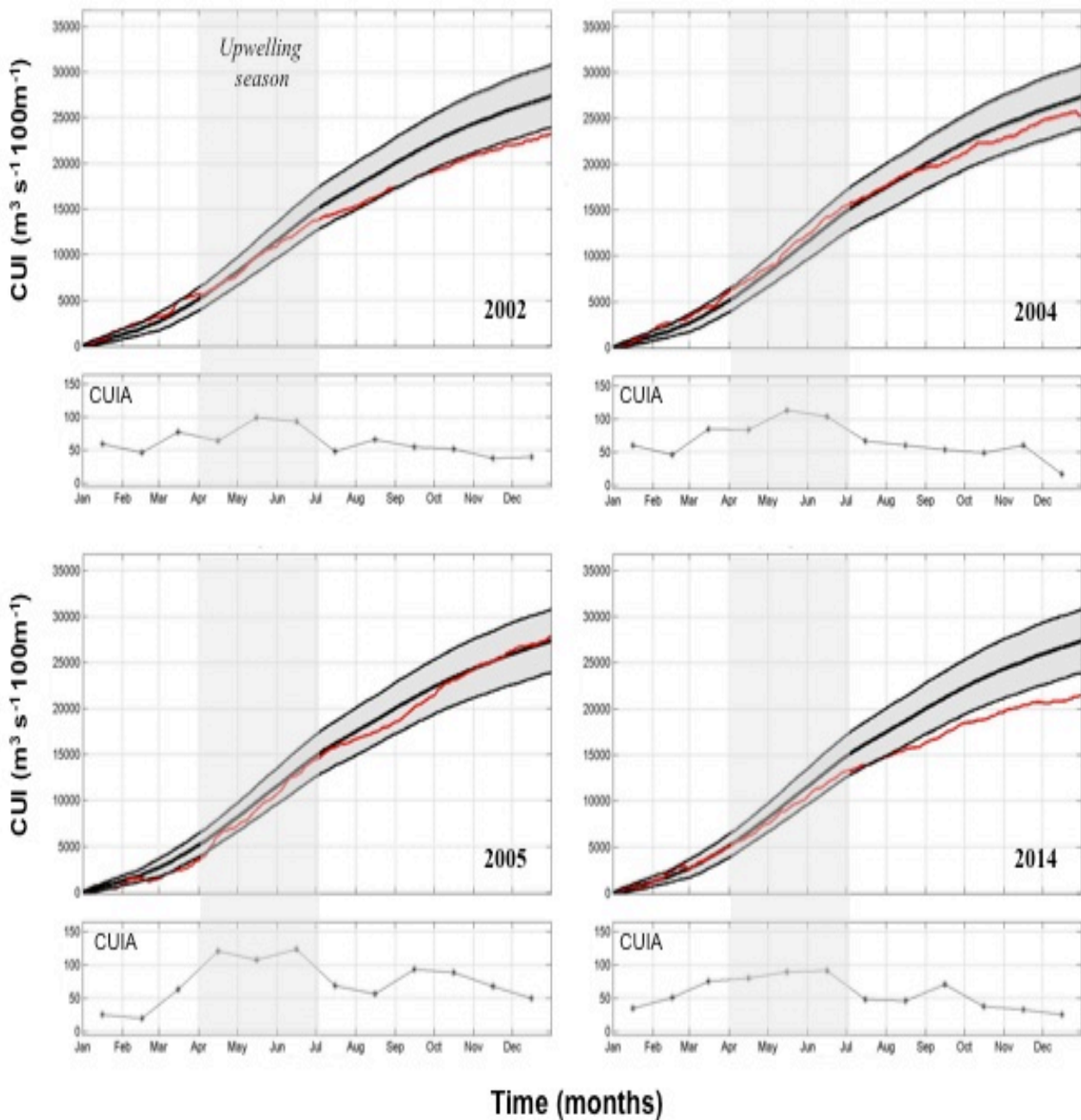
### *Characteristics and patterns of coastal upwelling waters*

In coastal waters off San Quintín Bay, 2005 upwelling season presented the maximum average upwelling index ( $216 \pm 23 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ ) followed by 2004, 2014 and 2002 periods ( $183 \pm 25 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ ;  $160 \pm 15 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$  and  $154 \pm 47 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ , respectively) (Table 1). In annual scale, 2014 was the year that presented weaker intensities of upwelling ( $95 \pm 50 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ ), while the respective annual means in 2002, 2004 and 2005 were  $103 \pm 43 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ ,  $113 \pm 53 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$  and  $128 \pm 50 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ . On the other hand, annual mean values of upwelling index anomaly were  $-16 \pm 23 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ ,  $-6 \pm 25 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ ,  $9 \pm 39 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$  and  $-23 \pm 26 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$  in 2002, 2004, 2005 and 2014, respectively (Table 1). Similar to upwelling index, maximum negative upwelling index anomalies were observed in 2014, while 2005 showed the maximum positive patterns in the study periods.

**Table 1.** Summary of seasonal average ( $\pm$ SD) of hydrological properties: **UI**, upwelling index ( $\text{m}^3 \cdot \text{s}^{-1} / 100 \cdot \text{m}^{-1}$ ); **UIA**, upwelling index anomaly ( $\text{m}^3 \cdot \text{s}^{-1} / 100 \cdot \text{m}^{-1}$ ); and **W**, wind speed ( $\text{m} \cdot \text{s}^{-1}$ ) in adjacent waters of San Quintín Bay during the different regional events analyzed. The whole system average of: **FCO<sub>2</sub>**, air-water CO<sub>2</sub> fluxes ( $\text{mmol m}^{-2} \cdot \text{d}^{-1}$ ) ( $\pm$ SD); and **NEP**, net ecosystem production ( $\text{mmol m}^{-2} \cdot \text{d}^{-1}$ ) ( $\pm$ SE) in each studied period is also presented.

Year	Large-scale event	UI ( $\text{m}^3 \text{ s}^{-1} / 100\text{m}^{-1}$ )	UIA ( $\text{m}^3 \text{ s}^{-1} / 100\text{m}^{-1}$ )	W ( $\text{m s}^{-1}$ )	FCO <sub>2</sub> ( $\text{mmol m}^{-2} \text{ d}^{-1}$ )	NEP ( $\text{mmol m}^{-2} \text{ d}^{-1}$ )
2002	LN- SAW	154 (47)	-26 (15)	4.5	4.0 (6.0)	25.8 (4.2)
2004	SAW	183 (25)	4 (11)	5.0	10.7 (3.6)	13.3 (2.0)
2004	SAW	90 (15)	-20 (33)	3.5	2.10 (0.7)	0.0 (3.9)
2005	SAW	216 (23)	36 (26)	6.2	12.2 (10.8)	28.2 (3.6)
2014	SCWA	160 (15)	-30 (29)	3.6	2.5 (2.7)	15.2 (3.1)
2014	SCWA	80 (38)	-19 (24)	3.1	1.6 (1.2)	-4.5 (8.8)

The climatological positive CUI values series show the large-scale winds upwelling favorably year-round off Baja California (Fig.2).

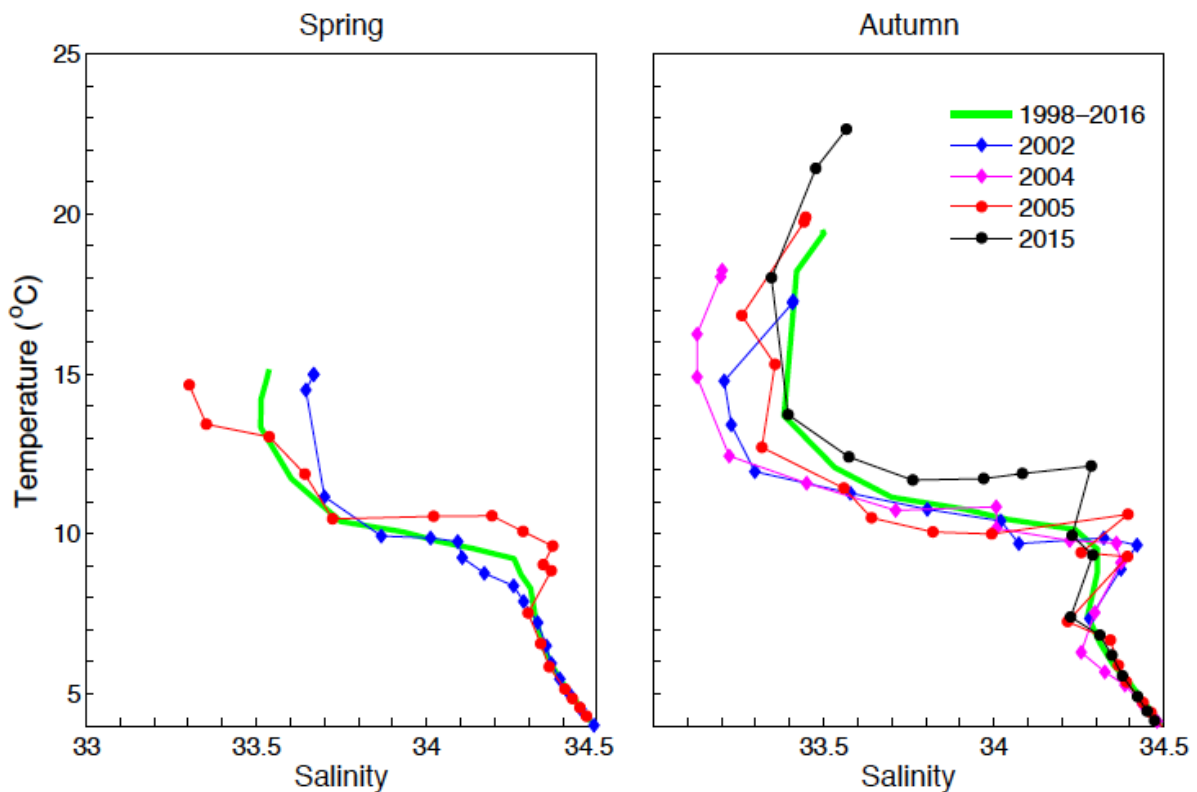


**Fig. 2.** Cumulative upwelling index (CUI:  $\text{m}^3 \cdot \text{s}^{-1} \cdot (100 \text{ m})^{-1}$ ) for location off San Quintín Bay ( $30^\circ\text{N}$ ;  $119^\circ\text{W}$ ) in the California Current. Mean and its respective standard deviations are shown for data series of 1967-2015 (black solid curves) and each study year (red curve). The panels below show the annual normalized CUI anomaly for the date of maximum mean upwelling (defined as the maximum slope of the climatological CUI) in each period. The shaded period represents the months of maximum favorable wind upwelling events (upwelling season).

There is significant variance in CUI over the period recorded (1967-2015) in this latitude, with the series sampled near the climatology condition during all the upwelling

season. Seasonal trends at the end of the year in 2002 and 2014 show greatest anomalous deviations with large shifts from the regional climatology. Upwelling peaks occurred during the favorable months upwelling season in May (2002 and 2004) and June (2005 and 2014), where 2005 shows the earlier and intense start of the seasonal upwelling. Interestingly, the year 2005 was preceded by a winter season with anomalously low CUI than normal mean, allowing the CUI for this season to reach the climatological mean by July. In contrast, 2004 CUI was preceded by a winter season with slightly high CUI than normal mean, reached the climatological mean in the end of July (Fig.2).

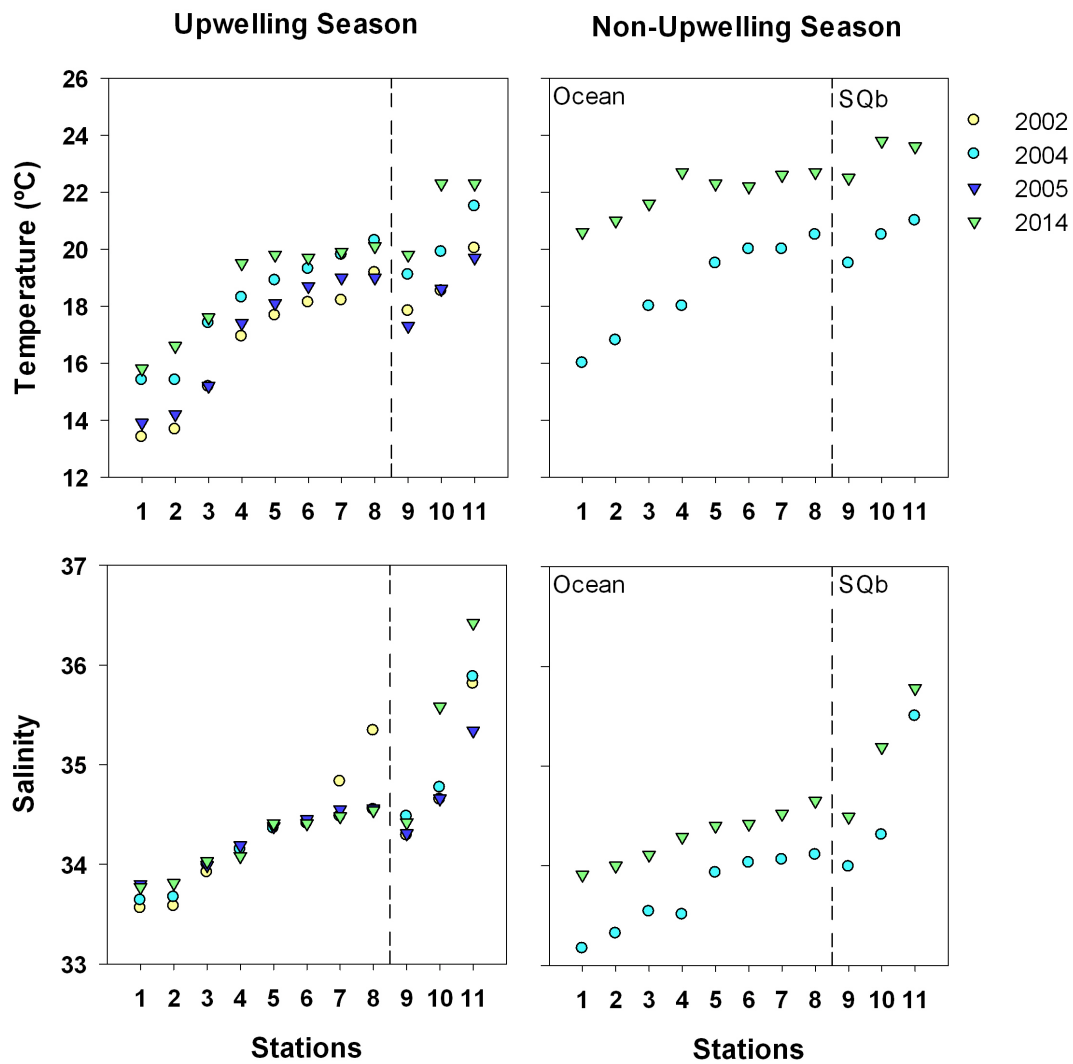
Near the surface across the marine area off San Quintín Bay, annual mean potential temperature ( $^{\circ}\text{C}$ ) versus salinity diagrams in upwelling season show variance in distributions between years (Fig.3). In general, surface temperatures were around  $18^{\circ}\text{C}$  and salinity shifted between years, presenting the lower values in 2004. Properties of the water mass in Spring of 2005 and 2002 were near the climatological mean with relatively low surface temperatures ( $\sim 15^{\circ}\text{C}$ ) and salinity values around 33.3 and 33.8, respectively. In Fall, the 2002 temperature-salinity diagram presented intermediate characteristics between 2005 and 2004, and a clear increase in 2015 seawater surface temperatures, similar to occurred in 2014. Results mainly show a predominant domain of relatively low temperatures ( $10^{\circ}\text{C} - 21^{\circ}\text{C}$ ) and a range of salinity between 33.1 and 33.7, which apparently identified subarctic waters (SAW) characteristic of the equatorward flow of the CCS (Fig.3). In contrast, 2015 salinity patterns show more dense water mass signal in surface waters with maximum temperatures recorded ( $23^{\circ}\text{C}$ ). As suggested by the temperature-salinity diagram in 2015, similarly in 2014, the influence of warmer and saltier waters during this period was observed to the water column (Fig.3). This modified water could be the results of solar heating and evaporation in the region, as well as mixing with offshore water masses more salty and warmer that converge therein, including the tropical surface water (TSW). Under the surface, characterized poleward flow of the California Undercurrent (CU) could be observed, typically presenting a relative salinity peak in deeper waters ( $\sim 100 - 250\text{ m}$ ), located at the lowest depth in 2015 Fall (Fig.3).



