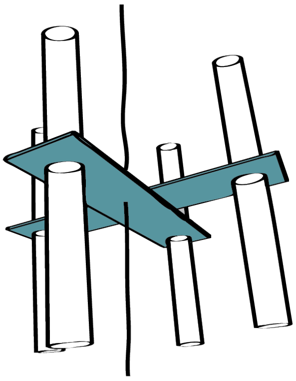

UNIVERSIDADE
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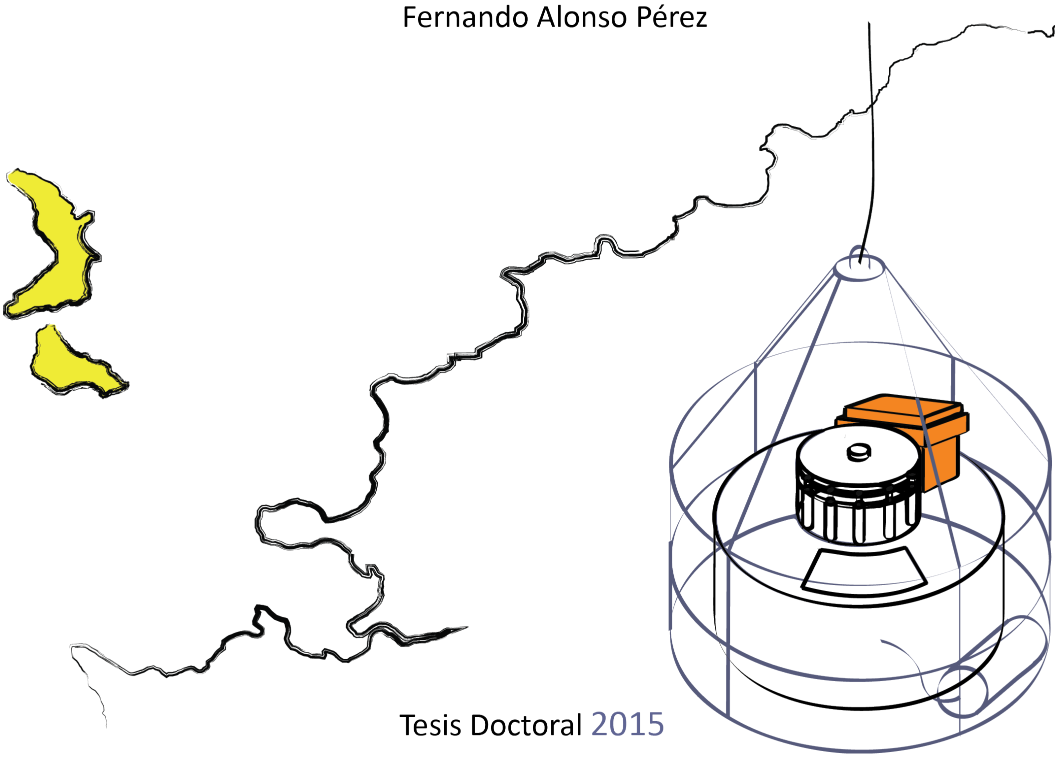
The importance of benthic fluxes

Fernando Alonso Pérez



Tesis Doctoral 2015

Universidade de Vigo

Facultad de Ciencias del Mar

Instituto de Investigaciones Marinas

BENTHIC-PELAGIC COUPLING IN A COASTAL UPWELLING SYSTEM (RÍA DE VIGO)

THE IMPORTANCE OF BENTHIC FLUXES

Fernando Alonso Pérez

Vigo 1015

PhD Thesis

Tesis Doctoral

CSIC

La doctora del Departamento de Oceanografía del Instituto de Investigacións Mariñas (IIM) perteneciente al Consejo Superior de Investigaciones Científicas (CSIC), **Dra. Carmen González Castro**, en calidad de directora de esta Tesis Doctoral

HACE CONSTAR

Que la presente memoria titulada "**Benthic-pelagic coupling in a coastal upwelling system (Ría de Vigo): the importance of benthic fluxes**" presentada por **Fernando Alonso Pérez** para optar al título de doctor por la Universidade de Vigo, fue realizada bajo mi dirección y cumple con las condiciones exigidas para su presentación, la cual autorizo.

Y para que así conste y surta los efectos oportunos, firmo la presente en Vigo, a 8 Abril 2015.

Carmen González Castro

Dra. Carmen González Castro

Esta Tesis Doctoral fue realizada dentro del grupo de Oceanoloxía del Instituto de Investigaciones Marinas (IIM) perteneciente al Consejo Superior de Investigaciones Científicas (CSIC). Fernando Alonso Pérez disfrutó de una beca predoctoral FPU del programa nacional de Recursos Humanos, durante el periodo 2002-2004. Los trabajos recogidos durante esta memoria se desarrollaron dentro de los proyectos TRACA: ‘Desarrollo de una plataforma observacional para la cuantificación de los procesos de sedimentación/resuspensión de material biogénico’, financiado por la Xunta de Galicia (ref: PGIDIT02RMA40201PR), FLUVBE: ‘Acoplamiento de los flujos verticales y bentónicos en la Ría de Vigo’, financiado por la Comisión Interministerial de Ciencia y Tecnología CICYT (ref: REN2003-04458/MAR) y MaBenE: ‘Managing benthic ecosystems in relation to physical forcing and environmental constraints’, financiado por la Unión Europea (ref: EVK3–CT–2002–00071).

Memoria de Tesis presentada por Fernando Alonso Pérez dentro del programa de doctorado en Oceanografía por la Universidade de Vigo, para optar al título de Doctor

Vigo , 8 de Abril de 2015

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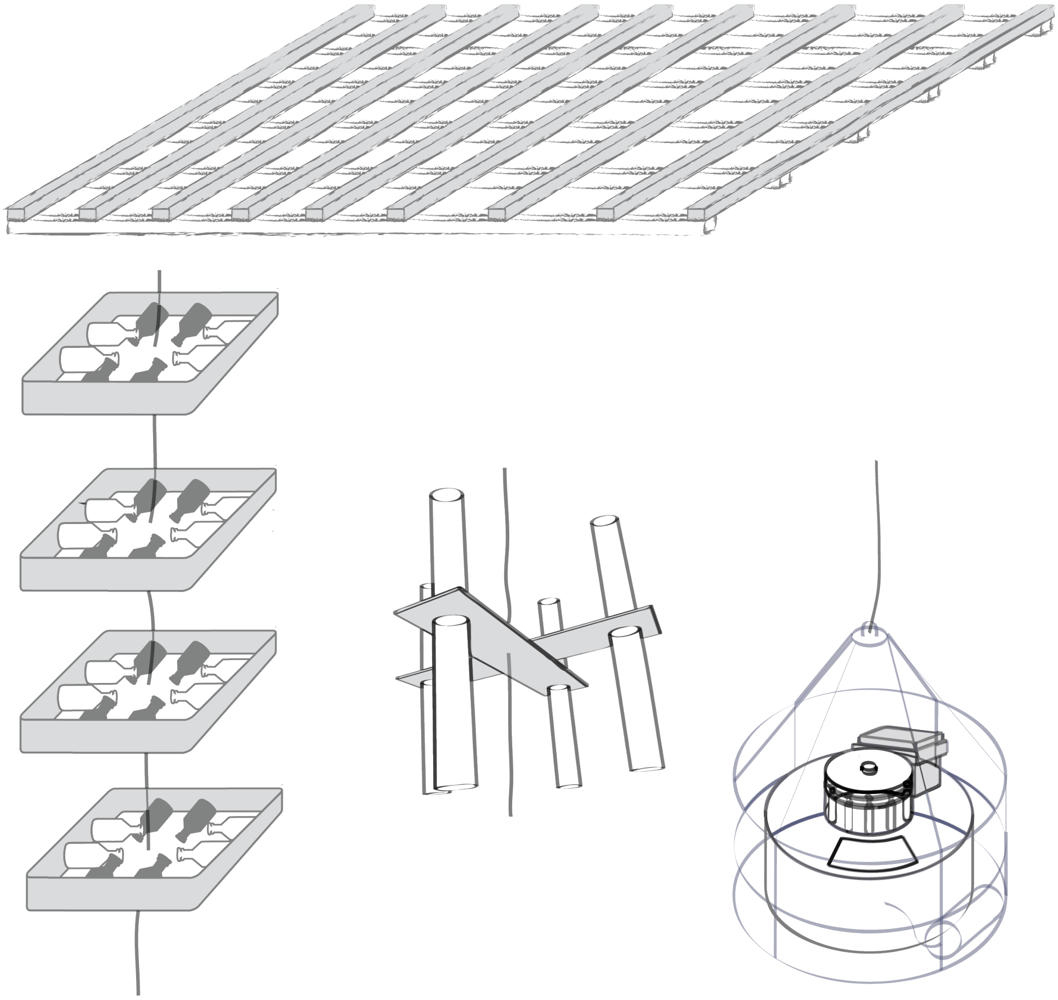
A mi familia

ÍNDICE

INTRODUCCIÓN Y OBJETIVOS



Capítulo I

1. Introducción

Los márgenes costeros se encuentran entre las áreas más activas biológica y geoquímicamente hablando de la biosfera (Falkowski et al. 1988, Walsh 1991, Liu et al. 2010). A pesar de ocupar <10% de la superficie oceánica global y <0.5% de su volumen total, entre un 10-50% de la producción primaria global tiene lugar en los mismos (Wollast 1998) y globalmente más del 90% del carbono orgánico que se incorpora a los sedimentos se produce por deposición de partículas en las zonas costeras (Berner 1989, Wollast & Chou 2001). El ciclo del carbono en las aguas costeras ha sido reconocido como un componente principal en el los ciclos y balances globales del carbono (Regnier et al. 2013) por lo que, resulta esencial conocer y entender los flujos de carbono en los sistemas costeros así como los factores que los regulan para establecer cuál es su importancia en los balances globales de carbono (Cai 2011, Bauer et al. 2013).

El destino del carbono orgánico fijado en las zonas costeras puede ser pérdida a través de los procesos heterotróficos, exportación al océano adyacente o bien exportación vertical y remineralización y/o deposición en los sedimentos de la plataforma y/o el talud continental (Joint & Wassmann 2001). Sólo una pequeña porción de esta materia orgánica queda definitivamente enterrada en el sedimento (Hedges & Keil 1995). La potencial exportación de carbono orgánico al océano adyacente varía entre las distintas regiones costeras, desde un 10% y 81% de la producción primaria anual (Falkowski et al. 1988, Pilskaln et al. 1996). La repartición del carbono fijado entre estos compartimentos es fundamental para evaluar el papel jugado por estos ecosistemas en el ciclo global del carbono.

Las zonas costeras son una frontera entre los sistemas terrestre, oceánico y atmosférico por lo que en ellas se produce un intenso gradiente tanto de energía, como de materia (Fig. 1). Además, una de las singularidades de las zonas costeras es su proximidad con el sedimento, que hace que los procesos de interacción con esta frontera se vean favorecidos (Soetaert et al. 2000, Zeldis 2004). De hecho, el acoplamiento pelágico – bentónico, es decir la conexión existente entre el ambos ambientes (Marcus & Boero 1998), se ve intensificado con la disminución de la profundidad (Suess 1980). El acoplamiento entre los sistemas bentónico y pelágico funciona en ambos sentidos: los ciclos de producción primaria en la columna de agua aportan materia orgánica lábil para su regeneración en el sedimento (Hatcher et al. 1994), de la que los organismos heterótrofos que habitan en el sedimento obtienen energía y nutrientes (Middelburg & Levin 2009), y a su vez los nutrientes reciclados en el sedimento constituyen una fuente importante para mantener las altas tasas de producción primaria en estos sistemas (Nixon et al. 1976, Hopkinson 1987, Grenz et al. 2010). Por lo tanto, el estudio de los procesos y reacciones que transforman y transportan elemento biogénicos entre el sedimento y la columna de agua son fundamentales para entender los ciclos biogeoquímicos marinos.

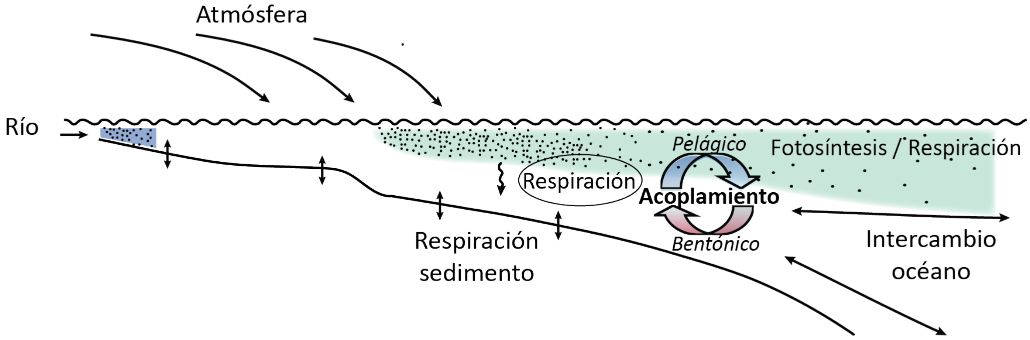


Figura 1. Vista esquemática dónde se reflejan los principales procesos biogeoquímicos que tienen lugar en las zonas costeras que actúan como frontera entre los sistemas terrestre, oceánico y atmosférico. Se muestra a su vez, la integración de estos procesos en el acoplamiento pelágico-bentónico.

Las mayores tasas de sedimentación de materia orgánica que tienen lugar en los márgenes costeros originan que el primer metro de sedimento en estas áreas constituya el mayor reservorio de carbono orgánico de la superficie oceánica (Jahnke 2005). Así, los sedimentos superficiales en las zonas costeras se convierten en emplazamientos donde se produce una intensa actividad de remineralización de la materia orgánica (Berner 1980, Boudreau 1997).

1.1 Remineralización bentónica

El flujo de solutos en la interfase sedimento-agua puede ser debido a su consumo o a su producción, además de ello, el movimiento de solutos y partículas se ve modificado por procesos físicos de transporte. El conjunto de estos procesos de transporte y de las reacciones químicas que consumen o aportan solutos y partículas se conocen como procesos diagenéticos (Jorgensen & Boudreau 2001). La regeneración bentónica, por su parte, es el resultado de procesos físicos, químicos y biológicos que tienen lugar en el sedimento e interfase sedimento-agua por los cuales se remineraliza la materia orgánica, generando carbono inorgánico y nutrientes, los cuales son liberados a la columna de agua.

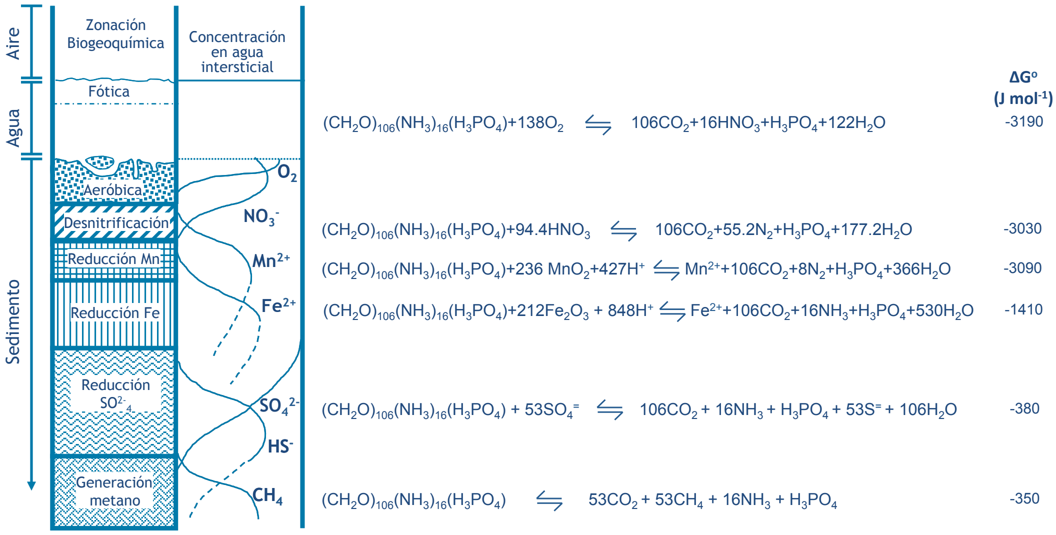


Figura 2. Secuencia vertical de las reacciones de remineralización de la materia orgánica en el sedimento así como la energía libre liberada asociada a cada una de ellas. Se muestra también la variación en la concentración de cada uno de los aceptores de electrones en el sedimento.

En principio, en los sedimentos la oxidación de la materia orgánica se produce secuencialmente en función de la energía libre, empleando como oxidantes primero oxígeno, nitrato, óxidos de Mn e Fe, sulfato y finalmente la propia materia orgánica via metanogénesis (Fig. 2; Froelich et al. 1979). Sin embargo, estas reacciones no son excluyentes, puede existir solapamiento entre los procesos de oxidación.

La oxidación aeróbica utiliza el oxígeno como aceptor de electrones y es la reacción que libera la mayor cantidad de energía (Fig. 2). Por lo que, cuando existe oxígeno disponible en el sedimento, los organismos capaces de utilizar oxígeno como oxidante predominarán y éste será consumido preferentemente. La respiración aeróbica predomina en sedimentos pelágicos debido a que estos reciben relativamente pequeñas cantidades de materia orgánica. La materia orgánica marina producida de forma natural es una mezcla compleja de proteínas, hidratos de carbono, lípidos y otros biopolímeros y una representación de la oxidación de este materia orgánica se puede expresar por la siguiente ecuación:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \text{ ---> } 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O$$

Esta ecuación establece que el estado de oxidación medio para el carbono en la materia orgánica es cero y que su ratio C:N:P es 106:16:1 (ratio Redfield). Además, lleva implícito que la remineralización aeróbica está acoplada a la oxidación del nitrógeno en el proceso de nitrificación llevado a cabo por bacterias litotróficas. Como consecuencia de ambos procesos, la concentración de oxígeno en el sedimento decrece con la profundidad de la misma forma que la concentración de nitrato aumenta (Fig. 2). Cuando la concentración de oxígeno se aproxima a cero el nitrato comienza a ser el aceptor de electrones preferido y se produce la desnitrificación, un proceso por el cual se genera preferentemente N_2 gas como producto final. Además de ello, también se acumulan los intermediarios en el proceso de reducción del nitrato (Codispoti et al. 2001), el cual se puede expresar de la siguiente forma:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

En la mayoría de los sedimentos costeros existe un acoplamiento fuerte entre los procesos de nitrificación y desnitrificación, de forma que gran parte del nitrato utilizado en la desnitrificación proviene del nitrato producido en el sedimento mediante la nitrificación (Burdige 2006). Codispoti et al. (2001), por ejemplo, muestran que la eliminación mediante procesos de desnitrificación de 'nitrógeno fijado', disponible biológicamente, tiene lugar casi exclusivamente en los márgenes continentales y sedimentos costeros.

Sin embargo, estudios recientes han descubierto que la desnitrificación no es la única ruta metabólica por la cual el nitrógeno fijado se pierde en forma de N_2 gas. En 1995, se identifica un nuevo proceso microbiano (anammpox) por el cual el amonio es oxidado anaeróbicamente por nitrito a N_2 gas (Mulder et al. 1995). Posteriormente en 2002, Thamdrup & Dalsgaard (2002) describen por vez primera el proceso de anammox en el medio marino. Actualmente, se estima que el anammox contribuye entre un 25 -30% de la producción de N_2(g) en el medio marino, considerando los sedimentos y las zonas de mínimo oxígeno (Lam & Kuypers 2011, Trimmer & Engström 2011).

Una vez que el nitrato es consumido la secuencia de remineralización de la materia orgánica continúa mediante la reducción de óxidos de Mn y Fe (Fig. 2) a sus formas solubles (Mn^{2+} y Fe^{2+}). La sulfatorreducción tiene una eficiencia energética menor comparada con los anteriores procesos por lo que tiene lugar en sedimentos donde existe un exceso de aporte de materia orgánica en relación a la cantidad de oxidantes disponibles (oxígeno, nitrato y óxidos de metales). Por lo tanto, la sulfatorreducción se produce en sedimentos ya muy reducidos, generalmente donde el oxígeno ha sido totalmente consumido. No es un proceso muy importante en sedimentos pelágicos sin embargo, puede ser predominante en sistemas costeros y márgenes continentales (Burdige 2006), alcanzando entre un 10-90 % de la remineralización de materia orgánica (Canfield et al. 1993). En la reducción de sulfato se genera sulfuro de hidrógeno (H_2S), el cual en muchos sedimentos costeros reacciona con el Fe para formar formas insolubles de sulfuros de Fe como es el caso de la pirita (Middelburg & Levin 2009).

Si todos los oxidantes son finalmente consumidos, la materia orgánica se respira y fermenta de forma anaeróbica, generando como resultado la formación de metano (metanogénesis). La producción de metano tiene mayor importancia en sedimentos fluviales dónde la concentración de sulfato es mucho menor que en sedimentos marinos (Burdige 2006). La remineralización de materia orgánica, fundamentalmente la respiración anaeróbica, produce la formación de varias sustancias reducidas (NH_4^+, Mn^{2+}, Fe^{2+}, H_2S y CH_4) las cuales pueden a su vez, volver a ser oxidadas ya que contienen una parte importante de la energía previamente contenida en la materia orgánica (Jørgensen 1982). Hasta un 90 % de las especies reducidas de Mn, Fe y S pueden llegar a ser re-oxidadas (Canfield et al. 1993).

1.2 Metabolismo neto del ecosistema

El conocimiento de la remineralización de la materia orgánica en la interfase sedimento-columna de agua nos aporta una pieza clave de la respiración del ecosistema cara a la estimación del metabolismo neto del ecosistema (Odum 1956). Este último es definido como la suma de todos los procesos anabólicos y catabólicos de todos los organismos incluidos en el sistema (Kemp et al. 1997). Por lo tanto, representa un balance entre la producción primaria (P) y la respiración total (R) en un sistema. La producción neta de materia orgánica se ve influenciada también por la entrada y salida de materia orgánica del sistema con los ecosistemas lindantes, ya que pueden modificar los procesos de respiración en el sistema (Testa et al. 2012). Los sistemas en los que $P > R$ se denominan autotróficos y normalmente son sistemas que reciben gran aporte de nutrientes inorgánicos en contraposición con los sistemas heterotróficos ($P < R$) los cuales reciben mayor aporte de materia orgánica. Mediante estudios del metabolismo de los ecosistemas costeros podemos obtener una medida integral de los cambios en los procesos ecológicos, que incluyen los ciclos biogeoquímicos de los elementos biogénicos así como de las interacciones entre los organismos de la cadena trófica (Odum 1956). Las tasas metabólicas de los ecosistemas costeros nos proporcionan de este modo una medida del estado ecológico del sistema en términos de sus transformaciones biogeoquímicas y su interacción con los ecosistemas adyacentes (Heath 1995).

Existe una demanda creciente de aproximaciones cuantitativas e integradoras sobre la respuesta de los sistemas costeros a diferentes combinaciones de cambios medioambientales (Kemp & Boynton 2012). Estos estudios de síntesis engloban diferentes disciplinas encaminadas a descubrir patrones, mecanismos e interacciones (Hobbie 2000) y en donde la información aportada por la cuantificación del metabolismo neto del ecosistema nos ayuda a entender mejor la estructura y funcionamiento del mismo (Odum 1971). Estas aproximaciones integrales deben ser aplicadas para mejorar la efectividad en la gestión de recursos costeros (Likens 1998).