**Fig. 3** Seasonal vertical distribution average values of the temperature (°C) and salinity diagram for the upper 500 m of the water column off San Quintín Bay (line 107.35, IMECOCAL) in the studied periods (2002, 2004 and 2005) and 2015 (no data for 2014), for Spring (left) and Autumn (right) seasons (graph provided by Dr. Reginaldo Durazo).

### *Local physical and chemical environmental water properties*

Increased gradients of temperature and salinity were observed from the mouth (with lower temperatures) to the inner part of both arms (with maximum temperatures) during all seasons and years sampled (Fig.4). During the four US, temperature values ranged between 13.4 to 20.0 °C in 2002; 15.4 to 21.5 °C in 2004; 13.9 to 19.7 °C in 2005 and 15.8 to 22.3 °C in 2014. Similarly, NUS show temperature values ranged between 16.0 to 21.0 °C in 2004, while in 2014 were between 20.6 to 23.6 °C. Average temperature values for 2002, 2004, 2005 and 2014 US were approximately  $17.2 \pm 2.2$  °C,  $18.7 \pm 1.9$  °C,  $17.4 \pm 2.0$  °C and  $19.4 \pm 2.4$  °C, respectively (Table 2).



**Fig. 4.** Seasonal average values of temperature (°C) and salinity, from ocean to the inner area of San Quintín Bay (eastern arm, SQb), during the study periods in favored upwelling condition (spring-early summer) and non-favorable upwelling condition (summer-fall).

On the other hand, average temperature values for NUS were  $19.1 \pm 1.6$  °C and  $22.3 \pm 1.0$  °C to 2004 and 2014, respectively. The 2014 year was the warmer environmental condition in compared with the rest of the periods, while temperatures were lowest in 2005 US event (Fig. 4). During US, temperature values appear to show two trends in the whole bay with higher temperatures in the water column in 2004 and 2014 ( $>15$  °C), while 2002 and 2005 were relatively cooler periods with lower temperatures in the oceanic stations ( $<14$  °C). These differences were more evident at NUS, clearly differing between 2004 and 2014 periods with more than 4 °C higher temperatures at the mouth of the bay during 2014 with respect to 2004, and approximately 3 °C at the inner parts of the bay (Fig. 4).

**Table 2.** Summary of temporal average ( $\pm$ DS) of hydrological and chemical properties observed in the outermost stations (oceanic signal) at San Quintín Bay during the studied upwelling condition: **T**, temperature ( $^{\circ}$ C); **Salinity**; **NO<sub>3</sub><sup>-</sup>**, nitrate ( $\mu$ M); **PO<sub>4</sub><sup>2-</sup>**, phosphate ( $\mu$ M); **DIC**, dissolved inorganic carbon ( $\mu$ mol kg<sup>-1</sup>); and **pCO<sub>2</sub>**, partial pressure of CO<sub>2</sub> ( $\mu$ atm).

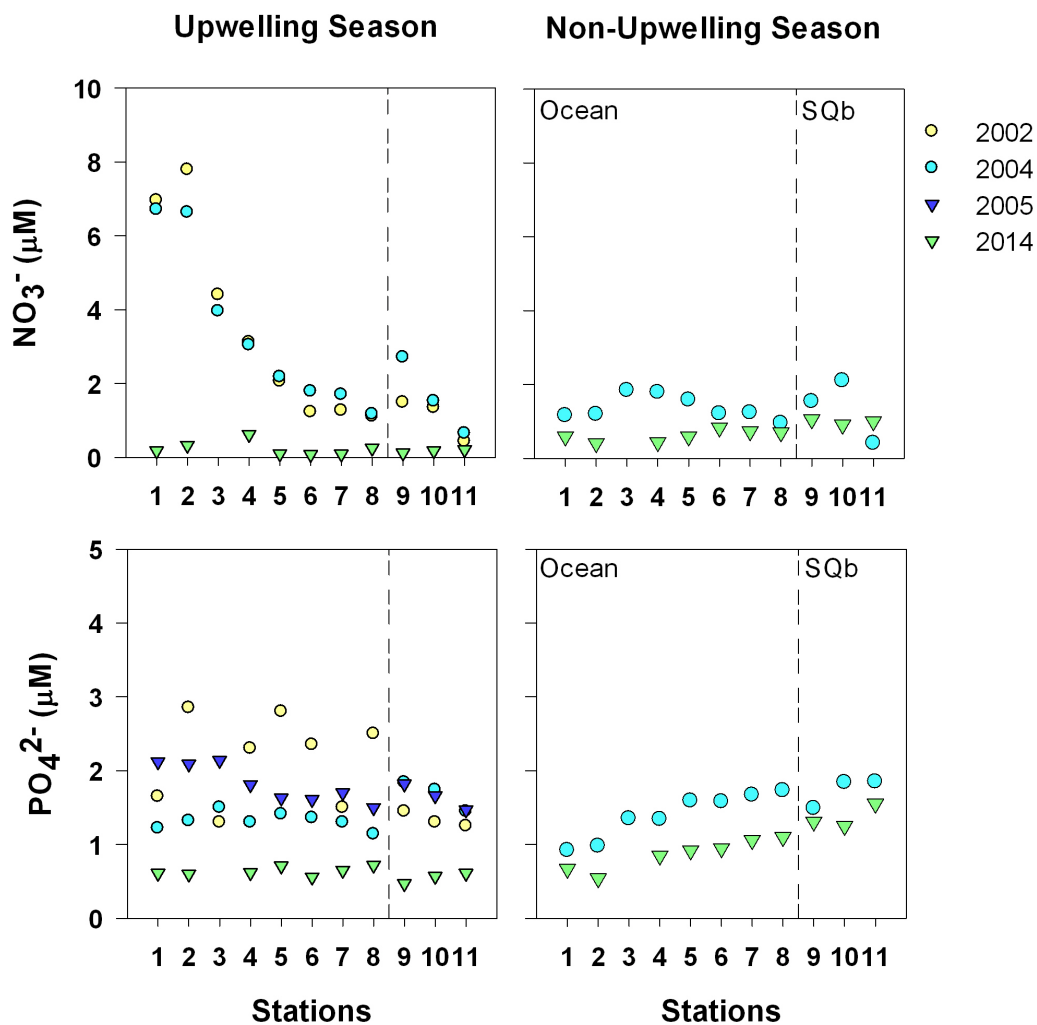
Year	Upwelling Condition	T ( $^{\circ}$ C)	Salinity	NO <sub>3</sub> <sup>-</sup> ( $\mu$ M)	PO <sub>4</sub> <sup>2-</sup> ( $\mu$ M)	DIC ( $\mu$ mol kg <sup>-1</sup> )	pCO <sub>2</sub> ( $\mu$ atm)
2002	Optimal	14.8 (0.2)	33.79 (0.03)	7.4 (2.3)	2.3 (0.8)	2126 (13)	577 (67)
2004	Weak	15.4 (0.0)	33.66 (0.02)	6.7 (0.1)	1.3 (0.5)	2074 (7)	659 (14)
2004	Relaxation	16.4 (0.5)	33.24 (0.11)	1.2 (0.1)	1.0 (0.1)	2044 (11)	461 (26)
2005	Intense	14.0 (0.2)	33.81 (0.01)	12.1*	2.1 (0.1)	2141 (1)	698 (1)
2014	Relaxation	16.2 (0.6)	33.19 (0.03)	0.3 (0.1)	0.6 (0.1)	2080 (6)	563 (14)
2014	Relaxation	20.8 (0.3)	33.96 (0.06)	0.5 (0.1)	0.6 (0.1)	2051 (3)	458 (60)

\* Maximum value observed by Ribas-Ribas et al. (2011) in San Quintín Bay's oceanic stations during the same study period.

Throughout the study periods, seawater salinity showed small temporal differences in US events, with the major variations observed towards the head of BFa in 2002 and SQb in 2004, 2005 and 2014. While for the NUS conditions, again both 2004 and 2014 seasons show noticeable differences in salinity along the system, probably linked to higher temperatures observed in 2014. Salinity ranged between 33.65 to 35.90, 33.56 to 35.81, 33.8 to 35.34 and 33.72 to 36.42, in 2002, 2004, 2005 and 2014 US, respectively (Fig.4). On the other hand, salinity values observed in NUS ranged between 33.17 to 35.50 and 33.91 to 35.77, in 2004 and 2014, respectively. Average salinity values were approximately  $34.45 \pm 0.77$  in 2002,  $34.40 \pm 0.61$  in 2004,  $34.37 \pm 0.44$  in 2005 and  $34.54 \pm 0.79$  in 2014, during the favorable US (Table 2). The higher increased salinities were generally observed at the inner portion of SQb, especially during 2014 with maximum values over 36.

A clear relationship was observed between nutrients concentrations and ocean-bay water exchanges, which suggest the presence of favorable upwelling events in adjacent coastal water off San Quintín Bay, with an exception in 2014 upwelling season (Fig. 5). The highest nutrient concentrations (NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) could be observed at oceanic

stations (1-2) during 2002 and 2004 study periods, however, also an intense upwelling event ( $\sim 12 \mu\text{M}$  of  $\text{NO}_3^-$ ) was developed in the northwestern coastal waters of Baja California during 2005 upwelling season (see Ribas-Ribas et al., 2011). The nitrate concentrations presented predictable trends with a decrease from the ocean stations (between  $7.0\text{-}8.0 \mu\text{M}$  of  $\text{NO}_3^-$ ) towards the heads of BFa and SQb ( $< 2.0 \mu\text{M}$  and  $< 1.0 \mu\text{M}$  of  $\text{NO}_3^-$ , respectively) mainly in US conditions, while in 2014 US period nitrate values were lower than  $1.0 \mu\text{M}$  in the whole system (Fig.5). In contrast, although in NUS periods nitrate values remained under  $2.0 \mu\text{M}$ , the results suggest a slightly increase from the outermost area of San Quintín Bay to the inner arms of the system.

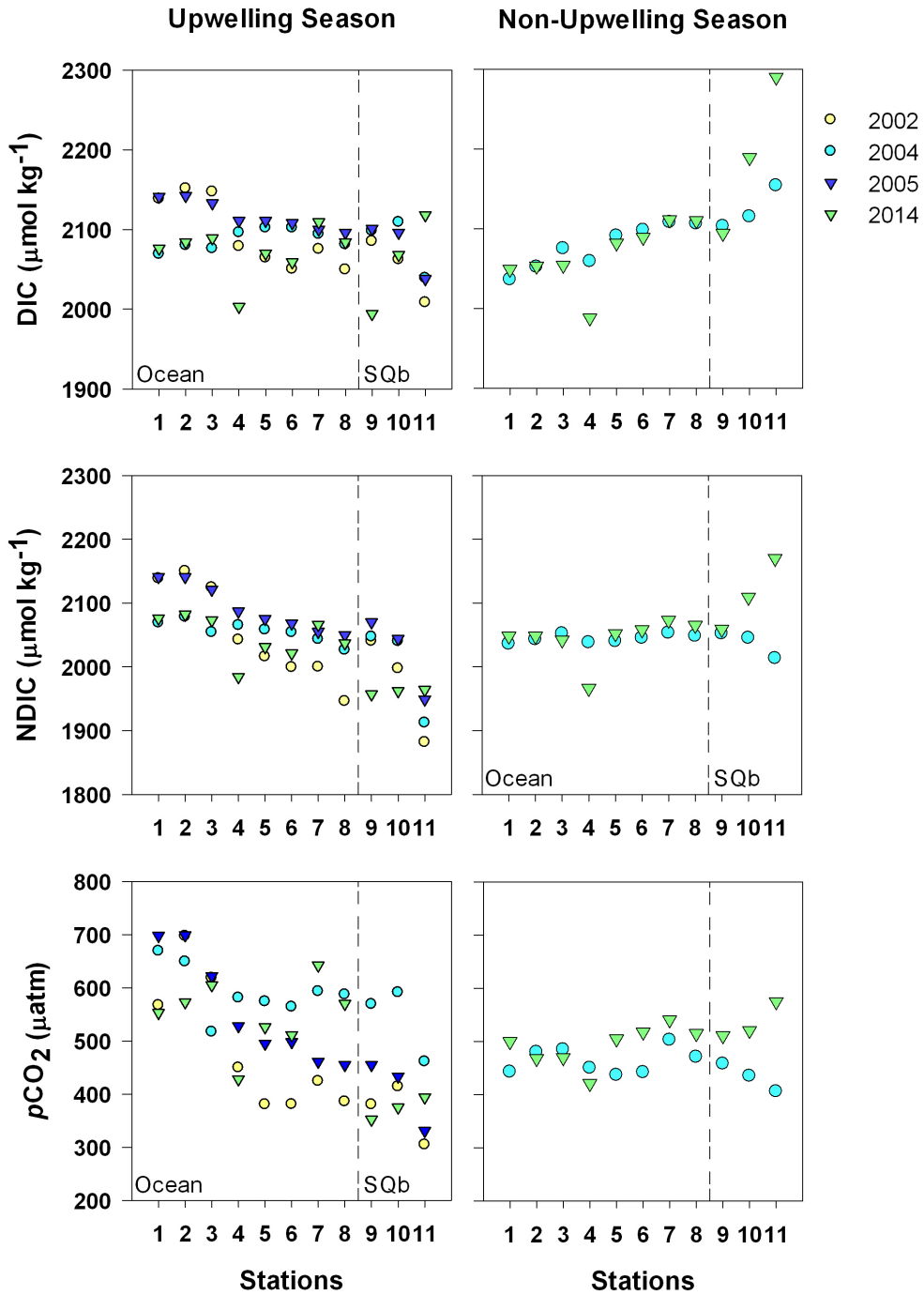


**Fig. 5.** Seasonal and temporal average values of nitrate ( $\text{NO}_3^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ), from ocean to the inner area of San Quintín Bay (eastern arm, SQb), during the study periods in favored upwelling condition (spring-early summer) and non-favorable upwelling condition (summer-fall).

Phosphate results ( $\text{PO}_4^{3-}$ ) show values higher than  $1.0 \mu\text{M}$  for the three main upwelling events during the study periods (2002, 2004 and 2005) with different patterns throughout the lagoon between years. Similarly to nitrate concentration, phosphate remained practically constant throughout the system during the 2014 US condition. A decrease of  $\text{PO}_4^{3-}$  concentrations towards the inner part of the bay in 2005 US was more evident, with maximum values in the outer area of the lagoon ( $2.1 \mu\text{M}$ ), similar to 2002 values observed, probably showing a signal of intense photosynthesis activity rather than organic matter degradation processes. Results under non-upwelling scenarios visibly show an increase into the bay (a respiration process signal), ranging between  $0.5$  and  $2.0 \mu\text{M}$  of  $\text{PO}_4^{3-}$  concentrations, which was consistent with patterns observed in the nitrate concentrations under the same seasons (Fig.5). Results show clearly difference between the six upwelling periods in San Quintín Bay, that suggest three upwelling season events and one suppressed upwelling season (US distributions), and two subsequent non-upwelling periods (NUS) (Table 1). Additionally, the values observed in wind velocity at San Quintín Bay across different study periods showed wind speeds of  $4.5$ ,  $5.0$ ,  $6.2$  and  $3.6 \text{ m}\cdot\text{s}^{-1}$  in 2002, 2004, 2005 and 2014, respectively for the upwelling season; and lower wind values for the non-upwelling season with  $3.5$  and  $3.1 \text{ m}\cdot\text{s}^{-1}$  in 2004 and 2014 periods, respectively (Table 1).

The interannual variation during the study periods also reflects changes in water column DIC concentrations, considering coastal upwelling like an important mechanism that brings waters with high  $\text{CO}_2$  concentrations to the surface marine waters off the lagoon. During favorable upwelling season, higher signal of enrichment DIC waters was observed at oceanic stations and at the mouth of the bay, with concentrations range of  $2038$  to  $2126$ ,  $2074$  to  $2095$ ,  $2078$  to  $2141$  and  $2046$  to  $2081 \mu\text{mol}\cdot\text{kg}^{-1}$ , during 2002, 2004, 2005 and 2014, respectively (Fig. 6). Maximum values of DIC were observed in 2005 period near the mouth of the bay, and the minimum was observed in 2002 event in the inner part of SQb. In contrast, DIC values in 2004 US condition remained throughout the system relatively similar to those observe in the oceanic station, with an average DIC concentration of  $2086 \pm 40 \mu\text{mol}\cdot\text{kg}^{-1}$ . In general, predictable trends were observed for DIC variations with a decrease from the mouth into the bay (Fig.6), more significant in the inner portion of SQb where large eelgrass meadows are located. On the other hand, DIC water column concentrations in 2014 period increase in the eastern arm, suggesting a major temperature control and higher evaporation rates into this shallow area of San Quintín Bay. Similarly trends to 2014 US event were observed into

SQb, with increases between 100 to 250  $\mu\text{mol}\cdot\text{kg}^{-1}$  during non-upwelling seasons (late summer-fall) (Fig.6). Nevertheless, as we expected, results show the lowest DIC concentrations in the open ocean stations under these scenario that is consistent with the hydrological water properties.



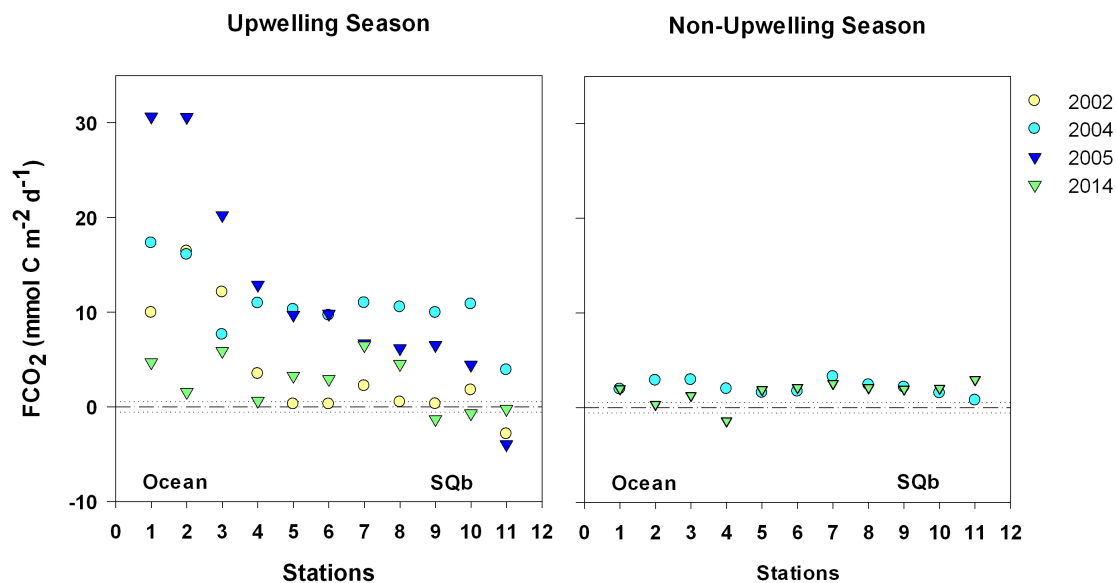
**Fig. 6.** Seasonal and temporal average in inorganic carbon dynamic from ocean to the inner area of San Quintín Bay (eastern arm, SQb), during the study periods in favored upwelling condition (spring-early summer) and non-favorable upwelling condition (summer-fall). **DIC**, dissolved inorganic carbon ( $\mu\text{mol}\cdot\text{kg}^{-1}$ ); **NDIC**, dissolved inorganic carbon normalized ( $\mu\text{mol}\cdot\text{kg}^{-1}$ );  **$p\text{CO}_2$** , partial pressure of  $\text{CO}_2$  ( $\mu\text{atm}$ ).

In addition, decrease variability throughout the bay of all the study seasons observed in DIC normalized by salinity (NDIC), signal of an evaporation effect in DIC measurements. The drop in NDIC along the system was evident during all US, maybe due to the biological uptake signal of the large primary producer communities located within it. In contrast, 2014 show different patterns during both seasons, with an increase mainly toward the inner part of SQb probably due to released DIC to the water column in this shallow area. In general, the DIC temporal patterns at the outermost bay stations seem to indicate two groups of DIC water characteristics during spring and summer time upwelling, with added CO<sub>2</sub> waters content mainly in 2002 and 2005 years, and lower average DIC concentrations for the region during 2004 and 2014 periods, the latest very similar in both sampling seasons (Fig. 6). The estimates of *p*CO<sub>2</sub> were consistent with DIC patterns in the water column, with a coupling decrease with the decreased DIC toward the inner areas of San Quintín Bay (Fig.6). The *p*CO<sub>2</sub> parameter was in the range of 350 to 700 µatm during all sampling period. The upwelling season event in 2004 presented the maximum *p*CO<sub>2</sub> along San Quintín Bay, with the respective estimates close to 700 µatm at the outer area of the mouth. In 2002 event, this variable showed the lowest value of *p*CO<sub>2</sub> (approximately 350 µatm) into the system (Fig.6). It is important to note that the high variability that is presented in the spatial and temporal distribution of *p*CO<sub>2</sub> could be a result of changes in DIC and AT concentrations; therefore additional mixing distribution diagrams analysis (DIC variation respect to salinity) are shown in discussion section.

### ***Temporal variability in carbon dioxide exchanges and metabolic status***

Interannual variations in air-water CO<sub>2</sub> fluxes (FCO<sub>2</sub>) resulted in different scenarios along San Quintín Bay, depending of the sampling period and local environmental condition (Fig.7). In general the whole system acted as a carbon source during all years (Table 1), with the highest values observed in stations located close to the mouth of the bay and open-ocean. During the favorable upwelling season, maximum CO<sub>2</sub> exchanges were observed in 2005 ( $12.2 \pm 3.6 \text{ mmol C}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) follow by 2004 US event ( $10.7 \pm 1.6 \text{ mmol C}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), 2002 ( $2.7 \pm 3.4 \text{ mmol C}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) and finally, 2014 US condition ( $2.5 \pm 1.9 \text{ mmol C}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) (Fig.7). The latest, presenting the lowest values throughout San Quintín Bay and acted as a weak carbon source to the atmosphere in this period. Independently of US sampling time, decreased trends were clearly showed from the

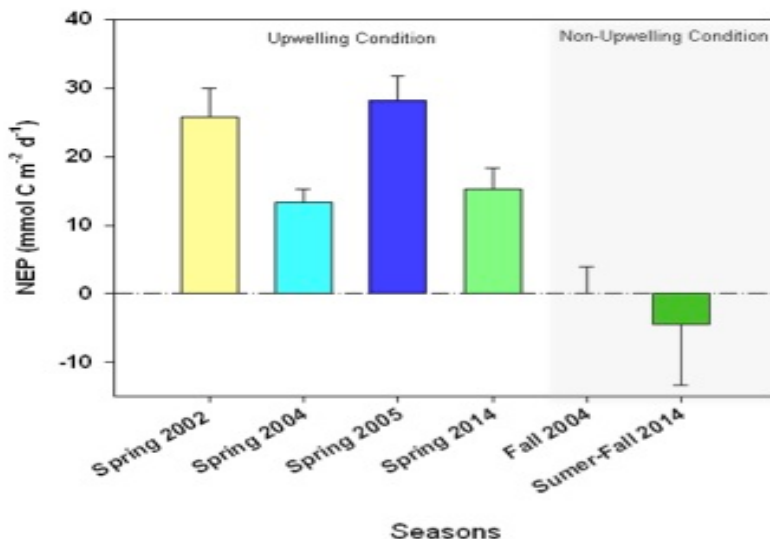
ocean into the bay, with negative carbon fluxes or near to the balance at the inner area of both BFa and SQb. In contrast, during the non-upwelling favorable condition, FCO<sub>2</sub> ranged between -1.4 and 3.3 mmol C·m<sup>-2</sup>·d<sup>-1</sup> (Fig. 7), with average values of approximately 2.1 ± 1.1 mmol C·m<sup>-2</sup>·d<sup>-1</sup> and 1.6 ± 1.2 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, in 2004 and 2014, respectively). As can be seen in the results, in warmer waters seasons, CO<sub>2</sub> degasification in San Quintín Bay remained close to balance, with minor positive FCO<sub>2</sub> values that indicate slightly gas transfer from water to the atmosphere.



**Fig. 7.** Spatial and temporal variability of air-water CO<sub>2</sub> fluxes (mmol C·m<sup>-2</sup>·d<sup>-1</sup>) during the sampling periods in San Quintín Bay. The zero line represents the equilibrium value of CO<sub>2</sub> exchanges and dotted line show the standard error of air-water CO<sub>2</sub> fluxes for the set data.

Estimated NEP clearly showed seasonality and interannual variations in San Quintín Bay (Fig.8). Results demonstrated a switched behavior between net heterotrophy (non-upwelling season) and net autotrophy (upwelling season) in this shallow ecosystem, strongly associated to upwelling conditions. NEP ranged approximately from -13 to 35 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, with negative values observed during non-upwelling season (late summer-fall), and positive values mainly during the favorable upwelling season (April-June) (Fig.8). The seasonal mean values of NEP estimate in San Quintín Bay during all scenarios were 27.4 ± 5.2 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, 17.8 ± 2.0 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, 31.3 ± 3.5 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, 16.7 ± 3.2 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, 1.3 ± 3.9 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, and -3.5 ± 8.8 mmol C·m<sup>-2</sup>·d<sup>-1</sup>, in 2002, 2004 US, 2005, 2014 US, 2004 NUS and 2014 NUS,

respectively (Table 1). Temporal variability in NEP results during the spring seasons seem to show similar trends to DIC concentrations observed at oceanic stations in figure 6; indicative of the functioning marine-dominated coastal systems in this region.



**Fig. 8.** Net Ecosystem Production (NEP) computed from non-conservative DIC fluxes ( $\Delta$ DIC) using a 1-box model. NEP estimates indicate that San Quintín Bay switched between net heterotrophy (organic respiration) and net autotrophy (inorganic uptake) in seasonal and interannual scales, apparently approaching a metabolic balance previous of winter seasons.

#### 4. DISCUSSION

Anomalous upwelling events are critical to the CCE because the coastal upwelling is one of the most important mechanisms that enrich surface waters to maintain its elevated productivity and the structure of the water column and marine habitats (Checkley and Barth 2009). This work was focused to examine coastal carbon dynamics in four years of altered coastal upwelling seasonal cycle in 2002, 2004, 2005 and 2014, associated with diverse basin-wide regimes like the cooling of *La Niña event* (LN), the unusual *strong subarctic event* during 2002-2006 (SAW) (Durazo 2009) and the atypical surface warming triggered by the *Southern California Warm Anomaly* (SCWA) in 2014 (Leising et al. 2015). Seasonal variability in upwelling conditions is mainly affected by equatorward wind patterns and consequent wind stress curl change that are primarily responsible for local oceanographic and chemical conditions (Linacre et al.

2010). Climatologically, coastal upwelling activity off Baja California during the studied years was unusual but not unprecedented within its natural variability (Fig. 2). As expected, the climatological positive CUI values series show the large-scale winds upwelling favorable year-round in the southern region of the CCS (Macías et al. 2012), with a gradual onset of the upwelling that reached its peak during spring-early summer months (*Upwelling Season*). The development of upwelling season in relation with climatological annual cycle of CUI series reflects intra-seasonal variations in upwelling intensity, controlled by the alongshore wind stress patterns (Bograd et al. 2009). Although all upwelling season studied remained near to climatological mean (Fig. 2), the timing and strength of maximum upwelling and its evolution toward the end of the winter season differ between years, apparently related to regional signal anomalies largely affected by climate conditions (i.e., wind patterns and oceanographic conditions) (García-Reyes and Largier 2012). The upwelling index anomalies data reported by NOAA for 30°N supported this assumption, with positive anomalies during upwelling season in 2005 and 2004 ( $36$  and  $4 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ , respectively), and negative anomalies in 2002 and 2014 at the same period ( $-26$  and  $-19 \text{ m}^3 \text{ s}^{-1} 100\text{m}^{-1}$ , respectively) (Table 1).

In regional context, recent descriptive studies exhaustively examine the seasonal and interannual variability of physical and chemical properties of the water column and their associated dynamics for the coastal ecosystem along Baja California Peninsula (e.g., Durazo 2009; Linacre et al. 2010; Macías et al. 2012; Durazo 2015). At the seasonal scale, air-sea exchange and wind patterns modulated coastal upwelling, stratification of the water column and regional circulation patterns (Linacre et al. 2010). Linacre et al. (2010) observed a marked seasonal hydrographic condition with two differenced climatological regimes, one in spring-summer months and a second during summer-fall and winter, respectively related to coastal upwelling-wind driven, mesoscale activity and wind stress patterns. Subarctic waters (SAW) dominate during the peak of the upwelling season in spring and summer, associated to equatorward flow of cold, low salinity and high nutrient concentration waters, which is consistent with observed in temperature-salinity vertical distribution (Fig. 3). During summer and fall, tropical and subtropical influences are commonly observed, linked to the poleward flow of warm, dense and oligotrophic characteristic waters, strengthened in a coastal band connected to the surface and subsurface mesoscale circulation in the CCS (Linacre et al. 2010). In addition to this seasonal variability, at the interannual to decadal time scale, coastal boundaries and upwelling shifted mostly associated with warm and/or cold basin-wide

variability dominated by large climate forcing events (Durazo, 2009; Checkley and Barth 2009). However, a recent study reported that changes in surface water mass properties are related to ENSO (El Niño Southern Oscillation) conditions while wind stress, and therefore upwelling activity, are affecting primarily by decadal scale remote forcing (like the North Pacific Gyre Oscillation) (Macías et al. 2012).