1.3 Área de estudio

El noroeste de la Península Ibérica, constituye la única zona de afloramiento de Europa. Dentro de este sistema se localiza la ría de Vigo, una de las cuatro Rías Baixas, valles tectónicos en forma de V (Fig. 3), de grandes dimensiones (> 2.5 km^3), inundados por la

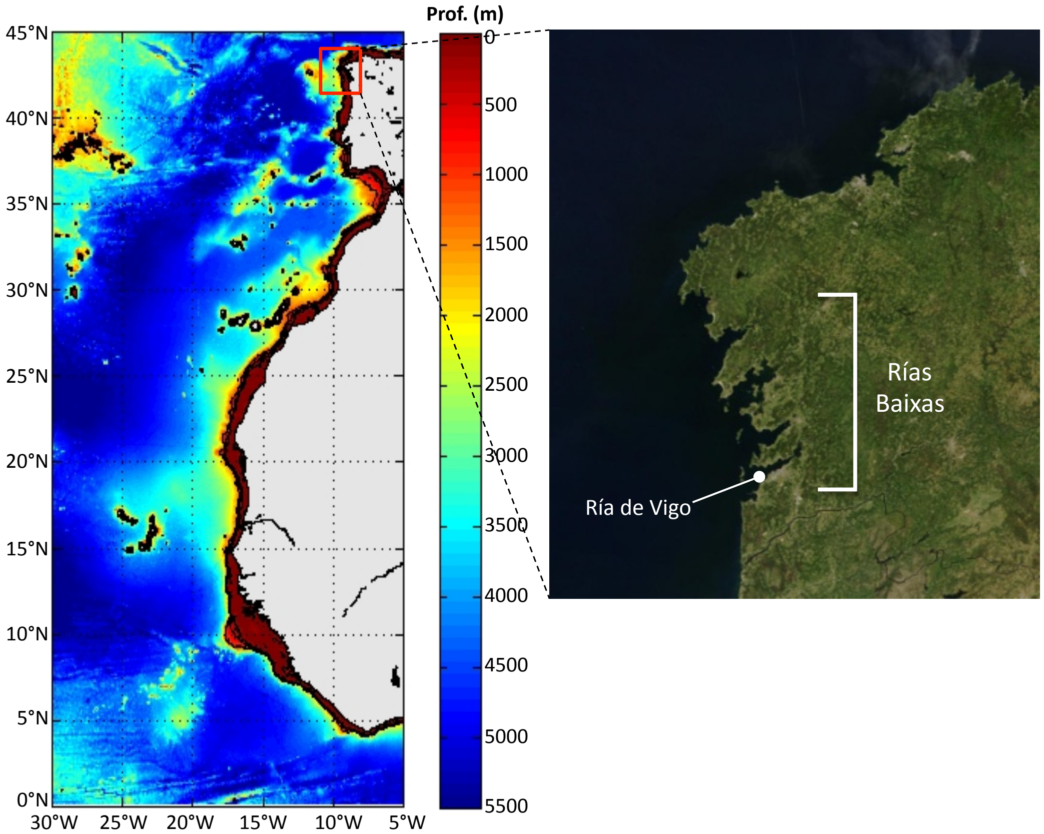


Figura 3. Área de estudio. En la izquierda se muestra el alfloramiento del noreste del Atlántico en el que se localiza mediante un rectángulo la zona de las rías Baixas, las cuales se muestran en mayor detalle en la figura de la derecha dónde, además, se localiza la ría de Vigo .

elevación del nivel del mar (Evans & Prego 2003). Las características hidrodinámicas de este margen costero están altamente influenciadas por el régimen estacional de viento. Entre Marzo-Abril a Septiembre-Octubre, el predominio de vientos de componente norte es el principal responsable del afloramiento de Agua Central Noratlántica del Este (ENACW; Eastern North Atlantic Central Water), caracterizada por un alto contenido en nutrientes (Fraga 1981, McClain et al. 1986, Castro et al. 2000). El agua aflorada es advectada hacia el oceáno abierto en forma de filamentos de afloramiento (Haynes et al. 1993), favoreciendo por tanto el intercambio de material desde la plataforma continental al océano adyacente. Durante el resto del año predominan los vientos de sur-suroeste, favoreciendo condiciones de hundimiento que provocan la entrada por superficie, de aguas de plataforma en la rías (Wooster et al. 1976, Castro et al. 1997). Las Rías Baixas se comportan como una extensión de la plataforma continental, respondiendo de forma directa al viento costero y la interacción entre el afloramiento costero y el patrón de circulación provocan una alta producción primaria dentro de las rías (~1.4 g C m^{-2} d^{-1} durante la época de afloramiento; Figueiras et al. 2002). Esta elevada producción primaria es la que ha permitido el crecimiento de una floreciente industria relacionada con el cultivo del mejillón *Mytilus galloprovincialis* Lamark. Las Rías Baixas sostienen la mayor producción mejillonera de Europa (250 x 10^6 kg yr^{-1}), dando empleo directo a 9000 personas y generando alrededor de unos 20,000 empleos indirectos (Figueiras et al. 2002) lo que implica que es una actividad de gran importancia socioeconómica en la zona.

Basándose en un intenso muestreo oceanográfico, con una frecuencia de dos veces por semanas, y mediante la aplicación de un modelo de circulación 2-D no estacionario, Álvarez-Salgado et al. (1996) y Rosón et al. (1999) establecieron los flujos y balances biogeoquímicos de C, N, P, Si y O_2 en la ría de Arousa durante la época de afloramiento. Estos autores cuantificaron la relación entre la fracción de la producción primaria que se regenera en la ría y la que se exporta a la plataforma en forma de materia orgánica particulada y/o disuelta, obteniendo que ~83% del carbono fijado en la ría es exportado a la plataforma, mientras que el 17% restante sedimenta en el interior de la misma. Sus resultados también muestran que del 83% de producción neta, un 55% es en forma de carbono orgánico disuelto, lo cual implica la ocurrencia de una intensa regeneración pelágica en el interior de la ría. Posteriormente, Gago et al. (2003a) mediante la aplicación de un modelo de circulación similar para la ría de Vigo, obtienen un porcentaje mucho mayor de la fracción sedimentada dentro de la ría (~ 62%) frente a la exportada (~ 34%). Si bien estos modelos nos dan un porcentaje del material que sedimenta en el interior de las rías no pueden llegar a diferenciar el destino final del mismo; qué fracción es incorporada ('enterrada') en el sedimento frente a la que sufre procesos de regeneración bentónica.

Estudios del incremento de la concentración de nutrientes del ENACW sobre la plataforma en relación al océano adyacente, ponen de manifiesto la ocurrencia de una intensa regeneración bentónica. Así, Álvarez-Salgado et al. (1997) muestran como este enriquecimiento aumenta hacia el fondo e interior de la plataforma, alcanzado máximos valores dentro de las rías (Prego et al. 1999). Por otro lado, Gago et al. (2003b) subrayan cómo la zona interior de la ría de Vigo se comporta como un manantial de CO_2 bajo diferentes condiciones oceanográficas, con excepción de la época invernal, lo cual también apunta a procesos de regeneración bentónica como causa de este comportamiento. Sin embargo, a pesar de estas evidencias indirectas, son muy pocas las medidas directas de estos procesos en la plataforma y todavía menos en el interior de las Rías Baixas. Epping et al. (2002) obtienen una tasa de deposición de carbono orgánico en los sedimentos de la plataforma de ~15 g C m^{-2} yr^{-1}, de los cuales un 33% pasa a incorporarse en los sedimentos. Si el valor medio de la producción primaria neta para la plataforma es de 547 g C m^{-2} yr^{-1} (Figueiras com. per.), la tasa de deposición supone tan sólo un 3% de la producción primaria neta.

Así pues aunque en las Rías Baixas se han realizado numerosos trabajos enfocados en el estudio de las condiciones hidrodinámicas y consecuencias biogeoquímicas bajo diferentes situaciones de forzamiento externo (escorrentía, viento local y costero, irradiancia...), la remineralización de la materia orgánica en la superficie del sedimento y la importancia de los flujos bentónicos es una de las asignaturas pendientes en este ecosistema de afloramiento costero.

2. Objetivos

La presente Tesis Doctoral se centra en el acoplamiento pelágico – bentónico, con especial interés en el estudio de los flujos bentónicos de nutrientes, oxígeno y carbono en el sistema de afloramiento costero de la ría de Vigo. Esta memoria se ha realizado en el marco de los proyectos de investigación TRACA: 'Desarrollo de una plataforma observacional para la cuantificación de los procesos de sedimentación/resuspensión de material biogénico', FLUVBE: 'Acoplamiento de los flujos verticales y bentónicos en la ría de Vigo' y MaBenE: 'Managing benthic ecosystems in relation to physical forcing and environmental constraints'.

La memoria comienza con el desarrollo de una cámara bentónica para medir *in situ* los flujos bentónicos y a partir de aquí, determinar el intercambio de nutrientes, carbono y oxígeno en la interfase sedimento - agua durante un ciclo anual, establecer cuáles son los factores que les afectan y estimar la importancia de la respiración bentónica en el metabolismo neto del ecosistema para incluirlos dentro de un balance anual de carbono. Por último, estudiar los efectos del cultivo de mejillón en los flujos bentónicos y a su vez en el posible acoplamiento pelágico-bentónico de la ría.

A fin de alcanzar el objetivo general se establecieron los siguientes objetivos específicos:

1. Diseño y construcción de una cámara bentónica para cuantificar el intercambio de solutos entre el sedimento y la columna de agua, que funcione de forma autónoma y que esté adaptada para trabajar en zonas costeras. Este sub-objetivo incluye la caracterización hidrodinámica en el interior de la cámara bentónica en condiciones controladas, así como la experimentación en campo para evaluar sus prestaciones y fiabilidad (*Capítulo II*).

2. Cuantificar los flujos bentónicos de nutrientes inorgánicos y oxígeno en la ría de Vigo cubriendo las principales épocas oceanográficas durante un año de estudio. Para determinar las variaciones estacionales de los flujos bentónicos y establecer los principales factores que los controlan, es necesario realizar simultáneamente una caracterización termohalina y biogeoquímica de la columna de agua y realizar medidas *in situ* de los flujos verticales de materia orgánica particulada. Analizar la importancia relativa de la

remineralización bentónica en los ciclos biogeoquímicos de nutrientes en la ría de Vigo (*Capítulo III*).

3. Utilizar los datos obtenidos *in situ* y de forma simultánea, de producción primaria, respiración pelágica, respiración bentónica y flujos verticales, durante el año de estudio, para determinar el metabolismo neto del ecosistema. Explorar la importancia de la respiración bentónica y evaluar hasta qué punto, influye en el estado trófico del sistema. Elaborar un balance anual de carbono para la ría de Vigo, en el que se incluyan además de estos datos, los potenciales aportes de aguas continentales, así como las pérdidas de carbono del sistema en forma de extracción de cultivo de mejillón, pesca y marisqueo (*Capítulo IV*).

4. Estudiar la influencia del cultivo de mejillón en el acoplamiento pelágico-bentónico mediante el estudio de la columna de agua, los flujos verticales y bentónicos en dos estaciones de la ría de Vigo, una localizada en un polígono de bateas y otra estación de referencia no directamente afectada por el cultivo de mejillón. Establecer un balance de carbono 1D para cada una de las localizaciones (*Capítulo V*).

3. References

Álvarez-Salgado XA, Castro CG, Pérez FF, Fraga F (1997) Nutrient mineralization patterns in shelf waters of the Western Iberian upwelling. Cont Shelf Res 17:1247–1270

Álvarez-Salgado XA, Rosón G, Pérez FF, Figueiras FG, Ríos AF (1996) Nitrogen cycling in an estuarine upwelling system, the Ría de Arousa (NW Spain). II. Spatial differences in the short-time-scale evolution of fluxes and net budgets. Mar Ecol Prog Ser 135:275–288

Bauer JE, Cai W-J, Raymond PA, Bianchi TS, Hopkinson CS, Regnier PAG (2013) The changing carbon cycle of the coastal ocean. Nature 504:61–70

Berner RA (1980) Early Diagenesis: A Theoretical Approach. Princeton University Press

Berner RA (1989) Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over phanerozoic time. Glob Planet Change 1:97–122

Boudreau BP (1997) Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments. Springer, Berlin

Burdige D (2006) Geochemistry of Marine Sediments. Princeton University Press, UK

Cai W-J (2011) Estuarine and Coastal Ocean Carbon Paradox: CO_2 Sinks or Sites of Terrestrial Carbon Incineration? Annu Rev Mar Sci 3:123–145

Canfield DE, Jorgensen BB, Fossing H, Glud RN, Gundersen J, Ramsing NB, Thamdrup B, Hansen JW, Nielsen LP, Hall POJ (1993) Pathways of organic carbon oxidation in three continental margin sediments. Mar Geol 113:27–40

Castro CG, Alvarez-Salgado XA, Figueiras FG, Perez FF, Fraga F (1997) Transient hydrographic and chemical conditions affecting microplankton populations in the coastal transition zone of the Iberian upwelling system (NW Spain) in September 1986. J Mar Res 55:321–352

Castro CG, Pérez FF, Álvarez-Salgado XA, Fraga F (2000) Coupling between the thermohaline, chemical and biological fields during two contrasting upwelling events off the NW Iberian Peninsula. Cont Shelf Res 20:189–210

Codispoti LA, Brandes JA, Christensen JP, Devol AH, Naqvi SWA, Paerl HW, Yoshinari T (2001) The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene? Sci Mar 65:85–105

Epping E, Zee C van der, Soetaert K, Helder W (2002) On the oxidation and burial of organic carbon in sediments of the Iberian margin and Nazaré Canyon (NE Atlantic). Prog Oceanogr 52:399–431

Evans G, Prego R (2003) Rias, estuaries and incised valleys: is a ria an estuary? Mar Geol 196:171–175

Falkowski PG, Flagg CN, Rowe GT, Smith SL, Whitledge TE, Wirick CD (1988) The fate of a spring phytoplankton bloom: export or oxidation? Cont Shelf Res 8:457–484

Figueiras FG, Labarta U, Reiriz MJF (2002) Coastal upwelling, primary production and mussel growth in the Rías Baixas of Galicia. Hydrobiologia 484:121–131

Fraga F (1981) Upwelling off the Galician Coast, Northwest Spain. In: Richards FA (ed) Coastal Upwelling. American Geophysical Union, Washington D.C., p 176–182

Froelich PN, Klinkhammer GP, Bender ML, Luedtke NA, Heath GR, Cullen D, Dauphin P, Hammond D, Hartman B, Maynard V (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim Cosmochim Acta 43:1075–1090

Gago J, Álvarez-Salgado XA, Gilcoto M, Pérez FF (2003a) Assessing the contrasting fate of dissolved and suspended organic carbon in a coastal upwelling system ('Ría de Vigo', NW Iberian Peninsula). Estuar Coast Shelf Sci 56:271–279

Gago J, Gilcoto M, Pérez FF, Ríos AF (2003b) Short-term variability of fCO2 in seawater and air–sea CO2 fluxes in a coastal upwelling system (Ría de Vigo, NW Spain). Mar Chem 80:247–264

Grenz C, Denis L, Pringault O, Fichez R (2010) Spatial and seasonal variability of sediment oxygen consumption and nutrient fluxes at the sediment water interface in a sub-tropical lagoon (New Caledonia). Mar Pollut Bull 61:399–412

Hatcher A, Grant J, Schofield B (1994) Effects of suspended mussel culture (*Mytilus* spp.) on sedimentation, benthic respiration and sediment nutrient dynamics in a coastal bay. Mar Ecol Prog Ser 115:219–235

Haynes R, Barton ED, Pilling I (1993) Development, persistence, and variability of upwelling filaments off the Atlantic coast of the Iberian Peninsula. J Geophys Res Oceans 98:22681–22692

Heath M (1995) An holistic analysis of the coupling between physical and biological processes in the coastal zone. Ophelia 42:95–125

Hedges JI, Keil RG (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar Chem 49:81–115

Hobbie JE (2000) Estuarine Science: A Synthetic Approach to Research and Practice. Island Press

Hopkinson CSH (1987) Nutrient regeneration in shallow-water sediments of the estuarine plume region of the nearshore Georgia Bight, USA. Mar Biol 94:127–142

Jahnke RA (2005) Transport processes and organic matter cycling in coastal sediments. In: Robinson AR, Brink KH (eds) The global coastal ocean. The sea: ideas and observations on progress in the study of the seas. Harvard University Press, Cambridge, p 163–191

Joint I, Wassmann P (2001) Lagrangian studies of the Iberian upwelling system—an introduction. A study of the temporal evolution of surface production and fate of organic matter during upwelling on and off the NW Spanish continental margin. Prog Oceanogr 51:217–220

Jørgensen BB (1982) Mineralization of organic matter in the sea bed—the role of sulphate reduction. Nature 296:643–645

Jorgensen BB, Boudreau BP (2001) Diagenesis and sediment-water exchange. In: Boudreau BP, Jorgensen BB (eds) The benthic boundary layer: transport processes and biogeochemistry. Oxford University Press

Kemp WM, Boynton WR (2012) Synthesis in Estuarine and Coastal Ecological Research: What Is It, Why Is It Important, and How Do We Teach It? Estuaries Coasts 35:1–22

Kemp WM, Smith EM, Marvin-DiPasquale M, Boynton WR (1997) Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Mar Ecol Prog Ser 150:229–248

Lam P, Kuypers MMM (2011) Microbial Nitrogen Cycling Processes in Oxygen Minimum Zones. Annu Rev Mar Sci 3:317–345

Likens GE (1998) Limitations to Intellectual Progress in Ecosystem Science. In: Pace ML, Groffman PM (eds) Successes, Limitations, and Frontiers in Ecosystem Science. Springer New York, p 247–271

Liu K-K, Atkinson L, Quiñones RA, Talaue-McManus L (2010) Biogeochemistry of Continental Margins in a Global Context. In: Liu PK-K, Atkinson PL, Quiñones PR, Talaue-McManus DL (eds) Carbon and Nutrient Fluxes in Continental Margins. Springer Berlin Heidelberg, p 3–24

Marcus NH, Boero F (1998) Minireview: The importance of benthic-pelagic coupling and the forgotten role of life cycles in coastal aquatic systems. Limnol Oceanogr 43:763–768

McClain CR, Chao S-Y, Atkinson LP, Blanton JO, Castillejo F De (1986) Wind-driven upwelling in the vicinity of Cape Finisterre, Spain. J Geophys Res Oceans 91:8470–8486

Middelburg JJ, Levin LA (2009) Coastal hypoxia and sediment biogeochemistry. Biogeosciences 6:1273–1293

Mulder A, Graaf AA van de, Robertson LA, Kuenen JG (1995) Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiol Ecol 16:177–183

Nixon SW, Oviatt CA, Hale SS (1976) Nitrogen regeneration and the metabolism of coastal marine bottom communities. In: Anderson JM, Macfaden A (eds) The role of

Terrestrial and Aquatic Organisms in Decomposition Processes. Blackwell Scientific Publications, London, p 269–283

Odum HT (1956) Primary production in flowing waters. Limnol Oceanogr 1:102–117

Odum HT (1971) Environment, power, and society. Wiley-Interscience, New York

Pilskaln CH, Paduan JB, Chavez FP, Anderson RY, Berelson WM (1996) Carbon export and regeneration in the coastal upwelling system of Monterey Bay, central California. J Mar Res 54:1149–1178

Prego R, Barciela M del C, Varela M (1999) Nutrient dynamics in the Galician coastal area (Northwestern Iberian Peninsula): Do the Rias Bajas receive more nutrient salts than the Rias Altas? Cont Shelf Res 19:317–334

Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, Laruelle GG, Lauerwald R, Luyssaert S, Andersson AJ, Arndt S, Arnosti C, Borges AV, Dale AW, Gallego-Sala A, Goddéris Y, Goossens N, Hartmann J, Heinze C, Ilyina T, Joos F, LaRowe DE, Leifeld J, Meysman FJR, Munhoven G, Raymond PA, Spahni R, Suntharalingam P, Thullner M (2013) Anthropogenic perturbation of the carbon fluxes from land to ocean. Nat Geosci 6:597–607

Rosón G, Álvarez-Salgado XA, Pérez FF (1999) Carbon cycling in a large coastal embayment, affected by wind-driven upwelling: short-time-scale variability and spatial differences. Mar Ecol Prog Ser 176:215–230

Soetaert K, Middelburg JJ, Herman PMJ, Buis K (2000) On the coupling of benthic and pelagic biogeochemical models. Earth-Sci Rev 51:173–201

Testa JM, Kemp WM, Hopkinson Jr CS, Smith SV (2012) Ecosystem metabolism. In: Day JW, Crump BC, Kemp WM, Yañez-Arancibia A (eds) Estuarine Ecology. John Wiley & Sons, p 381–416

Thamdrup B, Dalsgaard T (2002) Production of N2 through Anaerobic Ammonium Oxidation Coupled to Nitrate Reduction in Marine Sediments. Appl Environ Microbiol 68:1312–1318

Trimmer M, Engström P (2011) Distribution, activity, and ecology of anammox bacteria in aquatic environments. In: Ward BB, Arp DJ, Klotz MG (eds) Nitrification. ASM Press, Washington DC

Walsh JJ (1991) Importance of continental margins in the marine biogeochemicalcycling of carbon and nitrogen. Nature 350:53–55

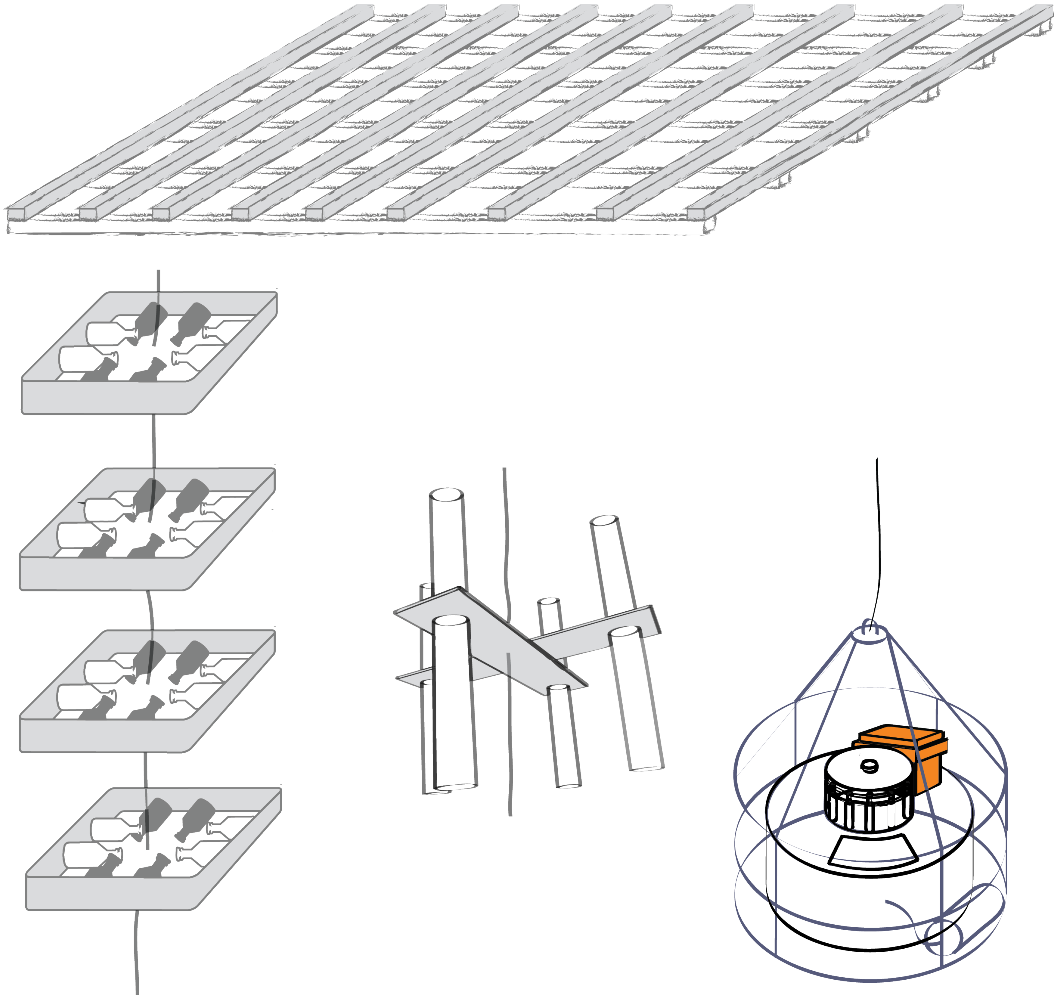
Wollast R (1998) Evaluation and comparisson of the global carbon cycling in the coastal zone and in the open ocean. In: Brink KH, Robinson AR (eds) The Sea, Brink, K.H. Wiley & Sons, New York, p 213–252

Wollast R, Chou L (2001) The carbon cycle at the ocean margin in the northern Gulf of Biscay. Deep Sea Res Part II Top Stud Oceanogr 48:3265–3293

Wooster WS, Bakun A, McLain DR (1976) Seasonal upwelling cycle along eastern boundary of North-Atlantic. J Mar Res 34:131–141

Zeldis JR (2004) New and remineralised nutrient supply and ecosystem metabolism on the northeastern New Zealand continental shelf. Cont Shelf Res 24:563–581

HYDRODYNAMIC CHARACTERIZATION AND PERFORMANCE OF AN AUTONOMOUS BENTHIC CHAMBER FOR USE IN COASTAL SYSTEMS



Capítulo II

Ferrón, S., Alonso-Pérez, F., Castro, C.G., Ortega, T., Pérez, F.F., Ríos, A.F., Gómez-Parra, A., Forja, J.M., 2008. Hydrodynamic characterization and performance of an autonomous benthic chamber for use in coastal systems. *Limnology and Oceanography: Methods 6, 558–571*.