During 2002-2006, a strong subarctic water regime dominated both coastal and oceanic waters of the CCS, noticeably freshening the upper marine waters off Baja California (Durazo 2009). Consistent with patterns observed by Durazo (2009), the excess of SAW was mainly detected during 2004 and 2005 in the temperature-salinity diagrams off San Quintín Bay (Fig. 3), with major anomalies observed in 2004 when deeper freshly waters (> 500 m) were observed in central Baja California. In particular, 2005 was an unusual year during which delayed coastal upwelling along the North U.S. west coast caused critical ecological shift in the nearshore marine ecosystems (Barth et al. 2007). Paradoxically, in coastal waters off Baja California, the intrusion of SAW resulted in large biological activity that caused high productivity along the coastal system (Hernández-Ayón et al. 2010; Ribas-Ribas et al. 2011), probably due to a weak LN state that sustained coastal upwelling off central and southern region of CCS (Durazo 2009). On the other hand, LN condition (increased upwelling) was observed from 1998 until mid to late 2002 in most of the southern region of the CCS (Durazo 2009). During this basin-wide period, Durazo (2009) observed a short-term cooling event in the region occurred in summer 2002, coinciding with the arrival of intense SAW regime, suggesting a major control by local wind processes over regional forcing. Expecting the development of typical features in regional circulation off Baja California (i.e., the alongshore near surface equatorward flows, a subsurface poleward current and coastal upwelling due the northerly winds), probably a mix of cold and nutrient-rich modified waters were carried to surface waters, showing a water mass signal near the climatological mean, which was detected in 2002 studied year (Fig. 3). In general, relatively low surface temperatures, favorable upwelling wind, increased upwelling and high DIC and nutrient concentrations were recorded for the upwelling season in 2002 and 2005 in coastal waters off San Quintín Bay, with relatively lower to moderate conditions in 2004 (Table 1 and 2). For summer-fall conditions in 2004, results showed typical signal for these seasons in physical and chemical properties.

A contrasting climate condition was observed in 2014 year characterized by a warm anomaly regime along the North Pacific Ocean (Leising et al. 2015). The surface warming in coastal waters off Baja California appeared in early spring 2014 season, induced by atmospheric forcing through weaker northeast trade winds and reduced latent heat flux; this warming was strengthened and expanded along the year in the coastal ecosystems (Newton et al. 2016, [http://www.nanoos.org/resources/anomalies\\_workshop/workshop2.php](http://www.nanoos.org/resources/anomalies_workshop/workshop2.php)). The anomalous oceanographic event markedly influenced the local dynamics of coastal waters off San Quintín Bay, affecting the local ocean-bay interactions and biogeochemical processes in this coastal system (Ávila-López et al. 2016). As showed in the vertical distribution of temperature-salinity diagram (Fig. 3), this pattern started as warming near surface waters and evolved toward deeper waters warming, which probably affected water column structure, chemical properties and local dynamic. According with the results obtained in 2014 for this study, warmer surface temperatures, weak local wind trends, decreased upwelling and low CO<sub>2</sub> and nutrient concentrations were recorded in spring-early summer off Baja California (Table 1 and 2), showing a completely different scenario for the California Current nearshore ecosystems compared with previous ones. As suggested in regional conditions examined, identifying the water masses involved in regional dynamic is a key component because the water origin and the characteristics of advected upwelling source waters will contribute differently to the ecosystem response and the water column biogeochemical processes.

Seasonal variation of transported upwelling waters and ocean-bay water exchange in San Quintín Bay is largely controlled by the seasonality in wind intensity and tidal amplitude (Ribas-Ribas et al. 2011). Decreased wind intensity probably induces a reduction in water exchange and higher residence times, which particularly affects biogeochemical distribution in this shallow system (Camacho-Ibar et al. 2003). Using as significant indicators of the local zone the chemical (nutrients and dissolved inorganic carbon) and physical (temperature and salinity) distributions in the water column (Zaytzev et al. 2003; Linacre et al. 2010), an evaluation of coastal upwelling patterns in San Quintín Bay was performed. In general, temperature and salinity patterns show expected trends in hypersaline coastal systems (Delgadillo-Hinojosa et al. 2008), as well as a clear consistency with observed regional condition in all years (Fig. 4). Most notably in 2014 due to the upgrading of warmer surface temperatures along the year, and in 2004 event where trends showed a seasonal evolution of salinity anomaly

associated to the strong SAW event (see Durazo 2009). Based on nutrients and temperatures as proxies widely used for upwelling intensities, 2002, 2004 and 2005 events reflected a coastal upwelling signal off San Quintín Bay; while 2014 event showed a relaxing upwelling condition along the year (Table 2).

Interestingly, two differentiated DIC concentrations were measured in the most oceanic stations sampled despite the marked regional differences in studied events (Table 2). In a first scenario, during 2002 and 2005 events, typical high subsurface waters DIC concentration ( $\sim 2134 \pm 11 \mu\text{mol}\cdot\text{kg}^{-1}$ ) was observed associated with relatively low surface temperatures ( $\leq 15 \text{ }^\circ\text{C}$ ), salinity upper than 33.6 and high nutrients concentrations ( $\geq 6 \mu\text{M}$ ), consistent with data measured in coastal waters during development of intense upwelling events along the CCS ecosystems (e.g., Fassbender et al. 2011; Ribas-Ribas et al. 2011; Muñoz-Anderson et al. 2015). In early upwelling season, the core of the equatorward flows (California Current) is located close to shore, bringing low salinity, temperature and high oxygen and nutrient concentrations during the maximum surface influence of the SAW (Linacre et al. 2010), where poleward flows can variably affect the water sources of the upwelling (Song et al. 2011). In a second scenario, during 2004 and 2014 upwelling season events, DIC concentrations were lower and close to equilibrium values ( $\sim 2011 \pm 10 \mu\text{mol}\cdot\text{kg}^{-1}$ ) in adjacent waters, associated with relatively higher surface temperatures ( $\geq 15 \text{ }^\circ\text{C}$ ) and similar salinity values, showing consistency with relaxation season of coastal upwelling along the CCS (García-Reyes and Largier 2012; Ávila-López et al. 2016). This condition, typical of declined upwelling season (summer-fall to winter) is related to local water sources for coastal upwelling (i.e., shallower source water) associated to farther offshore equatorward flow location and decreasing wind stress patterns (Song et al. 2011). Based on all features mentioned before and using oceanic signal of DIC concentrations as proxy to upwelling intensity, we propose four differentiated upwelling events in examined periods:

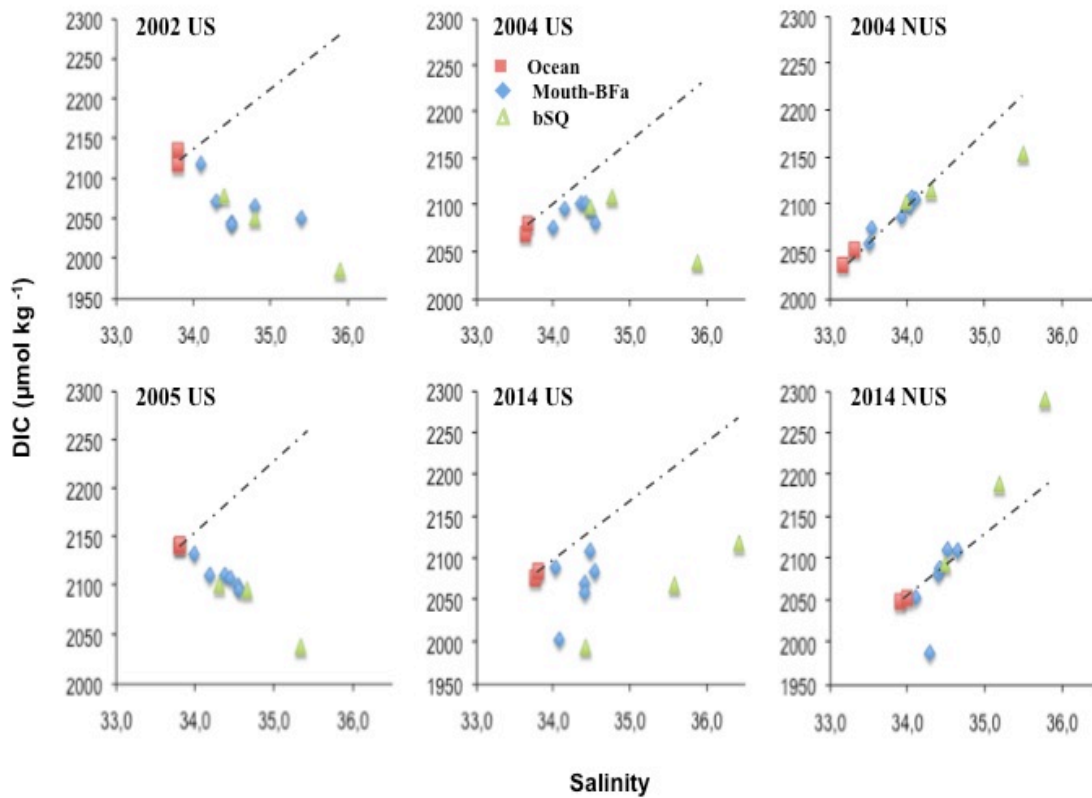
- a) *Intense upwelling event* in 2005, with persistent and intense wind stress ( $\geq 6.0 \text{ m s}^{-1}$ ) and therefore, deeper subsurface waters transported to surface, characterized by low temperatures ( $\leq 14 \text{ }^\circ\text{C}$ ), high nutrient ( $\geq 10 \mu\text{M}$ ) and DIC concentrations ( $\geq 2150 \mu\text{mol}\cdot\text{kg}^{-1}$ ), and high levels of  $p\text{CO}_2$  ( $\geq 700 \mu\text{atm}$ ) in contact with atmosphere nearshore.
- b) *Weak upwelling event* in 2004, intermittent wind stress ( $\sim 5.0 \text{ m s}^{-1}$ ) and the subsequent limited transportation of subsurface waters to upper layer, characterized by

relatively low temperatures (15-16 °C), moderate nutrient (2-7 μM), low DIC concentrations (2050-2100 μmol·kg<sup>-1</sup>) and high levels of pCO<sub>2</sub> (600-700 μatm) in contact with atmosphere nearshore.

**c)** *Relaxation upwelling event* in 2014 and summer-fall seasons, with low wind stress ( $\leq 3.6 \text{ m s}^{-1}$ ) and advected local waters characterized by relatively high temperatures ( $\geq 16$  °C), low nutrient ( $\leq 1 \text{ μM}$ ), DIC concentrations close to surface seawater equilibrium value ( $\leq 2050 \text{ μmol·kg}^{-1}$ ) and low levels of pCO<sub>2</sub> ( $\leq 600 \text{ μatm}$ ) in contact with atmosphere nearshore.

**d)** *Optimal upwelling event* in 2002, with favorable wind stress ( $\sim 4.5 \text{ m s}^{-1}$ ) and vertical advected subsurface waters characterized by moderate temperatures (14-15 °C), relatively high nutrient ( $\sim 8 \text{ μM}$ ), high DIC concentrations ( $\sim 2120 \text{ μmol·kg}^{-1}$ ) and low levels of pCO<sub>2</sub> ( $\leq 600 \text{ μatm}$ ) in contact with atmosphere nearshore.

A remarkable aspect in each of these events was the rapid and strong ecosystem response in San Quintín Bay to changes in physical and biogeochemical conditions, as has been observed in other areas impacted by altered climate regimens in the CCS (e.g., Grantham et al. 2004; Schwing et al. 2006; Thomas and Birckley 2006; Leising et al. 2015). The relationship between chemical properties (like DIC) and salinity has been broadly used in coastal systems to identify processes that can affect the conservative or non-conservative distribution patterns in water column. As suggested in mixing diagrams (Fig. 9), apparently coastal water DIC concentrations in this shallow upwelling-dominated habitat were a key feature that largely contributed to carbon distribution patterns within the bay and ecosystem response. Decreased DIC values below the conservative mixing line (mixing-dominated control) along San Quintín Bay in strengthened carbon upwelling seasons (mainly 2002 and 2005 events), suggested a remove in inorganic carbon probably by intense biological processes that occurred within the system as mentioned previously by others authors, also in nutrient distributions (e.g., Camacho-Ibar et al., 2003; Hernández-Ayón et al., 2004; Ribas-Ribas et al. 2011; Ávila-López et al. 2016).



**Fig. 9.** Distribution of DIC as functions of salinity for the upwelling seasons (US) and relaxation seasons (NUS) studied periods in San Quintín Bay. The mixing lines were calculated for a hypersaline system with only one end-member referred to the outermost ocean station DIC values in each season.

Contrasting trends were observed in studied 2004 and 2014 seasons (Fig. 9), possibly related to lower DIC concentrations exchanged with the adjacent waters, which showed higher variability along the bay that apparently reflected transition conditions from non-conservative distributions toward conservative patterns in summer-fall seasons. This change seems mainly controlled by horizontal advection (i.e., tides condition) and carbon addition processes (i.e., aerobic and anaerobic organic matter degradation) favored by limited exchange and higher residence time in this yearly season (Camacho-Ibar et al. 2003). Interestingly, it seems that temporal patterns observed in mixing diagrams showed the gradual evolution from an external planktonic-fueled to an internal benthic-fueled ecosystem strongly sensitive to coastal upwelling intensity and regional condition, as observed respectively by Ribas-Ribas et al. (2011) and Ávila-López et al. (2016).

Previous results were also supported by temporal trends in estimated NEP ranges that showed significant shift in interannual magnitude of net metabolic status between 2002-

2005 and 2004-2014 ( $\sim 10 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) (Fig. 8). Positive values in all studied events during US indicated that San Quintín Bay was a net autotrophic system (net organic carbon production) dominated by biological processes, independently of the anomalous upwelling event. Higher autotrophy ( $\sim 30 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) was consistent with values observed by Ribas-Ribas et al. (2011) in intense upwelling conditions, probably explained by the large nutrient inputs and high  $\text{CO}_2$  concentrations from upwelled waters that favored ecosystem productivity. During decreased coastal upwelling seasons (NUS), narrower and negative values were observed indicating the dominance of respiration processes (net heterotrophic system) in summer-fall conditions, which are broadly documented for this season in temperate coastal systems (Testa et al. 2013, and references therein). On an annual basis and year-to-year, the metabolic balance in the bay clearly indicated seasonal patterns between net heterotrophy and net autotrophy, mainly observed in summer-fall and upwelling season, respectively (Fig. 8).

According to the results obtained in this study, it would be expected that during weak upwelling events ( $\text{CO}_2$  subsaturated upwelled waters), the metabolic balance of San Quintín Bay reflect a net autotrophic condition, with low or close to the steady state values (Ávila-López et al. 2016). This metabolic status is probably favored by seagrass production, which dominates in coastal environments along the coast of the CCS and positively responds to lower upwelling intensity events (Hassing-Lewis and Hacker 2013; Ávila-López et al. 2016). On the other hand, based on values obtained in this work and previous studies results influenced by LN conditions ( $\sim -14 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) (intense upwelling events) in Ibarra-Obando et al. (2004), annual net heterotrophic conditions would be expected during deeper upwelling events, probably balanced by the net import of particulate organic matter produced in adjacent waters (Camacho-Ibar et al. 2003). These results are similar to the observed by Hernández-Ayón et al. (2010) in marine waters off Baja California, based on an historical  $p\text{CO}_2$  data series (1993-2007). These authors reported clear seasonal and interannual patterns in the region, acting as a carbon source to the atmosphere on annual basis; with positive values of  $\text{CO}_2$  fluxes to the atmosphere (carbon source) mainly in summer and fall, while negative values (carbon sinks) were observed in winter and spring seasons (Hernández-Ayón et al. 2010). This suggests that changes in regional oceanographic condition and upwelling activity (i.e., amplitude and phase) off Baja California, resulting primarily from basin-scale climate variability, drive considerable interannual fluctuations playing a critical role in seasonal function of the ecosystem status.

Shifts in metabolic balance would have important consequences for the efficiency of coastal ecosystems as CO<sub>2</sub> sinks or sources of carbon. The net flux of CO<sub>2</sub> across the air-water interface is largely modulated by this metabolic balance but also by other factors that contribute to this exchange like external inputs of DIC by upwelling, or river inputs, calcium carbonate (CaCO<sub>3</sub>) precipitation/dissolution, and merely thermodynamic effects related to temperature changes or mixing of water masses with different chemical properties (Gazeau et al. 2005). Although coastal ecosystems in upwelling systems (like the CCS) are generally considered source of CO<sub>2</sub> to the atmosphere, coastal waters have been relatively poorly examined (Chen et al., 2013). San Quintín Bay acted as a carbon source during all studied seasons independently to the coastal upwelling conditions, a point also reported by Ávila-López et al. (2016). In whole system scale during US, 2005 presented the greatest estimated FCO<sub>2</sub> ( $12.2 \pm 10.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ), while minimum values were observed in 2014 ( $2.5 \pm 2.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ), coinciding with the highest and lowest upwelling intensity events, respectively (Fig. 7). In summer-fall (non-upwelling condition), the bay acted as a slight carbon source as it was expected for this yearly season. For the four anomalous years, only 2004 and 2005 events were considered high carbon source to the atmosphere based on the FCO<sub>2</sub> criteria proposed by Paulmier et al. (2008) ( $\geq 5.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) for upwelling-dominate waters off Chile. High FCO<sub>2</sub> estimated in 2004 for the whole bay, in contrast with the relatively low DIC concentrations measured, possibly reflected the behavior observed by Chen et al. 2013 in North America and Europe coastal systems, which presented undersaturated waters in term of CO<sub>2</sub> but high CO<sub>2</sub> fluxes values strongly controlled by wind speeds. Another explanation could be the variation in *p*CO<sub>2</sub> resulted from changes in DIC and TA concentrations (data not shown), where 2004 US presented the lowest values observed during the study periods ( $\sim 2200 \text{ } \mu\text{mol kg}^{-1}$ ). Unlike NEP, FCO<sub>2</sub> are not closely related to regional oceanographic conditions, but probably wind patterns, which have significant influence in gas exchange magnitude; and biological processes, played a major role controlling surface CO<sub>2</sub> exchanges at the level of ecosystem, similar to observed in northern California coastal upwelling by Fassbender et al. (2011).

Inorganic carbon dynamic in coastal ecosystems is not only controlled by vertical and horizontal advection and CO<sub>2</sub> exchanges, but also by water temperature, residence time and biological processes, which are associated to the complexity of the biogeochemistry

carbon transformation in these environments (Chen et al. 2013). Regarding the future effects of global change, a downward (upward) trend in coastal upwelling has been projected by different authors for the southern region of the CCS (northern and central areas), mostly influenced by weakened (enhanced) wind speeds affected by poleward migration of ocean high-pressure systems (García-Reyes et al. 2015; Rycakzewski et al. 2015). As mentioned before, in addition to winds strength that largely modulate vertical transport (upwelling source depth) and nutrient supply to photic zone (Jacox et al. 2015), regional circulation associated to the depth of the upwelling cell and the alongshore-currents location, controlled the observed conditions related to the upwelling source waters in the CCS (Song et al. 2011). If we examine integrally the temporal patterns obtained in this study trying to understand how these patterns will change coastal ecosystems status, it might be expected, similar to observed in 2014 event, that weaker upwelling and coastal warming (increased thermal stratification) may limit inorganic carbon and nutrient enrichment of the photic zone (shallower source waters) (Jacox et al. 2015). Limited waters fertilization potentially impacts negatively phytoplankton production, which depends up to 70% on the DIC provided by upwelled waters (biological uptake of DIC and nutrients) in some regions of the CCS (Fassbender et al. 2011). Changes in plankton community composition and size structure from coastal-dominated species (phytoplankton fraction) to associated species to stratified waters and oligotrophic conditions (microplankton fraction) in coastal waters off Baja California from 2007 to 2015 was described by Gonzalez-Silvera et al. (in prep., Ocean Optics Conference XXIII 2016). Consequently, higher organic matter reactivity in lower plankton fraction may imply a decreased signal in primary production (decreased biological uptake of CO<sub>2</sub>) and faster nearshore organic matter turnover, which probably reflect positive carbon fluxes to the atmosphere and lower efficiency in coastal vertical (biological pump) and horizontal (exchange between coastal habitats) carbon transport between adjacent marine waters (Testa et al. 2013).

The increase in limited exchange to adjacent waters (greater residence time) may increase net heterotrophy favored by inorganic carbon and nutrients released to water column from increasing respired material time within the system (Camacho-Ibar et al. 2003); which in turn, favor primary production (net autotrophy), enabling the yield of organic matter that fuels respiration processes. At seasonal and large scales, where organic matter reactivity seems to be more critical than high surface temperatures in this system with upwelling waters dependence and benthic-dominated control (Ávila-López

et al. 2016; this study), ecosystem metabolism tend toward a metabolic balance condition, resulting in a major benthic-dominated metabolism (Fig. 9), favored also by low upwelling conditions. The mentioned above is in general agreement with patterns observed in a LOICZ synthesis of approximately 200 coastal ecosystems worldwide that provided key insight into the global trophic tendency of estuaries and bays toward close to zero net ecosystem metabolism with slightly more autotrophic than heterotrophic systems (Smith et al. 2005), as we observed in undersaturated CO<sub>2</sub> water scenarios in 2004 and 2014 events. Nevertheless, specific dependence not only in latitudinal location and temporal scale, but also in bathymetry, regional oceanographic condition, climate variability, primary production community dominance and local environmental conditions could be important factors that affect metabolic state in coastal systems. Therefore, increased effort in conducting studies regarding different spatial and temporal time-scale processes in these complex and valuable ecosystems is a priority and challenge for the scientific community in order to generate a major confidence understanding of how the coastal ocean and its marine habitats operate in a current and future changing world.

## **5. CONCLUSIONS**

Coastal carbon dynamic in San Quintín Bay is influenced by both local environment and temporal patterns in local oceanographic conditions. During the studied years (2002, 2004, 2005 and 2014), coastal upwelling activity off Baja California was unusual but not unprecedented within its natural variability. Upwelling source water associated to regional forcing, in addition to wind patters (favored and relaxation upwelling conditions) is a critical driver that largely modulated the observed biogeochemical conditions in this coastal lagoon. Furthermore, it seems that DIC concentration in upwelling-dominated coastal systems along Baja California Peninsula could be an important feature that largely contributes to ecosystem response and structure, as it was observed in San Quintín Bay.

Increased coastal upwelling intensity (like 2002 and 2005 studied years) implies the carrying of deeper waters, rich in nutrients and DIC to surface waters that lead an optimal development in primary productivity off Baja California. Intense upwelling also influence ocean-bay interactions, enhanced the ecosystems functioning with external supply of the organic matter produced, inorganic carbon and nutrients that maintained a

metabolic status at local scale in net heterotrophic conditions on annual basis, which suggested an ecosystem mainly fed by external plankton. In a contrasting scenario (weak or relaxation upwelling condition, like 2004 and 2014 periods), ecosystem resulted in numerous anomalies (i.e., low nutrients, low DIC, greatest surface waters temperatures, low inputs of organic matter and higher water residence time) that trigger ecosystem change to net autotrophy dominated by a benthic metabolism (i.e., seagrass meadows, macroalgae and microphytobenthos communities) surplus.

In both contexts, San Quintín bay acted as a carbon source to the atmosphere from higher CO<sub>2</sub> fluxes to lower or close to balanced at local scale, in the first and second scenarios, respectively. Under future projections in a global warming scenario, similar to the observed during 2004 and 2014 periods, this may be a potential future condition in upwelling-dominated coastal systems, where a continuous climate pressure would probably cause significant impact in the carbon budgets and exchanges, and likely in other important biogeochemical cycles, like the nitrogen and oxygen, as well.

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*Dinámica de flujos de carbono durante ciclos estacionales anómalos de surgencias costeras en una laguna costera de la región sur del Sistema de la Corriente de California*

## CAPÍTULO III

### El papel del sedimento en el control biogeoquímico del sistema de carbono en Bahía San Quintín



#### OBJETIVO PARTICULAR

- Examinar la variabilidad espacial y temporal de los flujos de intercambio sedimento-agua del sistema de carbono en Bahía San Quintín bajo diferentes condiciones ambientales locales, con la finalidad de conocer la influencia del metabolismo bentónico y los procesos implicados en el control de la biogeoquímica del carbono y el estatus trófico del sistema.

*\* Suplemento Capítulo 1: Nota Científica*

## CAPÍTULO III

### El papel del sedimento en el control biogeoquímico del sistema de carbono en Bahía San Quintín

*Suplemento Capítulo 1: Nota Científica*

#### RESUMEN

Este trabajo aborda el estudio de la variabilidad espacio-temporal de los flujos de intercambio del sistema de carbono (carbono inorgánico disuelto y alcalinidad total) en la interfase sedimento-columna de agua de Bahía San Quintín. La aproximación experimental de microcosmos estuvo basada en la incubación de núcleos de sedimento obtenidos en distintas zonas de la bahía, bajo condiciones controladas de laboratorio, y en dos estaciones del año (final-invierno vs verano en 2014). Los núcleos de sedimento analizados se seleccionaron bajo distintas condiciones ambientales con el objetivo de determinar el metabolismo bentónico del ecosistema y evaluar los procesos biogeoquímicos que contribuyeron a los cambios en la química de la columna de agua y el sedimento para estos periodos. Los resultados indican que los procesos heterotróficos en los sedimentos de Bahía San Quintín dominan los cambios del sistema de carbono para estos periodos, comportándose como eficaces fuentes de CO<sub>2</sub> hacia la columna de agua. La contribución de CO<sub>2</sub> debida al metabolismo bentónico somero de Bahía San Quintín al estatus metabólico neto del sistema fue del 61% y el 20% para Marzo y Julio de 2014, respectivamente. Esto sugiere que las comunidades bentónicas en los sedimentos profundos, podrían tener un importante papel en la dinámica del sistema de carbono y el estatus trófico en este hábitat costero. Los aportes de CO<sub>2</sub> provenientes de los procesos bentónicos junto con la influencia de las surgencias costeras en la bahía podrían explicar el comportamiento continuo como fuente de CO<sub>2</sub> observado en este sistema costero.

**Palabras clave:** Incubaciones de Microcosmos; Flujos bentónicos; Sistema de Carbono; Metabolismo del ecosistema; Bahía San Quintín.

## 1. INTRODUCCIÓN

La zona costera es un sistema heterogéneo complejo entre tierra y mar abierto, que reacciona en diferentes formas a la dinámica de estos sistemas adyacentes, así como a los cambios globales que se están viendo reforzados en la actualidad por el impacto de la actividad del hombre. En estos ambientes, la biogeoquímica del carbono, y otros nutrientes, está fuertemente condicionada por el metabolismo bentónico del sistema (~70% del total de NEP), asociado principalmente a comunidades de pastos marinos, macroalgas y microalgas bentónicas (e.g., Ibarra-Obando et al. 2004; Barrón et al. 2006; McGlathery et al. 2013). En particular, la producción primaria de las comunidades de macrófitos marinos (pastos y macroalgas) representan en torno al 5% de la producción marina global, pero su biomasa (reservorio del CO<sub>2</sub> removido de la atmósfera y almacenado como carbono orgánico) equivale a dos tercios de la biomasa total oceánica, representando sumideros de carbono mucho más eficaces que el fitoplancton (Duarte et al. 2005). El aumento de las concentraciones de CO<sub>2</sub> en el agua de mar, acoplado a las variaciones de pH en la columna de agua, es mediado en gran parte por la actividad biológica de estos productores primarios, que consumen el CO<sub>2</sub> disuelto y/o el ión HCO<sub>3</sub><sup>-</sup> (Marbá et al. 2006), desplazando el equilibrio químico del carbono inorgánico disuelto (CID) hacia la producción de carbonatos, que son de vital importancia para distintos organismos calcificadores. En este contexto, los ecosistemas costeros dominados por pastos marinos juegan un rol importante en la dinámica del ciclo del carbono y en el destino del CO<sub>2</sub> antropogénico, pudiéndose considerar ecosistemas clave en el control de futuros escenarios climáticos.

Bahía San Quintín es una laguna costera somera (~ 2 m) hipersalina de Baja California, localizada en el Océano Pacífico Norte, fuertemente caracterizada por el intercambio de agua con el océano adyacente y la presencia de extensas praderas de pastos marinos (*Zostera marina*) (Ribas-Ribas et al. 2011). Los eventos de surgencias característicos de la región sustentan el ecosistema de la bahía con el aporte externo de CID, nutrientes y fitoplancton, siendo éste último uno de los principales recursos que permite el desarrollo sustentable de la ostricultura en la bahía (Emery et al. 2015). El conjunto de estos componentes que interactúan dinámicamente en la laguna (i.e., surgencias, pastos marinos y ostricultivos), juegan un papel substancial en la regulación de los procesos biogeoquímicos del carbono, entre otros elementos, en la columna de agua y en el sedimento (Hernández-Ayón et al. 2004; Sandoval-Gil et al. 2016).