Abstract

A benthic chamber (covering 5030 cm^2 of seafloor) with real time control of sampling and sensor data transmission has been developed for studying benthic fluxes in coastal sediments. Enclosed water is stirred by three submersible centrifugal pumps, which are connected to power circuits that regulate their input voltage and thus, the current velocity inside the chamber. The complete mixing of the incubated water is achieved within 4 minutes. The 3D velocity field and the distribution of the diffusive boundary layer (DBL) inside the chamber were characterized at different pump rates in a laboratory tank with a bottom layer of sediment or a false bottom supporting alabaster dissolution plates. Two different outlet devices from the pumps were tested. For the one finally selected, averaged tangential velocities at 5 cm above the bottom ranged from 2.0 cm s^{-1} to 4.8 cm s^{-1}, depending on the voltage applied to the pumps, providing averaged DBL thicknesses that ranged from 125 µm to 279 µm. Average tangential velocity and average DBL thickness were found to correlate according to: $V_T = 615x[DBL]^{-1.02}$ (R^2= 0.97). Successful field chamber measurements were performed in two shallow coastal systems: Ría de Vigo (NW Spain) and Bay of Cádiz (SW Spain).

Resumen

El presente trabajo muestra el desarrollo y la caracterización de una cámara bentónica, que cubre una superficie de sedimento de 5030 cm^2, para el estudio de flujos bentónicos en sedimentos costeros. El equipo dispone de control en tiempo real de los datos de muestreo así como sensores de medida en continuo. El agua incubada en la cámara es homogeneizada mediante tres bombas sumergibles, conectadas a los sistemas de energía, los cuales pueden regular el voltaje de entrada y por lo tanto, la velocidad de corriente dentro de la cámara. La mezcla completa del agua incubada se consigue en 4 minutos. Se estudió el campo de velocidades en 3D así como la distribución de la capa límite de difusión (DBL) dentro de la cámara bentónica en un tanque de laboratorio, utilizando como fondo una capa de sedimento o un falso fondo de neopreno incluyendo placas de disolución de alabastro. Se compararon dos sistemas distintos de expulsión del agua a través de las bombas. Las velocidades tangenciales a 5 cm sobre el fondo, para el sistema finalmente escogido, estuvieron en un rango entre 2.0 cm s^{-1} y 4.8 cm s^{-1}, dependiendo del voltaje aplicado a las bombas, lo que generó espesores promedio de la DBL desde 125 µm a 279 µm. La velocidad tangencial y los espesores promedio de la DBL correlacionaron siguiendo la siguiente fórmula: $V_T = 615x[DBL]^{-1.02}$ (R^2= 0.97). Finalmente, se realizaron satisfactoriamente medidas de flujos bentónicos en dos sistemas costeros someros: la ría de Vigo (NO de España) y la bahía de Cádiz (SO de España).

1. Introduction

The importance of solute exchange across the sediment-water interface has become increasingly recognized during recent years (Sayles 1981, Jorgensen & Boudreau 2001, Hammond et al. 2004), as it influences the water column concentrations and speciation of several elements (Aller 1980). Furthermore, benthic exchange rates give information about the diagenetic reactions occurring in the sediments (Berner 1980). Solute transport across the sediment-water interface is mainly affected by biological and chemical processes within the sediments (Jorgensen & Boudreau 2001), as well as by the hydrodynamic conditions near the bottom (Boudreau & Guinasso 1982).

Different methods have been used to study benthic fluxes (for a recent review see Viollier et al. 2003). Diffusive fluxes can be indirectly calculated from the concentration gradients measured in sediment pore water (Aller 1980, Sayles 1981, Reimers et al. 1986). An alternative approach is the direct measure of benthic fluxes from the concentration evolution in an enclosed water volume in contact with the sediment, in core or benthic chamber incubations (Pamatmat & Banse 1969, Rowe et al. 1975, Hammond et al. 2004, Ferguson et al. 2007). Among these techniques, the benthic chambers offer several advantages. Apart from avoiding sediment manipulation, the sediment surface covered by the chamber can be relatively large, and therefore, it can take into account the variability caused by fine scale sediment heterogeneity, as well as the contribution of benthic fauna. In fact, the presence of meio- and macrobenthos in natural environments can significantly enhance sediment-water exchange by bioturbation and bioirrigation (Aller & Aller 1986, Forja & Gómez-Parra 1998, Glud et al. 2003). To correctly represent the faunal activity when measuring benthic fluxes, measurements should preferably be made *in situ* and with relatively large benthic chambers (Glud & Blackburn 2002).

When using benthic chambers the sediment is isolated from the influence of natural hydrodynamics. A major consideration in the use of benthic chambers is therefore, the stirring of the water phase (Boynton et al. 1981, Hartman & Hammond 1984). Most chambers are equipped with a stirring mechanism (e.g. pumps, paddles, magnetic stirring bars) in order to simulate natural hydrodynamic conditions and avoid stratification of the incubated water. The water flow near the bottom affects the bottom stress and thus the thickness of the diffusive boundary layer (DBL) (Jorgensen & Des Marais 1990, Glud et al. 2003, 2007). The DBL represents a thin viscous film of water at the sediment-water interface where molecular diffusion becomes the principal mechanism for mass transport (Santschi et al. 1983, Boudreau & Jorgensen 2001). In some cases, the DBL can act as an important diffusion barrier and limit the exchange of solutes across the sediment-water interface (Boudreau & Guinasso 1982, Jorgensen & Revsbech 1985, Archer et al. 1989, Jorgensen & Des Marais 1990, Jorgensen & Boudreau 2001). In deep-sea sediments with low biogeochemical activity, the DBL resistance to exchange rates can often be neglected. However, in active coastal sediments the hydrodynamic conditions and DBL impedance can be very significant (Jorgensen & Boudreau 2001).

In an attempt to characterize the hydrodynamics imposed by the chambers and make sure that they do not affect *in situ* flux measurements, DBL thicknesses inside stirred chambers have previously been measured directly with microelectrodes (e.g. Glud et al. 1995, Black et al. 2001) or calculated from alabaster dissolution (Santschi et al. 1983, Buchholtz-ten Brink et al. 1989, Tengberg et al. 2004). Chambers differing in shape, size and with variable styles of stirrers will have different specific hydrodynamic conditions. A comprehensive review and comparison of different autonomous benthic chamber designs and modes of operation, as well as the different stirring devices used can be found in Tengberg et al. (1995) and Tengberg et al. (2005).

Benthic fluxes of inorganic carbon, nutrients and oxygen have previously been measured *in situ* in coastal waters of the Iberian Peninsula by means of opaque plexiglass stirred chambers (Forja & Gómez-Parra 1998, Forja et al. 2004, Ortega et al. 2005, 2008). These chambers, apart from requiring SCUBA divers for their correct placement over the sea-bottom, had to be physically connected to a vessel or a dock at the sea surface so that sample collection could be triggered manually. This issue considerably limited the potential sites where they could be used. Moreover, they did not enable independent ship motion as the ship has to stay on station attached to the chambers. In this context, this work reports the development and testing of a new autonomous stirred benthic chamber designed for shallow coastal waters. The chamber is large in size in order to obtain representative measures of benthic exchange, taking into account sediment heterogeneity. The chamber is provided with an innovative mechanism to verify that it has correctly landed on the sea-bottom, which avoids the need of SCUBA divers, and it uses a two-way communication system that allows the user to control all the operational components during the incubations. The hydrodynamic properties of the chamber were investigated at different stirring flow rates by measuring the horizontal and vertical current velocities as well as the DBL thicknesses inside the chamber.

2. Materials and methods

2.1 Chamber description

2.1.1 Structure and components

A detailed diagram of the benthic chamber is given in Fig. 1. The equipment is composed of a stainless steel frame on which all the operational components are mounted. The weight of the entire structure, including batteries and ballast, is approximately 245 kg. In the center of the structure, a 28 cm high cylindrical opaque PVC chamber (1 cm wall thickness) covers 5030 cm^2 of sea-bottom. The volume of the chamber is 140.8 ± 3.5 L. An 8 cm rim assures proper insertion of the chamber into the sediment. On top of the cylindrical structure, three PVC lids operate by means of an external 12 V DC motor through nylon fishing lines fitted on pulleys. During the landing process they remain open to minimize disturbance of the sediment and to guarantee that the enclosed water comes from water overlying the sea-bottom and not from a mixture of the entire water column. A tight seal between the openings and the lid is ensured by the use of gaskets and stainless steel coil springs which provide sealing pressure. Prior to field experiments, the chamber was tested for leakage by placing it inside a large tank filled with water and sediment and injecting a colored tracer (eosine) into the chamber. No loss of tracer was visually observed.

Up to twelve 50 mL water sample syringes can be withdrawn during deployment, with a multiple water sampler (KC Denmark) located on top of the chamber (Fig. 1). The timing of the samples is software controlled. The volume of sample withdrawn, representing ~0.03% of the incubated water, is compensated by using a latex sheath. When a sample is

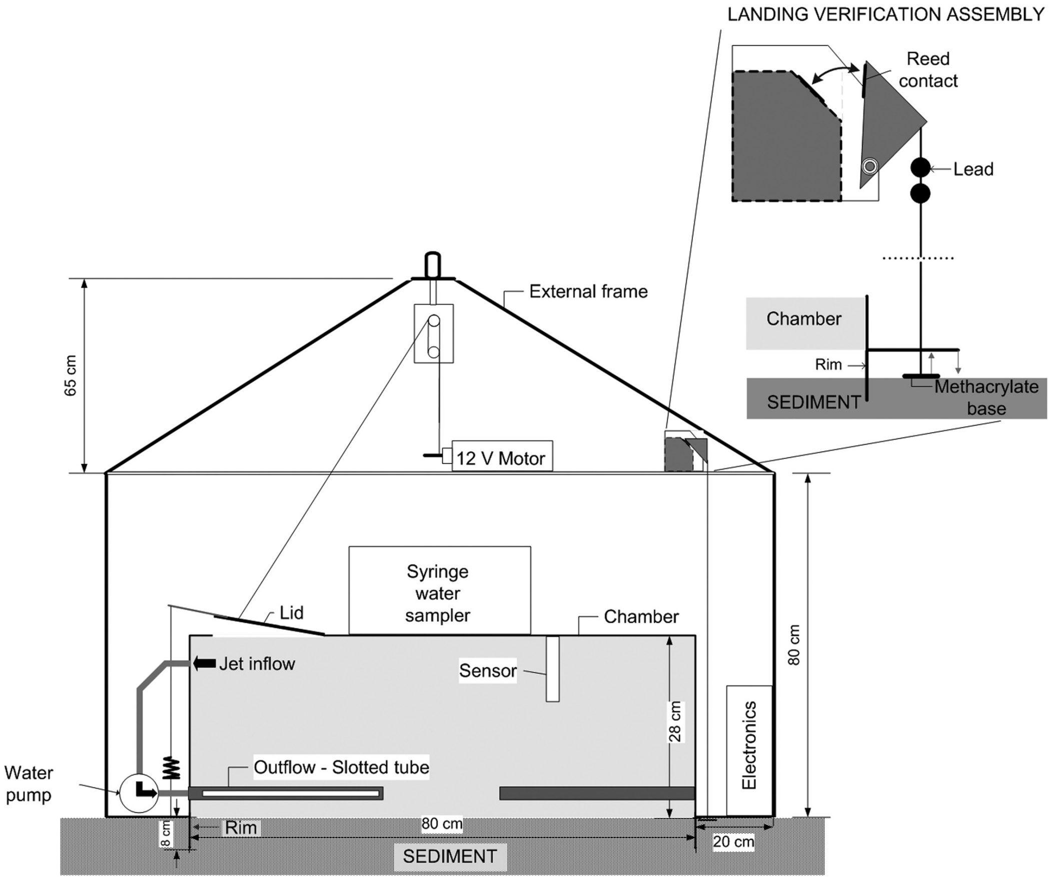


Figure 1. Schematic side-view drawing of the benthic chamber equipment, including a zoomed view of the land verification assembly. Expanded image is not to scale. Material shown: sensors (1 of 4), water pumps (1 of 3), lids (1 of 3), outlet slotted tubes (2 of 3) and electronic cases (1 of 3).

withdrawn, it fills up with external water that remains isolated from the incubated water, so that it avoids a pressure change inside the chamber as well as the input of external water.

Inside the chamber, sensors for temperature (SBE-39), pH (SBE-18), oxygen (SBE-43) and turbidity (Seapoint Turbidity Meter), which were provided by the company Sea-Bird Electronics, Inc, give a continuous recording of these variables during the incubation time. All electronic components are housed inside watertight titanium pressure-cases, which are fixed to the frame and interfaced through 4- to 8-pin marine connectors. Power to operate the chamber is derived from different sources. Two 12 V-7.2 Ah rechargeable batteries power the sensors, the electronic equipment and the water sampler, while a rechargeable oil pressure compensated battery (12 V-76 Ah) powers the stirring mechanism and the motor that opens and closes the lids, providing power for approximately 12 hours of autonomous operations.