En este trabajo, se realizó una primera aproximación de la variabilidad espacio-temporal de los flujos de intercambio del sistema de carbono (CID y alcalinidad total, AT) entre el sedimento y la columna de agua durante Marzo y Julio de 2014, a partir de cámaras de incubación de microcosmos controladas en laboratorio (McGlathery et al. 2001). Los núcleos de sedimento analizados se seleccionaron bajo distintas condiciones ambientales, que incluyeron áreas en interacción con las comunidades de *Zostera marina* y en ausencia de las mismas, así como en zonas influenciadas por ostricultivos y surgencias costeras (Fig. 1); el objetivo principal fue determinar el metabolismo bentónico del ecosistema y evaluar los procesos biogeoquímicos que contribuyeron a los cambios en la química de la columna de agua para este periodo. Además, cabe mencionar que durante 2014, se desarrollaron distintas anomalías excepcionalmente cálidas a lo largo del Pacífico Norte, afectando la dinámica regional y la condición oceanográfica frente a la costa de Bahía San Quintín, lo que condujo a la ausencia de surgencias costeras a lo largo del año (Ávila-López et al. 2016, ver Capítulo 1). Por tanto, el análisis tuvo como objetivo final, explorar la hipótesis propuesta en Ávila-López et al. (2016) que sugiere el papel de los flujos bentónicos de carbono y nutrientes reciclados como un componente clave en el comportamiento de Bahía San Quintín como fuente de CO<sub>2</sub> hacia la atmósfera, en un escenario de intercambio oceánico limitado y el calentamiento de la superficie del agua de mar.

## 2. METODOLOGÍA

### *Descripción del área de estudio*

Bahía San Quintín, es una laguna costera poco profunda (~ 2 m) localizada en la costa oriental del Océano Pacífico en la península de Baja California, México (30° 30'N, 116° W). Principalmente, en este sistema costero se distinguen tres subsistemas que presentan diferencias biogeoquímicas significativas (Camacho-Ibar et al. 2003): la Boca de la bahía, el brazo oeste o Bahía Falsa y el brazo este o brazo San Quintín (Fig. 1). La *boca* de la bahía es la única conexión del sistema con el océano abierto. A través de ella se realizan los principales procesos de intercambio de nutrientes, fitoplancton y carbono inorgánico disuelto hacia el interior de la bahía por acción de las mareas, que oscilan entre 1.0 y 2.5 m (Ribas-Ribas et al. 2011). *Bahía falsa*, con 5.6 Km de largo, se caracteriza por una elevada producción fitoplanctónica (12 mg C m<sup>-3</sup> h<sup>-1</sup>) (Camacho-

Ibar et al. 2003) e importantes floraciones estacionales de macroalgas (Zertuche-González et al. 2009; Ávila-López et al. 2016), que sustentan de forma natural la importante industria acuícola de ostión (*Crassostrea gigas*) que se desarrolla en la región (Emery et al. 2015). En el *brazo San Quintín*, con 11.5 km de largo, se localizan las principales praderas de *Zostera marina*, que crecen en abundancia en toda la bahía, cubriendo aproximadamente el 40% de la extensión superficial del área (~ 42 km<sup>2</sup>) (Ward et al. 2004). Los gradientes de temperatura y salinidad aumentan desde la boca de la bahía hacia el interior de ambos brazos como resultado de la baja precipitación anual, intensos procesos de evaporación y el tiempo de residencia del agua en el sistema, que oscila entre 13 y 26 días durante el verano y el invierno, respectivamente (Camacho-Ibar et al. 2003).



**Fig.1.** Localización geográfica de Bahía San Quintín en la costa noroccidental de la Península de Baja California. Los círculos negros indican los puntos de muestreo seleccionados a lo largo de la laguna costera para marzo y Julio de 2014: Boca de la bahía (BM), brazo San Quintín (BSQ), parte externa Bahía Falsa (o-BF), parte interna Bahía Falsa (i-BF) (modificado de Sandoval-Gil et al. 2015).

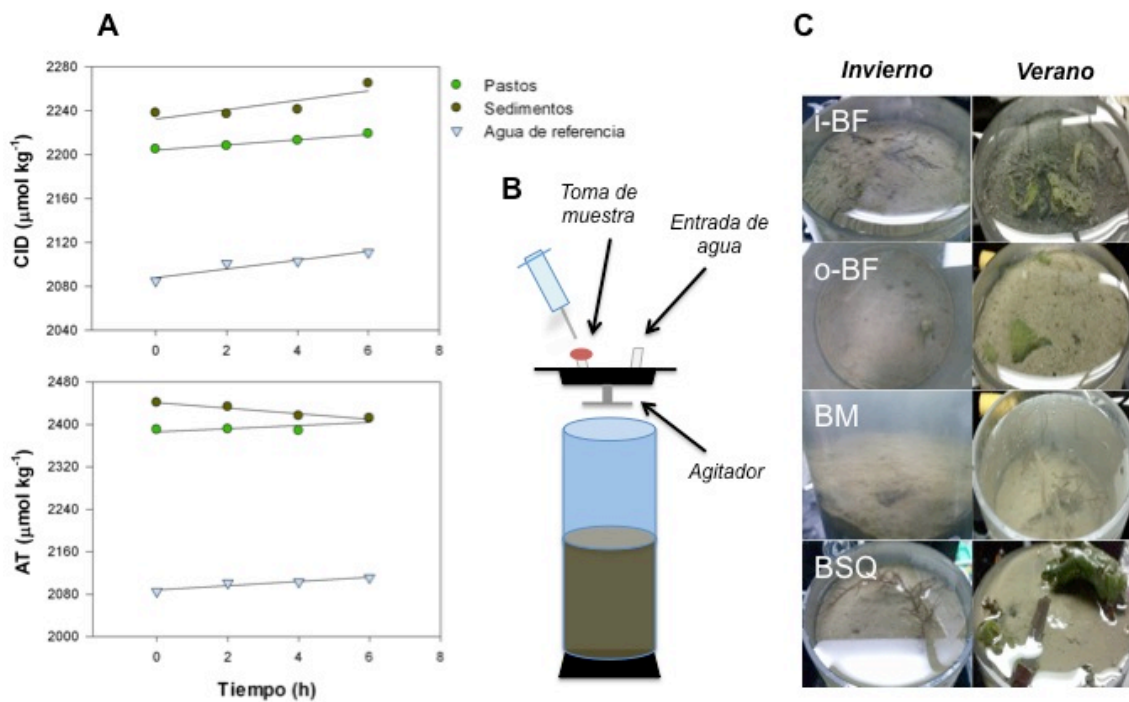
### *Metabolismo bentónico*

Para determinar el papel del sedimento en la dinámica del sistema de carbono, cuatro estaciones expuestas a condiciones ambientales contrastantes fueron seleccionadas a lo largo de la laguna (Fig. 1): a) Una estación localizada en la Boca de la bahía con influencia directa de eventos de surgencias (BM); b) Dos estaciones ubicadas en la zona externa e interna de Bahía Falsa (o-BF e i-BF, respectivamente), con influencia directa de las actividades acuícolas y condiciones ambientales ligeramente diferentes; c) Una estación localizada en la porción externa del brazo San Quintín (BSQ) influenciada por condiciones físico-químicas similar a las dos anteriores, pero sin presencia de cultivos. En cada una de ellas, se colectaron núcleos de sedimento en presencia y ausencia de pastos marinos (n=3) para los meses de Marzo y Julio de 2014, con el fin de captar la señal de las condiciones de invierno y verano del ciclo anual en el metabolismo bentónico de la laguna costera. Las principales características físico-químicas de la columna de agua para ambas temporadas en cada uno de los subsistemas de Bahía San Quintín se muestran en la Tabla 1.

Una vez transportados los núcleos de sedimento al laboratorio, se dejaron aclimatar durante 7-10 h previas al comienzo de la incubación. Las condiciones experimentales fueron simuladas en laboratorio a la temperatura e irradiancia observadas en campo para invierno ( $16\text{ }^{\circ}\text{C}$  y  $353 \pm 22\text{ }\mu\text{mol fotones m}^{-2}\text{ s}^{-1}$ ) y verano ( $19\text{ }^{\circ}\text{C}$  y  $664 \pm 48\text{ }\mu\text{mol fotones m}^{-2}\text{ s}^{-1}$ ) de 2014, en cámaras de incubación de microcosmos siguiendo las recomendaciones propuestas por Tengberg et al. (2004). Se colectaron muestras discretas de agua de mar al comienzo de la incubación y a intervalos de aproximadamente 2 h (0-6 h) para el análisis del sistema de carbono (CID y AT), siguiendo el mismo procedimiento descrito en los Capítulos 1 y 2. El volumen muestreado en cada toma fue reemplazado por agua de mar de referencia, manteniendo el mismo volumen de incubación durante todo el periodo. Los datos de CID y AT fueron corregidos a partir del cambio en la pendiente del agua de mar de referencia (actividad metabólica de la columna de agua) colectada en campo en cada una de las estaciones y periodos muestreados (Fig. 2).

**Tabla 1.** Características físico-químicas (promedio  $\pm$  DS) (i.e., temperatura, salinidad, CID, AT y pH (en escala de agua de mar)) observadas en la columna de agua en invierno y verano del 2014 para las diferentes áreas de Bahía San Quintín.

	Boca	Bahía Falsa	Brazo San Quintín
<i>Invierno</i>			
Temperatura (°C)	17.3 (0.9)	18.0 (0.3)	18.0 (0.6)
Salinidad	33.51 (0.14)	34.07 (0.14)	34.09 (0.31)
CID ( $\mu\text{mol kg}^{-1}$ )	2020 (65)	2124 (33)	2155 (49)
AT ( $\mu\text{mol kg}^{-1}$ )	2236 (8)	2320 (16)	2361 (82)
pH <sub>(CID-AT)</sub>	8.02 (0.10)	7.96 (0.06)	7.97 (0.06)
<i>Verano</i>			
Temperatura (°C)	20.2 (2.2)	23.2 (0.4)	24.2 (1.5)
Salinidad	33.73 (0.21)	34.25 (0.09)	34.99 (0.79)
CID ( $\mu\text{mol kg}^{-1}$ )	2074 (33)	2146 (14)	2174 (66)
AT ( $\mu\text{mol kg}^{-1}$ )	2254 (15)	2297 (8)	2369 (71)
pH <sub>(CID-AT)</sub>	7.90 (0.07)	7.77 (0.01)	7.84 (0.03)



**Fig. 2.** A) Variaciones típicas de las concentraciones de carbono inorgánico disuelto (CID) y alcalinidad tota (AT) durante las incubaciones de microcosmos para los núcleos muestreados en áreas sin vegetación (círculos café), en praderas de pastos marinos (círculos verdes) y en el agua de mar de referencia (triángulos celestes). B) Diagrama simplificado de las cámaras de incubación de microcosmos utilizadas durante el experimento. C) Ejemplo de las condiciones observadas en los núcleos sedimentarios en las distintas estaciones de muestreo para los meses de Marzo (izq.) y Julio (dcha.) de 2014.

Los flujos de intercambio bentónico de CID (*FCID*) y AT (*FAT*) se estimaron a partir de los cambios en el tiempo de las concentraciones de cada uno de los parámetros durante el periodo de incubación de los núcleos de sedimento, usando la ecuación propuesta por Dollar et al. (1991):

$$J = V \cdot (C_t - C_0) / (A \cdot T) \quad (1)$$

Donde, J es flujo bentónico por unidad de área (moles  $\text{cm}^{-2} \text{s}^{-1}$ ); V es volumen de agua incubado en la cámara ( $\sim 1000 \text{ cm}^3$ );  $C_0$  y  $C_t$  son la concentración disuelta al comienzo y final del periodo de incubación ( $\text{mol cm}^{-3}$ ); A es el área de sedimento incubado ( $\sim 71 \text{ cm}^2$ ); y T es el tiempo de incubación (s). Cabe mencionar que los flujos positivos representan la liberación del componente disuelto a la columna de agua, mientras que los flujos negativos representan la remoción del mismo.

El metabolismo bentónico del carbono debido a procesos de producción/respiración de la materia orgánica (CID\*) (i.e., sin el efecto de los procesos de disolución/precipitación de carbonatos) se calculó a partir de los valores de CID y AT de acuerdo con Broecker y Peng (1982), en Barrón et al. (2006):  $\text{CID}^* = \text{CID} - 0.5\text{AT}$ ; con el fin de identificar los principales procesos biogeoquímicos implicados en la producción y degradación de materia orgánica en la superficie de los sedimentos que modulan las variaciones de los flujos del sistema de carbono observadas entre éste y la columna de agua subyacente.

### *Análisis estadístico*

Se usó una prueba de signo de Wilcoxon para comparar las diferencias estadísticas espaciales y temporales en los flujos de intercambio de sedimento-agua para CID y AT medidos en los núcleos de sedimentos dentro de las comunidades de pastos marinos y en los sedimentos sin vegetación. Se consideraron diferencias estadísticamente significativas en  $P < 0.05$ .

## **3. RESULTADOS**

### *Condiciones locales*

Los parámetros físico-químicos observados en la localidad de estudio para ambas temporadas, presentaron un aumento desde la boca de la bahía hacia las áreas más

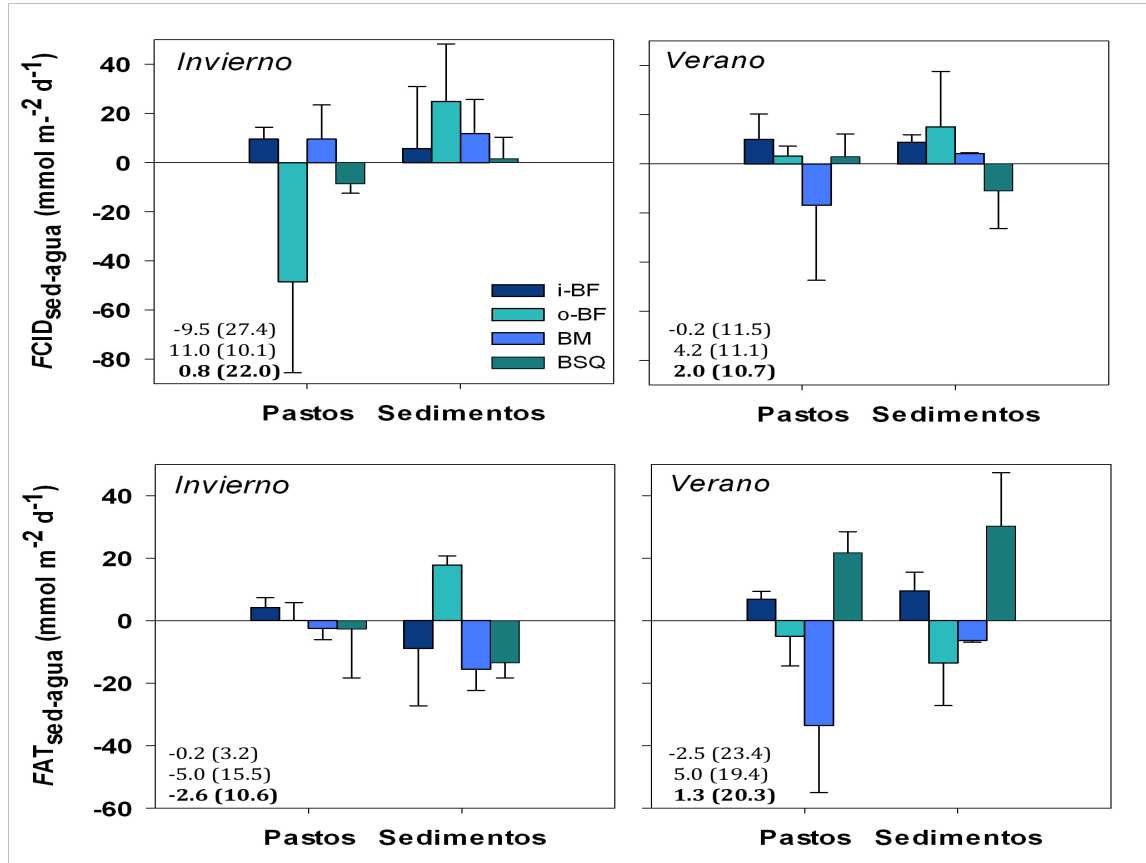
internas, a excepción del pH que disminuyó en ambos brazos del sistema con respecto a su valor más oceánico (boca) (Tabla 1). Los valores promedio de temperatura en las diferentes áreas de Bahía San Quintín para Marzo fueron de aproximadamente 17 °C para la región de la boca de la bahía, y 18 °C para ambos brazos. Para el mismo periodo de estudio, la salinidad aumentó de 33.5 a 34.1 hacia los brazos de la bahía, mientras que CID y AT presentaron incrementos por encima de 100 y 90  $\mu\text{mol kg}^{-1}$ , respectivamente. Como se esperaba en las condiciones ambientales para la temporada de verano (aumento de las temperaturas y la irradiancia estacional), los valores de las variables medidas fueron mayores en el mes de Julio, presentando una mayor variabilidad hacia las partes internas de la laguna (Tabla 1). Los valores medidos de temperatura y salinidad aumentaron de 20 °C y 33.7 en la parte más externa de la laguna a 24 °C y 34.9 hacia el brazo Este, con valores intermedios para Bahía Falsa; mientras que las concentraciones de CID y AT aumentaron más de 100  $\mu\text{mol kg}^{-1}$  hacia ambos brazos de la laguna con magnitudes superiores (20–40  $\mu\text{mol kg}^{-1}$ ) a los datos observados para Marzo. Para esta condición de estudio, los valores de pH calculados para toda la bahía estuvieron por debajo de 8.0, indicativo de un mayor dominio de procesos respiratorios en el interior de la laguna (Tabla 1).

### *Estimaciones de los flujos bentónicos*

Como se puede observar en la figura 3, los valores estimados de los flujos de intercambio sedimento-agua para CID y AT en las incubaciones de los núcleos sedimentarios mostraron gran variabilidad espacial y temporal. Los flujos promedio de CID fueron positivos hacia la columna de agua para ambas temporadas ( $0.8 \pm 22.0$   $\text{mmol m}^{-2} \text{d}^{-1}$  y  $2.0 \pm 10.7$   $\text{mmol m}^{-2} \text{d}^{-1}$  en Marzo y Julio de 2014, respectivamente), mientras que se observó la remoción de AT desde la columna de agua hacia el sedimento para Marzo ( $-2.6 \pm 10.6$   $\text{mmol m}^{-2} \text{d}^{-1}$ ). En contraste, en el mes de Julio los flujos fueron positivos ( $1.3 \pm 20.3$   $\text{mmol m}^{-2} \text{d}^{-1}$ ), lo que sugiere un cambio en los procesos bentónicos dominantes para este periodo. Las incubaciones de microcosmos de los sedimentos situados en praderas de *Zostera marina* mostraron en promedio una señal de autotrofia neta, aunque con estatus tróficos muy variables, a diferencia de los núcleos de sedimento localizados afuera de las mismas, en los cuales se observa principalmente un comportamiento heterotrófico neto para los periodos de estudio (Fig. 3). En ambos casos, las magnitudes promedio observadas fueron mayores en el mes de Marzo con grandes variaciones que oscilaron de -48.5 a 24.8  $\text{mmol m}^{-2} \text{d}^{-1}$ , mientras que

en Julio los valores promedio fueron más cercanos al balance metabólico fluctuando de -33.5 a 30.3  $\text{mmol m}^{-2} \text{d}^{-1}$ . Las distintas condiciones ambientales analizadas (i-BF, o-BF, BM y BSQ) mostraron importantes diferencias espaciales en la distribución del sistema de carbono, influenciadas por las características locales y las condiciones físico-químicas de las temporadas de estudio (Fig. 3).

**Fig. 3.** Flujos de intercambio de FCID y FAT en la interfase sedimento-agua observadas en Marzo y Julio

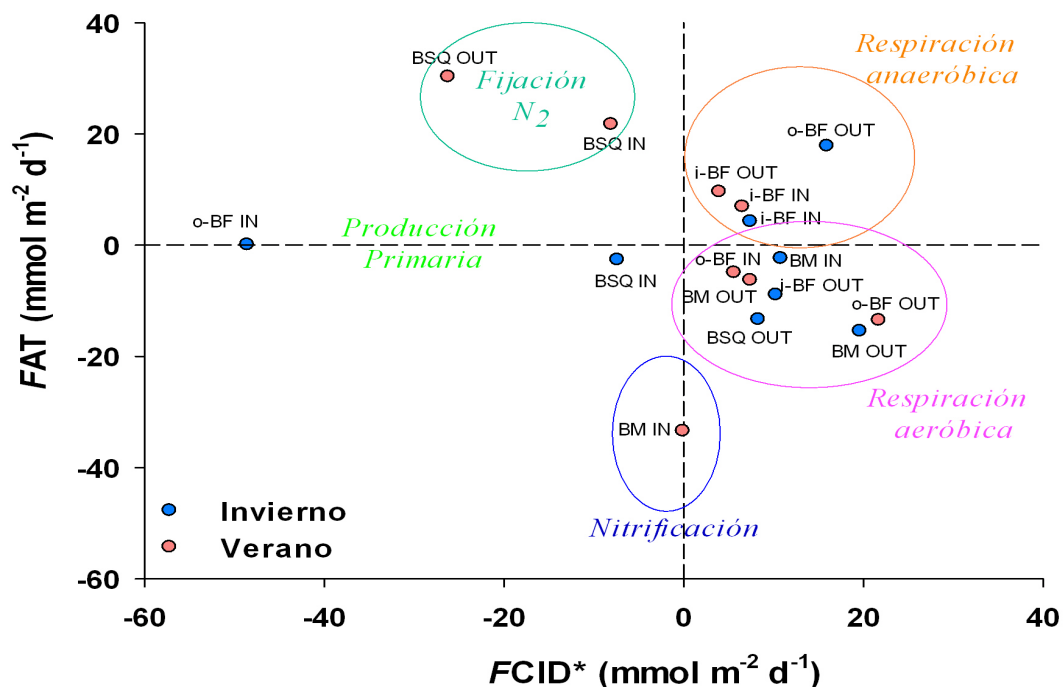


del 2014, para los núcleos localizados dentro (Pastos) y afuera (Sedimentos) de las praderas de *Zostera marina* en cada una de las estaciones muestreadas durante el periodo de estudio. En la esquina inferior izquierda de cada uno de los gráficos se muestran los promedios ( $\pm$  DS) de las incubaciones de microcosmos en Pastos, Sedimentos y Total de las muestras experimentales estimadas para cada variable y temporada de estudio.

#### 4. DISCUSIÓN

Los estudios encaminados a examinar el metabolismo de un ecosistema están implícitamente relacionados con el balance de carbono orgánico, sin embargo, las propiedades metabólicas generalmente se miden a partir de cambios en la producción o consumo de oxígeno disuelto o de carbono inorgánico (Testa et al. 2013). Los cambios en los parámetros del sistema de carbono en cámaras de incubación reflejan el equilibrio

entre: 1) el consumo/producción de carbono por los organismos autótrofos; 2) la producción durante el período de incubación debida al zooplancton, la fauna bentónica y las bacterias; 3) la señal del metabolismo inorgánico asociado a cambios no mediados biológicamente (Barrón et al. 2006). Para simplificar el análisis de los valores estimados para los flujos bentónicos de CID asociados al metabolismo debido a procesos de producción/respiración de la materia orgánica ( $FCID^*$ ) y AT ( $FAT$ ) durante el periodo de incubación experimental en las distintas condiciones de estudio, se presentan sus variaciones relativas en la figura 4, como indicador de los componentes y procesos biogeoquímicos dominantes en el sedimento que afectan directa o indirectamente a estas cantidades.



**Fig. 4.** Variaciones relativas de los flujos de intercambio de CID\* ( $FCID^*$ ) y AT ( $FAT$ ) en la interfase sedimento-agua observadas en Marzo y Julio del 2014, para los núcleos localizados dentro (IN) y afuera (OUT) de las praderas de *Zostera marina* en cada una de las estaciones muestreadas durante el periodo de estudio. Asimismo, se presentan posibles procesos biogeoquímicos involucrados en la liberación o captación de CID y AT entre el sedimento y la columna de agua que afectan directa o indirectamente a estas cantidades.

Como se observa en la figura 4, las variaciones en las concentraciones de CID durante las incubaciones de los núcleos de sedimento de Bahía San Quintín mostraron, en la mayoría de los casos de estudio, la producción bentónica de CID dentro de las cámaras de microcosmos (procesos heterotróficos), con una gran variabilidad espacial y

temporal característica de sistemas costeros someros dominados por macrovegetación (Barrón et al. 2004). En Bahía San Quintín, al igual que en otros sistemas costeros templados, ha sido ampliamente estudiado el comportamiento heterotrófico neto (dominancia de procesos de respiración) de estos ambientes en las temporadas de invierno y verano a lo largo de un ciclo anual (e.g., Smith and Hollibaugh 1997; Camacho-Ibar et al. 2003; Ibarra-Obando et al. 2004; Delgadillo-Hinojosa et al. 2008). El aumento de las tasas metabólicas de respiración en Bahía San Quintín está influenciado principalmente por la importación y/o producción *in situ* de material orgánico (particulado y disuelto), modulado por eventos de surgencias costeras que son máximas en los meses de primavera y principios de verano (Ribas-Ribas et al. 2011), así como exudados asociados tanto a los productores primarios, como a los cultivos de ostión que se desarrollan en la laguna (Hernández-Ayón et al. 2007b; Sandoval-Gil et al. 2016; Camalich-Carpizo, 2006). La disponibilidad de material orgánico en el sistema permite la intensificación de los procesos bentónicos, también influenciados por los ciclos de luz y temperatura, promoviendo la liberación de CID a la columna de agua que, a su vez, sustenta el metabolismo heterotrófico de la columna de agua para estas temporadas. Esto es consistente con los resultados observados en las variaciones de los flujos de CID\* y AT, donde se observa una mayor importancia relativa de los procesos de degradación (aeróbica y anaeróbica) de la materia orgánica para ambas temporadas (Fig. 4).

En Bahía San Quintín, los procesos bénticos dominan el metabolismo a nivel del sistema, representando aproximadamente el 70% de la respiración y la producción primaria total, controlado hasta en un 80% por la actividad de las comunidades de pastos marinos (Ibarra-Obando et al. 2004). La actividad metabólica y la estructura de las comunidades asociadas a estos macrófitos, pueden modificar las propiedades físicas y químicas del ambiente donde se desarrollan (Barrón et al. 2004), promoviendo: 1) la oxigenación de la rizosfera sedimento a través de las raíces, y por tanto, la intensificación de procesos aeróbicos entre el sedimento y la columna de agua; 2) el aporte de material orgánico producido por exudados o por el recambio del tejido vegetativo; y 3) la retención de material particulado proveniente del sistema, que queda atrapado por el dosel vegetal de la pradera. En consecuencia, los procesos biogeoquímicos que tienen lugar en las praderas de pastos marinos y sus comunidades microbianas bentónicas asociadas, pueden contribuir a un cambio en la condición metabólica del sistema hacia una heterotrofia neta y acontecer a la intensificación de

procesos sedimentarios anóxicos (Marbá et al. 2006). Importantes procesos de respiración anaeróbica (esencialmente procesos de desnitrificación y sulfatorreducción) pueden ocurrir en los sedimentos localizados principalmente en la parte interna de Bahía Falsa (i-BF), probablemente modulados por la retención de altos aportes de materia orgánica y tiempos de residencia ligeramente más altos (Fig. 4). Para este brazo de la laguna y el área de la boca, Camacho-Ibar et al. (2003) ya han reportado la dominancia de importantes procesos de desnitrificación y remineralización bentónica durante los meses de verano y, en menor intensidad, para la temporada de invierno. Estos autores, sugieren que estos procesos están fuertemente influenciados por altas concentraciones de materia orgánica lábil de origen fitoplanctónico, y probablemente, al aporte de material orgánico debido a importantes floraciones de macroalgas (Zertuche et al. 2009; Ávila-López et al. 2016), así como a los extensos cultivos de ostión localizados en esta área (Emery et al. 2015). La intensa variación observada para Julio en los flujos de AT dentro de praderas de pastos marinos localizadas en la boca de la bahía (BM), posiblemente se deban al acoplamiento de procesos de nitrificación en la superficie de los sedimentos y la columna de agua adyacente a los antes mencionados (Camacho-Ibar et al. 2003), y/o el consumo preferente de  $\text{NH}_4^+$  por *Zostera marina* (en hojas y raíces) observado en Bahía San Quintín por Sandoval-Gil et al. (2015), que es una importante fuente de nitrógeno inorgánico para el desarrollo y crecimiento de estos productores primarios. Ambos procesos son reconocidos como importantes promotores del sumidero de alcalinidad en condiciones ambientales más cálidas y oligotróficas (Wolf-Gladrow et al. 2007), siendo consistente con los resultados obtenidos en el presente estudio (Fig. 3 y 4).

Cambios estacionales e interanuales en la temperatura y el aporte de carbono inorgánico y nutrientes pueden afectar directa e indirectamente las tasas de fotosíntesis (producción de carbono orgánico) en los ecosistemas acuáticos, debido a que estos aportes son generalmente mejorados por la acentuación de las tasas de reciclamiento en la columna de agua y en el bentos (Testa et al. 2013; McGlathery et al. 2013). Aunque en sistemas costeros templados como Bahía San Quintín, la fijación de nitrógeno es un proceso que afecta en menor medida que la desnitrificación en praderas de *Zostera marina* (< 5%) (Camacho-Ibar et al. 2003; McGlathery et al. 1998), recientemente Hernández-López et al. (2017) han observado que este proceso también puede contribuir de forma significativa en los sedimentos costeros de esta laguna (~10% del nitrógeno total aportado a la columna de agua). Asimismo, se ha estimado que la fijación de nitrógeno

en sedimentos de sistemas marinos tropicales y subtropicales, sustenta más del 50% de la demanda de nitrógeno de los productores primarios (Welsh, 2000, y referencias en él).

Teniendo en cuenta la condición climática desarrollada durante el periodo de estudio, con bajos intercambios océano-bahía y anomalías de temperatura de hasta 2 °C para los meses de verano en el interior de la laguna (Ávila-López et al. 2016), el aumento de los flujos de AT, acoplados a la disminución de CID en la localidad más externa del brazo San Quintín (BSQ) en Julio, podría ser indicativo de importantes procesos de fijación de N<sub>2</sub> mediadas por comunidades de microalgas bentónicas en los núcleos de sedimento de fuera y dentro de las praderas de pastos para dicha localidad (Fig. 4). Además, los intensos procesos de captación de CO<sub>2</sub> observados durante las incubaciones realizadas en invierno con sedimentos obtenidos dentro de praderas de pastos localizados en la parte externa de ambos brazos de la bahía (o-BF y BSQ), también sugieren una importante presencia de estos productores primarios, que pueden llegar a contribuir del 20-25% de la producción primaria béntica total en ecosistemas templados con presencia de pastos marinos (McGlathery et al. 2013).