2.1.2 Stirring mechanism

Water recirculation inside the chamber is achieved using three submersible centrifugal pumps (Totton DC 30/5), which are located outside the chamber, attached to the frame and connected to the chamber through silicone tubing (3 mm wall thickness). The 12 V DC stepper-motors are placed inside watertight housings, useable up to 100 m depth, and magnetically coupled with the impeller. The three pumps flush water from the upper part of the chamber wall and jet it back into the chamber through adjustable inlet nozzles located near the bottom (Fig. 1). The jet outflows and inflows are placed every 120° apart, for an even current flow. The stirring assembly is connected to power circuits that regulate the output voltage applied to the pumps, so that current velocity inside the chamber can be controlled. Five different output voltages (up to 8 V) can be easily set at the power circuit box. At maximum pumping rate the total consumption of the system is below 6 A.

2.1.3 Deployment and landing verification assembly

During a typical deployment, the benthic chamber is lowered from the ship by a mooring line, stopping at a few meters above the seabed to allow the sensors to stabilize. The lids remain open and the stirring system is already working to avoid possible contamination with water from upper layers. After several minutes, the chamber is slowly lowered, minimizing sediment disturbance, until it reaches the bottom. The turbidity sensor is a good indicator to check re-suspension effects from the landing process. Once on the sea-bottom, the lids are closed and the communication surface buoy, which is connected to the chamber data logger by an electromechanical cable, is released from the ship. The cable is always released in excess to overcome changes in water column height due to waves and tides. The estimated floatability of the communication buoy is ~ 20 times smaller than the in-water weight of the chamber (~ 200 kg). Occasionally, in sites with strong water currents or waves, an auxiliary intermediate ballast may be released on the sea-bottom, between the benthic chamber and the buoy, to prevent the transmission of currents and wave motions from the buoy to the chamber instrument.

An innovative mechanism, based on reed switches, was designed to verify proper landing of the chamber on the sea-bottom (Fig. 1, upper right). When the chamber contacts the sea-bottom and the rim sinks into the sediment, three methacrylate bases, located at the bottom collar surrounding the chamber, elevate three steel bars, making the reed switches contact with a magnet. This contact is checked by applying an electrical signal to the system. As these three devices are placed 120° apart, it is assumed that a signal coming from the three reeds indicates a correct horizontal landing of the chamber and, therefore, that the chamber is level and right side up. A similar procedure using reed switches is applied to confirm closure of the lids.

2.1.4 Data Acquisition and Communication

The whole system is controlled by a CR10X Campbell Scientific Data Logger. Two different telemetry communication mechanisms have been successfully tested:

(i) a two-way Global System for Mobile communications (GSM) that enables data acquisition in real time, as well as monitoring sample withdrawn, pump rates, batteries and confirmation mechanisms. The GSM communication system is housed in a watertight case mounted on the communication buoy at sea surface, and is connected to an 8 db antenna that assures good transmission coverage, and to the benthic chamber data logger through a submersible electromechanical cable. The main advantage of this system is not being distance limited within phone coverage.

(ii) a 869 MHz radio frequency, two way communication system (SATELLINE-3AS, SATEL). The receiver is mounted on the communication buoy at sea surface and the transmitter is mounted on board, covering distances up to 4 km.

The software controlling all the operational components of the chamber has been developed from Campbell's commercial scientific software. The computer interacts with the data logger to verify the proper insertion of the chamber into the sediment, to operate the lids, to set sample time collection and to select the output voltage applied to the stirring system. The software also displays the signals of the sensors as well as the battery voltage in real time.

2.2 Water sample handling and analytical methods

Water samples for NH_4^+ analysis, collected during the field chamber incubations reported in this work, were filtered and determined with a segmented flow Alpkem autoanalyzer (± 0.05 µmol kg^{-1}). Water samples for N_2O and CH_4 analysis were carefully drawn, immediately after they were recovered, in 25 mL air-tight glass bottles. Samples were preserved with saturated mercuric chloride, sealed with Apiezon grease and stored in the dark until analysis. Dissolved N_2O and CH_4 concentrations were determined with a gas chromatograph (Varian CX 3600) provided with an Electron Capture Detector (ECD) and a Flame Ionization Detector (FID). In-syringe head space equilibration was used to extract the dissolved gases from the water samples. The precision of the method, including the equilibration step, expressed as the coefficient of variation based on replicate analysis (n =25) of a seawater sample saturated with CH_4 and N_2O, was 4.8% and 6.6%, respectively. The concentrations of the gases in the water samples were calculated from the concentrations measured in the head space, using the functions for the Bunsen solubilities given by Wiesenburg & Guinasso (1979) for CH_4, and Weiss & Price (1980) for N_2O.

3. Assessment

3.1 Mixing time

A set of experiments were made in order to estimate the mixing time of the stirred water inside the chamber and the total volume of incubated water. The chamber was placed inside a tank and incubated after injecting 50 mL of a 20 mM sodium nitrite solution. Immediately after the injection, twelve water samples were withdrawn and analyzed for $[NO_2^-]$ (Grasshoff et al. 1983). Once the NO_2^- concentration remains constant with time, it is assumed that complete mixing is achieved. Incubations were performed applying a range of voltages (4 V-8 V) to the submersible pumps. In one of the experiments water samples were withdrawn at different heights (3 cm, 15 cm and 25 cm above sea-bottom) in the water column inside the chamber, in order to test possible gradient formation.

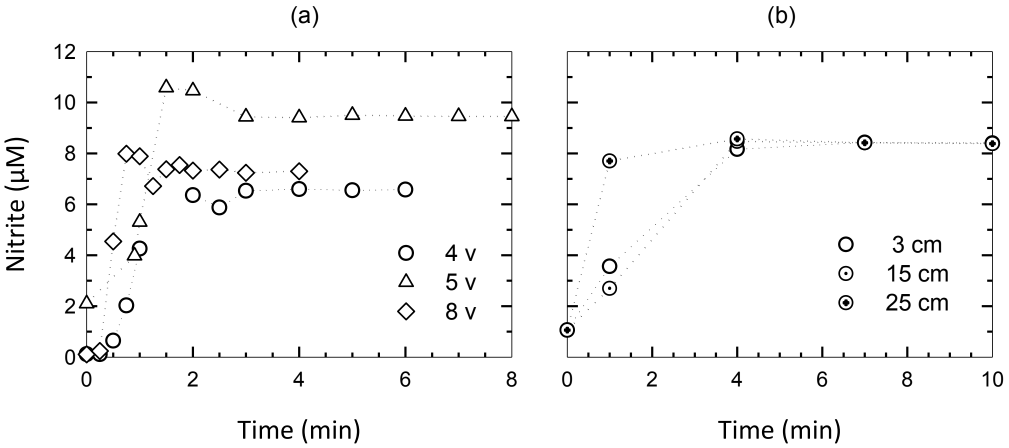


Figure 2. Time series evolution inside the chamber of nitrite concentration after injection applying three different voltages to the water pumps (a) and sampling at three depths (output voltage : 4 V)(b).

Results showed that the nitrite injected inside the chamber achieved a constant concentration 3-4 min after the injection at the lowest voltage (4 V, Fig. 2a,b) and this time was reduced to 3 min and 1.5 min when the output voltage was increased to 5 V and 8 V, respectively. Regarding the gradient formation, the experiment with samples collected at different heights showed that after 4 minutes the nitrite concentration was the same for the three depths (Fig. 2b). These results confirm that water is homogenized in less than 4 minutes and that there is no stratification inside the chamber, which means that the sampled water is representative of the entire incubated water. The mixing time for this chamber is within the range reported by Tengberg et al. (2005) for 14 different designs of chambers, which cover sediment surface areas between 78 and 12100 cm^2. These authors measured a wide range of mixing times, with values varying from less than 1 min to more than 60 min (in most cases between 0.5 min and 8 min).

3.2 Hydrodynamics inside the chamber

The 3D velocity field inside the chamber was characterized by means of a NORTEK Acoustic Doppler velocimeter. The experiments were carried out in the same tank used for testing for leakage. Two different mechanisms for the jet outflow were tested for their ability to duplicate the hydrodynamic conditions and bottom DBL thickness of the natural environment: (i) mechanism A, a 10 cm-long PVC tube ending in an elbow (2 cm of inner diameter) (Fig. 3a), and (ii) mechanism B, a 23 cm long PVC tube (2 cm of inner diameter) with a 1 cm-wide slot and sealed at the end (Fig. 1, Fig. 3b). Both systems are hereinafter called elbow and slotted tube, respectively. In the former, the water comes out the tube in a single water jet, whereas in the latter, the water exits the tube and forms a wider water stream throughout the slot. The outlets are located 5 cm above the bottom and are horizontally oriented in the same direction, with a slight upward inclination.

Water velocities for testing mechanism A were measured with a NORTEK Acoustic Doppler velocimeter provided with three receiver arms (Vector 3D current meter), whereas when testing mechanism B an improved velocimeter (Vectrino) was used, which is comprised of four streamlined receiver arms and a substantially smaller probe. The latter allowed broader velocity coverage inside the chamber due to its smaller dimensions. The factory-calibrated instrument's accuracy is ± 0.1 cm s^{-1}.

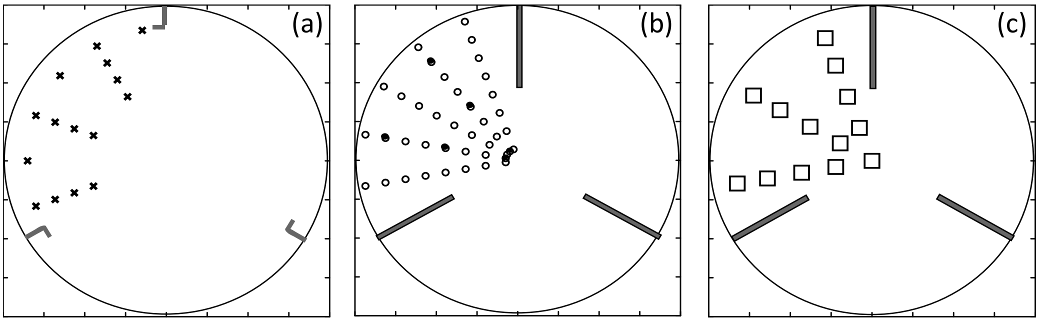


Figure 3. Schematic drawings showing the location of (a) velocity measurements at 5 cm above the sediment using elbows as outlet system; (b) velocity measurements at 5 cm above the sediment using slotted tubes as outlet system (solid circles represent the positions where vertical velocity profiles were performed); (c) alabaster plate locations for the estimation of DBL thicknesses. Space between ticks is 10 cm.

The PVC chamber cover was replaced by a methacrylate top, in which a 2 cm wide radial groove allowed the current meter to be moved inside the chamber. Once the current meter was fixed at the sampling point, the rest of the groove was sealed. Sampling locations were distributed along 5 radials (A-E) at 20° intervals (Fig. 3), covering a 100° section situated between the inflows and outflows of two pumps. Therefore, results can be inferred for the rest of the cylindrical chamber. Velocities were measured in a horizontal layer at 5 cm above the sediment, applying five different voltages to the stirring system. Vertical velocity profiles were also measured at some locations, as shown in Fig. 3b.

For the two stirring mechanisms, the horizontal velocity measurements indicated that the flow is mainly tangential and rather uniform along the circumference. The contour map of the tangential velocity inside the chamber (5 cm from the bottom), using the elbow system (Fig. 4a) reflects a high concentric gradient of the horizontal velocity field. Measured horizontal velocities ranged from 0.3 cm s^{-1} to 4.4 cm s^{-1} at 4 V and 0.7 cm s^{-1} to 9.8 cm s^{-1} at 6 V. Higher velocity values were obtained close to the chamber wall, as a result of the proximity to the elbow water outlet. The module of horizontal velocity decreases rapidly towards the center, so that the flow velocity is lower than 1 cm s^{-1} in approximately 25 % of the total chamber area when applying 6 V to the pumps. The area affected by this very low horizontal velocity increases to up to 42 % when applying 4 V to the pumps.

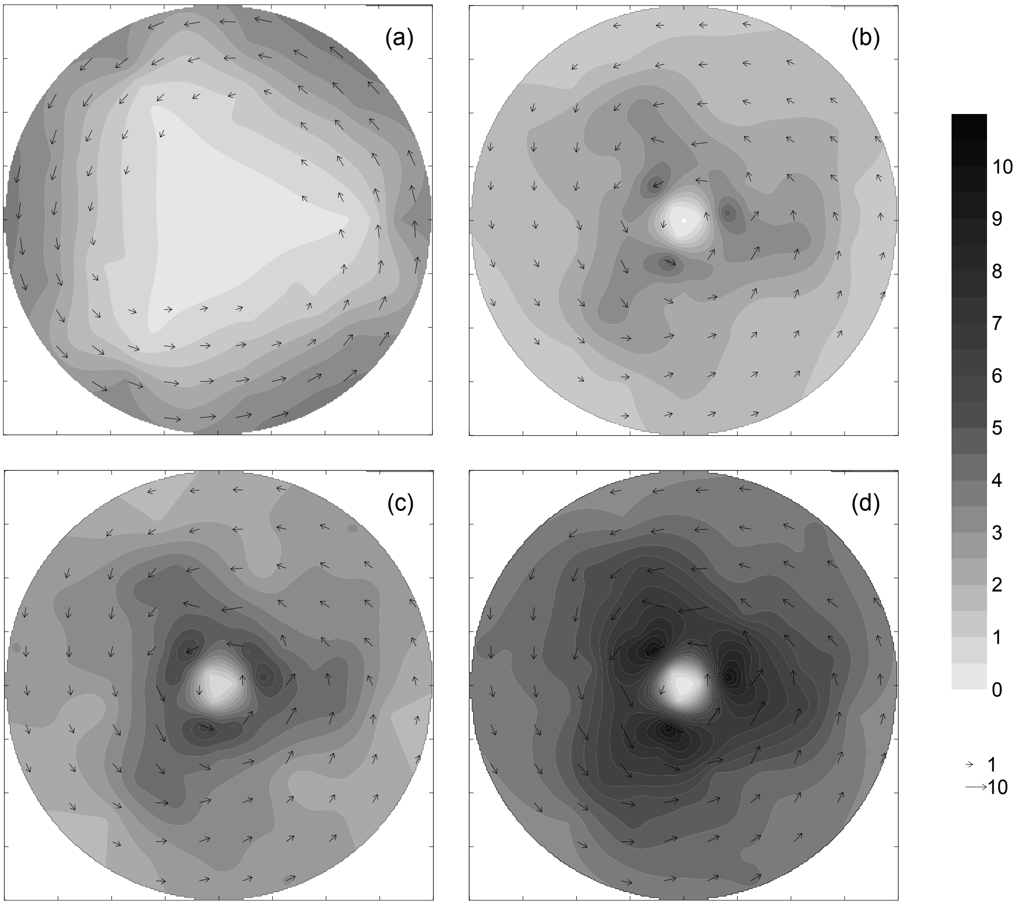


Figure 4. Distribution of the tangential velocity (cm s^{-1}) measured at 5 cm above the bottom, comparing two outlet systems: elbows (a) and slotted tubes (b-d). Voltage applied to the pumps: (a) 5 V; (b) 4 V; (c) 6 V and (d) 8 V. Arrows show the direction of the flow, and their dimension reflects the horizontal velocity module (cm s^{-1}). Space between ticks is 10 cm.

The slotted tube system appears to be a more reliable stirring mechanism. Table 1 presents the averaged tangential velocities at each of the applied voltages. The vector velocity distribution (Fig. 4b-4d) reveals that the flow inside the chamber is characterized by a tangential and relatively uniform flow in the horizontal layer. The result is a rotary flow generated inside the chamber, with average tangential velocities between 2 cm s^{-1} and 5 cm s^{-1}, depending on the voltage input to the submersible pumps (Table 1). Although velocity slightly increases towards the centre of the chamber, it shows a minimum in the centre due to the rotating circulation. This portion of the chamber, characterized by velocities under 1 cm s^{-1}, occupies only 0.6 % of the total chamber area. Vertical profiles of the horizontal velocity (Fig. 5) also indicate a constant profile in the water column.

Table 1. Input voltage to the stirring system (V), pump rate (L min^{-1}), averaged tangential velocities (V_T) and range of vertical velocities (V_Z) measured at 5 cm above the bottom; averaged DBL thicknesses calculated both from individual alabaster plates (weighted by the area represented by each plate) and from Ca^{2+} increase, and estimated mixing time at different pump rates and input voltages. The last line corresponds to the experiments done using the elbow system.

Voltage (V)	Pump rate (L min^{-1})	V_T (cm s^{-1})	V_z (cm s^{-1})	DBL individual plates (μm)	DBL Ca^{2+} increase (μm)	Mixing time (min)
4	13.9 ± 0.9	2.04 ± 0.64	-0.64–1.33	279 ± 75	333.2	< 4
5	18.4 ± 0.7	2.49 ± 0.73	-0.40–1.95	231 ± 98	229.2	< 3
6	22.9 ± 0.6	3.10 ± 0.83	-0.79–2.13	180 ± 80	--	--
7	27.4 ± 0.5	3.71 ± 1.02	-1.48–2.78	139 ± 59	197.0	--
8	32.0 ± 0.4	4.77 ± 1.30	-1.08–2.73	125 ± 55	195.4	< 1.5
5	18.4 ± 0.7	1.79 ± 1.06	-0.72–0.96	309 ± 120	369.5	--

Regarding the vertical velocity field inside the chamber, weaker velocities were measured compared to the horizontal velocity range (Table1). Negative values indicate a downwards flow and vice versa. The contour map of the vertical velocity at 5 cm above the bottom (Fig. 6a) shows that water inside the chamber ascends from the center (positive values) and descends mainly close to the wall, creating a circular flow. This feature is confirmed by the vertical velocity profile from the chamber wall to the center (Fig. 6b).

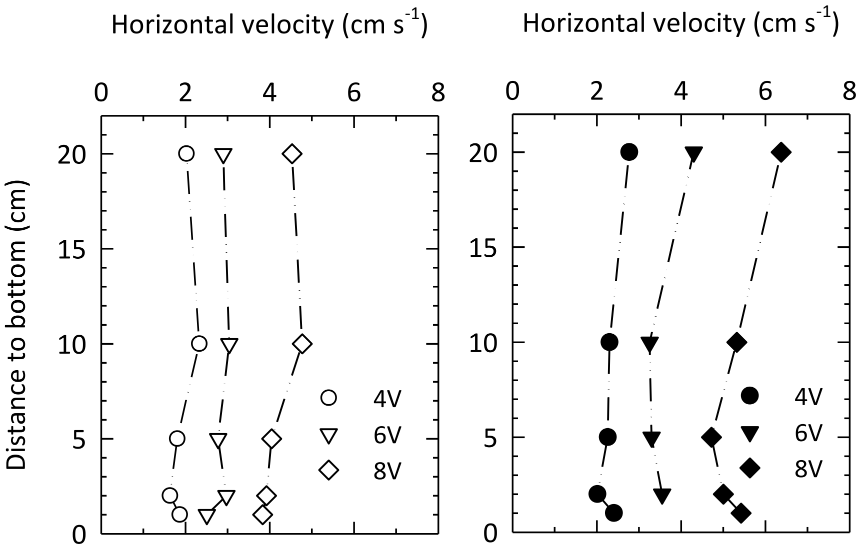


Figure 5. Horizontal velocity profiles applying three different voltages to the water pumps. (a) Profile D2 (30 cm to the chamber centre, see Fig. 3). (b) Profile D5 (15 cm to the chamber centre, see Fig. 3).

3.3 DBL thickness

DBL thicknesses inside the chamber were estimated using the alabaster dissolution method, both through weight loss of individual alabaster plates and through the [Ca^{2+}] increase in the overlying water (Santschi et al. 1983, Buchholtz-ten Brink et al. 1989). Thirteen 5 x 5 x 1 cm square alabaster plates were pre-weighed and mounted on a neoprene bottom at different positions inside the chamber (Fig. 3c). The alabaster pieces were painted on the sides and bottom with polyurethane to prevent dissolution from non-exposed surfaces, and were fitted into the neoprene so that they did not protrude from it. For the experiments, a tank was filled with fresh water and the neoprene bottom with the alabaster plates was inserted. Immediately after, the chamber was placed on top of it to start the experiment. Approximately 14 hours were needed for measurable weight losses in the alabaster plates.

During this period, twelve water samples were collected for Ca^{2+} analysis. [Ca^{2+}] were measured by means of an inductively coupled plasma mass spectrometer (ICP-MS). After each experiment, the alabaster plates were carefully removed, air-dried and weighed.

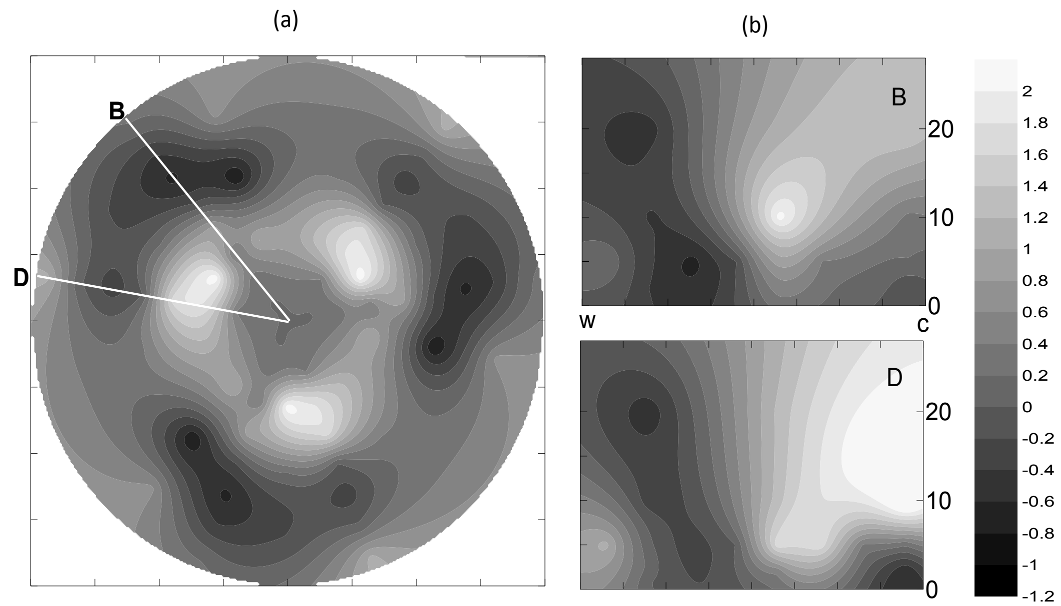


Figure 6. (a) Contour map of the vertical velocity over the chamber surface at a height of 5 cm above the bottom. The locations of the water outlets are the same as in Fig. 3. Positive values: ascending velocities. (b) Profiles B and D of the vertical velocity field from the wall (W) to the centre (C); height in cm. Velocity units: cm s^{-1}. Voltage applied to the pumps: 6V. Space between ticks is 10 cm.