Considerando la totalidad de Bahía San Quintín, donde los bancos de sedimentos someros desprovistos de vegetación y las áreas de praderas de *Zostera marina* cubren aproximadamente el 20% y el 40% de la superficie del sistema, respectivamente (Ward et al. 2004), la producción neta béntica del ecosistema (basados en los flujos de CID estimados para estas comunidades) para invierno y verano de 2014, sería de  $-1.59 \pm 4.25$  y  $0.76 \pm 0.66$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectivamente. Estos resultados son consistentes con la tendencia general estacional de la producción neta del ecosistema (NEP, siglas en inglés) observada en Bahía San Quintín por Ávila-López et al. (2016), calculados a partir de los flujos de DIC no conservativos en la columna de agua aplicando el modelo biogeoquímico de LOICZ. Las estimaciones obtenidas de las incubaciones de microcosmos sugieren una contribución del metabolismo béntico al estatus trófico del sistema para Marzo y Julio de 2014 de 61% y 20%, respectivamente. Sin embargo, hay que tener en consideración: 1) no se tiene en cuenta la contribución de la heterotrofia neta anaeróbica correspondiente al metabolismo béntico en sedimentos profundos, que parecen ser los responsables del carácter metabólico neto de este sistema en una escala anual (Ibarra-Obando et al., 2004); 2) limitaciones debidas a la propia metodología usada, que puede inducir errores difíciles de cuantificar en las tasas estimadas y/o “efectos de botella” artificiales en las distintas unidades incubadas (i.e.,

agua, sedimentos y organismos), así como la limitación de recursos, que alteran en sí mismo las tasas medidas, siendo éstas muy diferentes a las condiciones naturales (Testa et al. 2013). Sin embargo, los cambios en las concentraciones del sistema de carbono durante los periodos de incubaciones no mostraron signos de limitación de CID, que hubieran conducido a la subestimación del metabolismo (Fig. 2A).

Por tanto, aunque existe la dificultad inherente de inferir en el balance metabólico global de un ecosistema extrapolando las tasas metabólicas obtenidas de las incubaciones de microcosmos en escalas de horas, los datos obtenidos en el presente estudio parecen sugerir que las comunidades bentónicas en los sedimentos profundos podrían tener una importante contribución a la dinámica del sistema de carbono y al estatus trófico en este hábitat costero.

## 5. CONCLUSIÓN

La distribución de los flujos de intercambio de los parámetros del sistema de CO<sub>2</sub> entre el sedimento y la columna de agua subyacente en las incubaciones de microcosmos de los núcleos de sedimento de Bahía San Quintín, mostró una gran heterogeneidad espacio-temporal dentro del sistema para los periodos de estudio. En balance, las comunidades bentónicas estudiadas de Bahía San Quintín mostraron una señal neta heterotrófica en Marzo y Julio de 2014 ( $0.8 \pm 22.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$  y  $2.0 \pm 10.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , respectivamente), no observándose diferencias claras estacionales entre ambas temporadas. Nuestro estudio indica que los procesos biogeoquímicos de respiración aeróbica y anaeróbica en los sedimentos de Bahía San Quintín dominan los cambios del sistema de carbono para estos periodos, comportándose como eficaces fuentes de CO<sub>2</sub> hacia la columna de agua que pueden jugar un papel importante en el mantenimiento de los procesos biológicos de la laguna. A nivel ecosistema, los resultados obtenidos fueron consistentes con los patrones observados en Bahía San Quintín por Ávila-López et al. 2016 para el 2014. Sin embargo estos flujos parecen explicar sólo la contribución debida al metabolismo bentónico de las áreas más someras de la laguna, donde las comunidades bentónicas en los sedimentos profundos podrían tener una importante contribución a la dinámica del sistema de carbono en este hábitat costero. Los resultados observados en este trabajo sugieren que la combinación de los aportes de CO<sub>2</sub> provenientes de los sedimentos, en su conjunto, y los eventos de surgencias costeras podrían explicar la paradoja de autotrofia-heterotrofia que mantiene el ciclo

estacional del metabolismo neto observado en Bahía San Quintín, donde el sistema es fuente continua de CO<sub>2</sub> hacia la atmósfera a lo largo del año.

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El efecto del cambio climático global en los entornos naturales es una prioridad y un reto para la comunidad científica, con el fin de conocer cómo será la evolución de estos sistemas ante las proyecciones globales futuras, donde el ciclo del carbono costero desempeña un papel clave en la regulación de los patrones climáticos y el funcionamiento de los ecosistemas. El Sistema de la Corriente de California, una de las regiones de surgencias costeras con mayor productividad por unidad de área a nivel mundial (Checkley y Barth, 2009), es una de las zonas del océano global más vulnerable a los principales estresores causados por las crecientes emisiones de CO<sub>2</sub> a la atmósfera (i.e., el calentamiento superficial, la acidificación y la desoxigenación del océano) (Gruber, 2011). A pesar de su importancia socioeconómica y ambiental, aún se conoce muy poco sobre la dinámica del ciclo del carbono en los ecosistemas internos a lo largo de sus costas, así como al impacto al que pueden verse sometidos bajo las condiciones de proyección climáticas futuras.

En este contexto, el trabajo de investigación generado en la Tesis Doctoral se ha centrado en aportar nueva información a la base de datos que existe sobre la dinámica del carbono y su biogeoquímica en Bahía San Quintín, una laguna costera de Baja California localizada en el Pacífico Mexicano, dentro de la región sur de la Corriente de California. Este trabajo caracteriza por primera vez la variabilidad espacial y temporal del sistema de carbono, en relación con el estado metabólico del sistema, en un ambiente costero mexicano, influenciado por eventos de surgencias costeras y macrovegetación. Con base en muestras in situ de los parámetros del sistema de carbono generadas a lo largo de un ciclo anual (2014) y bases de datos de 2002, 2004 y 2005, se estimaron los flujos de intercambio de CO<sub>2</sub> aire-agua y el metabolismo neto de Bahía San Quintín, para identificar los principales procesos que modulan la respuesta del ecosistema bajo distintos escenarios regionales en las condiciones oceánicas adyacentes. Además, se examinó la variabilidad espacio-temporal de los flujos de intercambio sedimento-agua del sistema de carbono para Marzo y Julio de 2014, bajo distintas condiciones ambientales locales, con el objetivo de determinar el metabolismo bentónico del ecosistema y evaluar los procesos biogeoquímicos que contribuyeron a

los cambios en la química de la columna de agua y el sedimento para estos periodos. A continuación se resumen los principales resultados obtenidos bajo las distintas condiciones oceanográficas regionales, que constituyen las conclusiones generales de estas investigaciones.

1. La dinámica del carbono costero en Bahía San Quintín está influenciada por el ambiente local y los patrones temporales en las condiciones oceanográficas de la región. El origen del agua advectada hacia la laguna, asociada al forzamiento regional, así como la intensidad del viento (condiciones favorables o de relajación de las surgencias) jugaron un papel crítico en el control de las condiciones biogeoquímicas observadas en esta laguna costera, modulados por los productores primarios dominantes.
2. Durante el desarrollo de la anomalía cálida que afectó la región costera de Baja California en 2014 se observó una condición de verano continuo para Bahía San Quintín, con ausencia de surgencias favorables a lo largo del año.
3. Pese a las altas temperaturas observadas en Bahía San Quintín durante el desarrollo de la anomalía cálida de 2014, la actividad biológica dentro de la laguna controló, sobre los procesos físicos, la distribución estacional observada en los parámetros del sistema de carbono en 2014.
4. Bahía San Quintín se comportó como una fuente débil de CO<sub>2</sub> a la atmósfera en 2014 ( $3.3 \pm 4.8 \text{ mmol C m}^{-2} \text{ día}^{-1}$ ), consistentemente a lo observado en sistemas costeros dominados por surgencias, con los flujos promedios positivos más altos observados principalmente en los meses de verano ( $9.0 \pm 5.3 \text{ mmol C m}^{-2} \text{ día}^{-1}$ ) y un rango de variación entre  $-0.32$  a  $15.06 \text{ mmol C m}^{-2} \text{ día}^{-1}$ .
5. El patrón espacial y temporal estimado en los flujos netos de CO<sub>2</sub> aire-agua durante 2014 parece reflejar una señal basal de las transformaciones biogeoquímicas del carbono promovidas por un ecosistema dominado por comunidades bentónicas de productores primarios.
6. Pese a que las biomásas de las comunidades de macroalgas dominantes (*Ulva* sp., *Gracilaria* sp., y *Chondracanthus squarulosus*) fueron mucho menores durante la anomalía cálida de 2014 que las observadas durante surgencias

intensas para Bahía San Quintín, el aporte de material detrítico debido a estas comunidades contribuyó aproximadamente en un 45% al CO<sub>2</sub> liberado a la columna de agua (vía detritus), lo que sugiere su importante papel como fuente interna de materia orgánica hacia el sistema, aparentemente vinculados, al menos parcialmente, a los patrones de variación estacional del balance de carbono en Bahía San Quintín para este periodo.

7. El metabolismo neto del ecosistema cambió estacionalmente entre una condición de heterotrofia neta, en invierno y verano, a una condición de autotrofia neta durante la estación de surgencias máximas (Abril-Junio), fuertemente influenciado por la condición de surgencia costera (procesos externos) y la actividad del metabolismo bentónico (procesos internos); éste último modulado principalmente por el ciclo de vida de los productores primarios dominantes (i.e., macroalgas y pastos marinos) en Bahía San Quintín, en respuesta a los ciclos anuales de luz y temperatura.
8. El promedio anual de la producción neta del ecosistema fue de  $2.2 \pm 7.1$  mmol C m<sup>-2</sup> día<sup>-1</sup>, indicando una dominancia de la autotrofia neta del ecosistema para 2014, con rangos de variación entre -9.27 y 15.14 mmol C m<sup>-2</sup> día<sup>-1</sup>, consistente con lo observado en otros sistemas someros templados.
9. La anomalía cálida favoreció las tasas de respiración en Bahía San Quintín que liberaron carbono inorgánico a la columna de agua, estimulando la producción de materia orgánica que alimentó la respiración bentónica y un suministro local de nutrientes reciclados para los productores primarios en ausencia de los aportes provenientes de las surgencias costeras.
10. Los resultados de las incubaciones de mesocosmos mostraron la dominancia de procesos heterotróficos (aerobios y anaerobios) en los sedimentos de Bahía San Quintín durante invierno y verano de 2014, comportándose como eficaces fuentes de CO<sub>2</sub> hacia la columna de agua.
11. A escala del ecosistema, los patrones estacionales del metabolismo bentónico neto fueron consistentes con los patrones estacionales estimados por el modelo biogeoquímico de LOICZ para el metabolismo neto del ecosistema, mostrando una señal de autotrofia neta ( $-1.59 \pm 4.25$  mmol C m<sup>-2</sup> d<sup>-1</sup>) y heterotrofia neta

( $0.76 \pm 0.66 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) en los sedimentos de Bahía San Quintín para Marzo y Julio de 2014, respectivamente.

12. La contribución debida al metabolismo bentónico (pastos marinos y sedimentos someros sin vegetación) de Bahía San Quintín al estatus metabólico neto del ecosistema fue del 61% para Marzo y del 20% para Julio de 2014.
13. Climatológicamente, la actividad de afloramiento costero de Baja California durante los años estudiados en 2002, 2004, 2005 y 2014, asociados con diversas condiciones climáticas regionales, fue atípica pero no sin precedentes dentro de su variabilidad natural.
14. Se observó una respuesta rápida e intensa del ecosistema en Bahía San Quintín a las condiciones atípicas en los ciclos estacionales de las surgencias costeras estudiados, con variaciones estacionales e interanuales de los flujos de intercambio de  $\text{CO}_2$  entre la atmósfera y el medio marino y el estatus trófico del sistema, principalmente influenciadas por la velocidad del viento, el origen del agua advectada hacia la laguna y el régimen climático dominante, así como por la actividad biológica en el interior del sistema.
15. Bahía San Quintín actuó como una fuente de carbono hacia la atmósfera durante todas las estaciones de surgencias costeras estudiadas, oscilando entre  $1.6 \pm 1.2$  a  $12.2 \pm 10.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$  a lo largo del sistema, principalmente influenciada por la condición ambiental.
16. La concentración de carbono inorgánico disuelto (DIC) en las aguas de surgencias que interactúan con la laguna contribuye en gran medida a los patrones de distribución de carbono inorgánico dentro de la bahía, así como a la respuesta y estructura del ecosistema, pudiendo ser una variable clave para explicar el funcionamiento de este tipo de ecosistemas someros hipersalinos, dominados por surgencias y macrovegetación.
17. El equilibrio metabólico en la bahía indicó claramente un cambio estacional en los procesos dominantes entre la producción de materia orgánica (autotrofia neta) y la respiración (heterotrofia neta) en el sistema, principalmente durante el

máximo de la estación de surgencia (Abril-Junio) y verano, respectivamente, oscilando de -13 a 35 mmol C m<sup>-2</sup> d<sup>-1</sup>.

18. Los aportes de CO<sub>2</sub> provenientes de los procesos bentónicos junto con la influencia de las surgencias costeras en la bahía podrían explicar el comportamiento continuo como fuente de CO<sub>2</sub> observado en este sistema costero, a diferencia del metabolismo neto del ecosistema que mantiene un ciclo estacional entre autotrofia y heterotrofia neta, principalmente asociado a una mayor influencia del ciclo de vida de los macrófitos marinos dominantes.

Finalmente y con base en las observaciones anteriores, la disminución de la velocidad del viento y, por consiguiente, la intensidad de la surgencia costera frente a Baja California en las proyecciones de calentamiento global futuras, pueden afectar particularmente la distribución biogeoquímica del carbono en este hábitat costero poco profundo, con la tendencia hacia el equilibrio del estatus metabólico del ecosistema y un intercambio débil de CO<sub>2</sub> con la atmósfera. Bajo este escenario, el metabolismo basal de las comunidades bentónicas y su capacidad de almacenamiento y transformación de materia orgánica y nutrientes, desempeñan un papel regulador clave en la dinámica del sistema de carbono en este hábitat costero.

La relevancia de este trabajo radica en:

- Se contribuyó al conocimiento del ciclo del carbono en un sistema costero de México, integrando distintas escalas temporales y espaciales, así como su interacción con la oceanografía regional y los procesos internos involucrados en su dinámica.
- Se reporta por primera vez para Bahía San Quintín, su comportamiento como fuente de CO<sub>2</sub> a la atmósfera a lo largo del año y la variación estacional del metabolismo neto del ecosistema en una escala anual e interanual.
- Provee información importante ante un posible escenario de cambio climático global en sistemas costeros someros dominados por macrovegetación y eventos de surgencia, que pueden ser usados para alimentar modelos climáticos que nos ayuden a predecir de forma más aproximada la evolución de estos ecosistemas de un alto valor ecológico y económico para el ser humano.

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