The DBL thickness, calculated through Ca^{2+} accumulation in the overlying water, is given by the following expression:

$$z = D_{Ca2+}(C_{sat}-C_0)/F \qquad (1)$$

where D_{Ca2+} (cm^2 s^{-1}) is the molecular diffusion coefficient for Ca^{2+} at a given temperature, C_{sat} is the Ca^{2+} concentration at saturation (g cm^{-3}), C_0 is the initial Ca^{2+} concentration (g cm^{-3}) and F is the dissolution flux of Ca^{2+} (g cm^{-2} s^{-1}). D_{Ca2+} and C_{sat} were taken from Buchholtz-ten Brink et al. (1989). Besides, the DBL thicknesses of individual plates were also calculated from their weight loss by modifying equation (1) as:

$$z = D_{Ca2+}(C_{sat}-C_0)At/0.2328 \times \text{wt loss} \quad (2)$$

where A is the surface area of the alabaster plate (cm^2), t is the time exposed to dissolution (s), wt loss is the measured weight loss from the alabaster plate (g) and the constant 0.2328 is the relative Ca^{2+} weight in alabaster. DBL thickness inside the chamber was estimated for the two different pump outlet devices as stirring system (elbows and slotted tubes). As expected from the velocity distribution inside the chamber, the DBL thickness obtained for

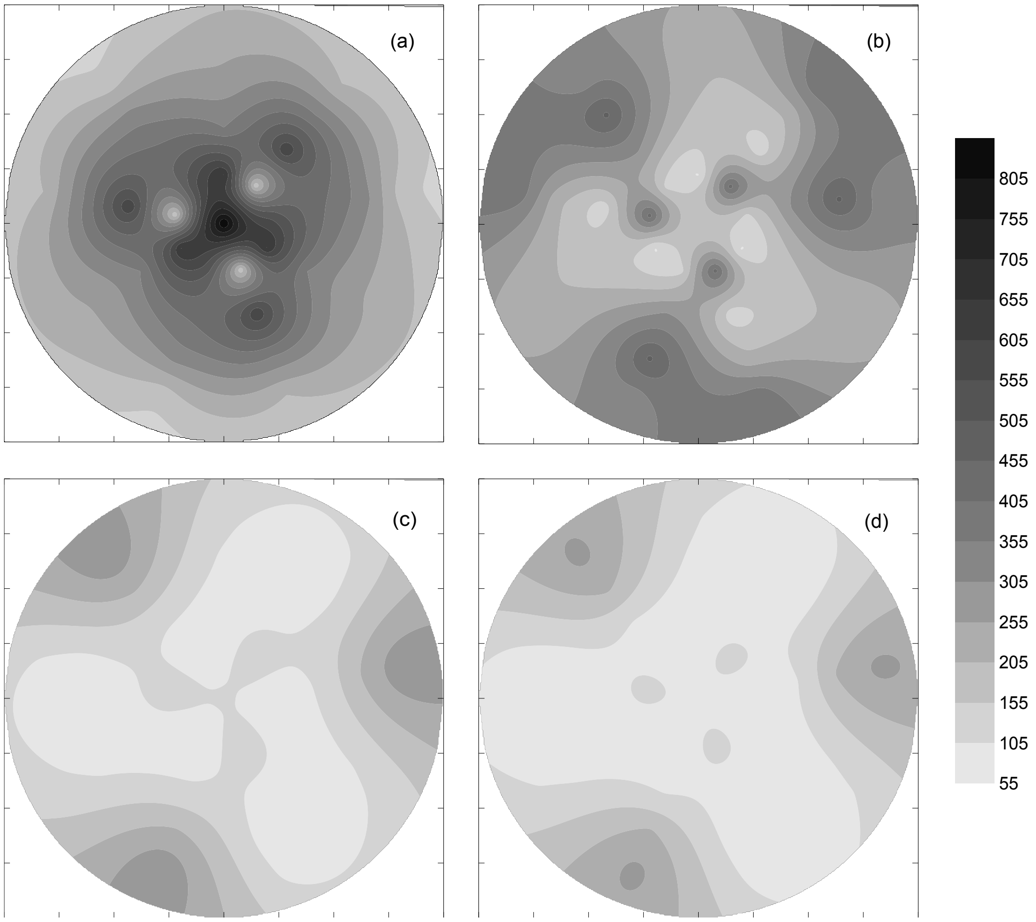


Figure 7. Contour maps of the DBL thickness inside the chamber obtained from alabaster plate observations, comparing two outlet systems: elbows (a) and slotted tubes (b-d). Voltage applied to the water pumps: (a) 5 V; (b) 4 V; (c) 6 V and (d) 8 V. Units are in µm. The locations of the water outlets are the same as in Fig. 3. Space between ticks is 10 cm.

individual alabaster plates reflected the velocity pattern, with thicker DBL at low velocities and thinner DBL at high velocities. The DBL thickness using the elbow outlet device (Fig. 7a) was only measured for purposes of comparison, applying an output voltage of 5 V to the pumps, as it had already proven to be less appropriate (from the velocity measurements) than the slotted tubes system to reproduce natural hydrodynamics. Thus, DBL thickness using the elbows system was, as expected, highly variable and showed a concentric distribution with values increasing from 165-235 µm at the chamber wall to 820 µm at the center. The DBL thickness distribution obtained using the slotted tubes (Fig. 7b-7d) presented comparatively less variability throughout the chamber surface, with values decreasing towards the center. Radial C, which is the one located 60° from the pump outflow, showed in all cases a higher gradient than the other two, with values decreasing along this transect from 330 µm (265 µm) near the chamber wall to 163 µm (97 µm) at the center, for output voltages of 4 V (8 V) respectively. This results in a portion of the chamber near the wall and between two pumps characterized by a DBL which is about 2.5 times thicker than the DBL in the rest of the chamber, as seen in the contour maps (Fig. 7b-7d). This portion of the chamber represents around 20 % of the total chamber area.

The average DBL thickness calculated from individual plates, weighted according to the area represented by each plate, and from the dissolution of Ca^{2+} is presented in table 1 for each experiment. There was a good correlation between the weighted average DBL thickness obtained from the weight loss of individual alabaster plates and DBL thickness calculated from the rate of increase of Ca^{2+} concentration (R^2= 0.88) (Fig. 8a). When applying different pump rates to the stirring system, weighted average DBL thickness inside the chamber ranged from 278 µm to 125 µm (Fig. 8b) and a high power correlation (DBLthickness= 3641 $[\text{Pump Rate}]^{-0.97}$; R^2= 0.98) was obtained between these two variables. In general, averaged DBL thicknesses estimated for the different pump rates are at the low range of those measured in other benthic chambers (Tengberg et al. 2004, 2005).

As expected, when comparing the tangential velocity (5 cm above the bottom) with the averaged DBL thickness, the latter gets thinner as the horizontal velocity inside the chamber increases (Fig. 8c), obtaining a high power relationship ($V_T = 615 \times [DBL]^{-1.02}$) ($R^2$= 0.97).

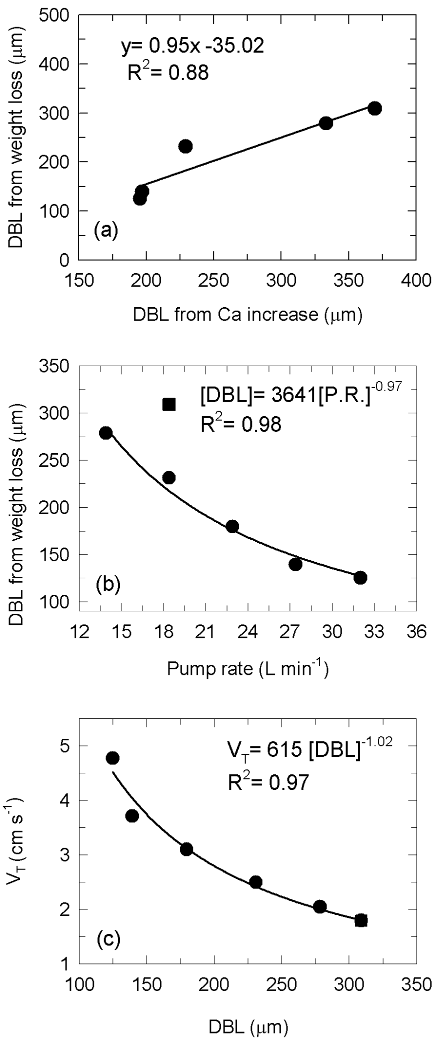


Figure 8. (a) Plot showing the relationship between average DBL thickness estimated from weight loss of individual plates and DBL thickness estimated from the Ca^{2+} increase inside the chamber. (b) Average DBL thickness estimated from weight loss plotted versus pump rates (c) Weighted average DBL thickness plotted versus average tangential velocity. Solid circles represent data using the slotted tubes as outlet system. Solid square shows the only datum obtained using the elbow system.

3.4 Benthic flux determinations

In Fig. 9 we present, as an example, the results of two recent benthic chamber deployments in two shallow coastal systems: Ría de Vigo (NW Spain) and Río San Pedro creek (salt marsh area of the Bay of Cádiz, SW Spain). The former deployment was performed at 20 m depth, average wave height < 1m, sediment characterized as muddy sand containing 6-8 % of organic matter (Vilas et al. 2005) and the average depth obtained for 0.1 % PAR was 16.5 ± 3.2 m. The other deployment was located at a 4 m-depth station, characterized by muddy sediments with 2-3 % of organic carbon and a porosity of 0.8 (at the top 5 cm of sediment). Measuring benthic exchange rates of major oxidants and nutrient or reductant species allows constraining the stoichiometries of the reactions taking place in the sediments during organic matter remineralization. The concentration evolution of the variables studied in the plotted examples suggested that incubation times of around 5-8 hours were sufficient to calculate benthic fluxes at these sites. In both examples dissolved oxygen decreases approximately 20% in around 5 hours. In the Ría de Vigo, a linear decrease in pH and in the concentration of dissolved oxygen and a consequent linear increase in the concentration of the nutrient NH_4^+, collected as discrete samples, are well represented as a result of the benthic metabolism inside the chamber during the incubation. Results from the turbidity sensor also indicate that the system is able to maintain the initial hydrodynamic conditions

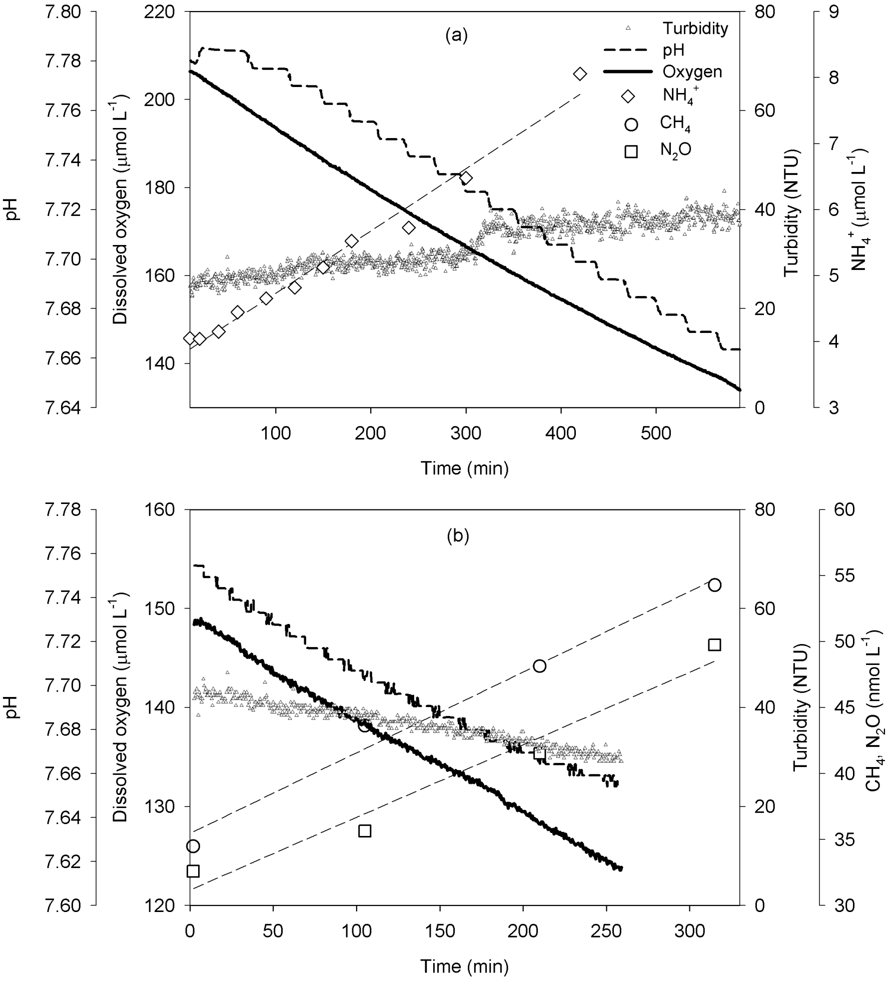


Figure 9. Two examples of the evolution of the response of the sensors (dissolved oxygen, pH and turbidity) measured during *in situ* benthic chamber incubations. (a) Incubation at the Ría de Vigo, NW Spain. Ammonium measurements are included (b) Incubation at Río San Pedro creek, Bay of Cádiz, SW Spain. Measurements of dissolved methane and nitrous oxide are included.

throughout the whole incubation. Similar sensor responses are found in the creek, where discrete samples were taken to analyze dissolved methane (CH_4) and nitrous oxide (N_2O), which increased linearly during the incubation.

4. Discussion

The sediment surface covered by the chamber (5030 cm^2) and the incubated water volume (140 L) make this chamber one of the largest compared to other benthic chambers in the literature (Berelson & Hammond 1986, Jahnke & Christiansen 1989, Glud et al. 1995, Tengberg et al. 2004, 2005). Although this feature makes it a high energy demanding chamber due to its need for a stirring system able to homogenize such a water volume, Glud & Blackburn (2002) have shown that increasing the chamber radius results in a better precision of the estimated benthic oxygen fluxes, as it better accounts for the spatial heterogeneity in sediments with high macrofauna abundance. Thanks to the large radius of the chamber (40 cm), one single benthic flux measurement can be considered as reliable, as it may have similar or even better precision than 8 replicate measurements made with a 5 cm radius chamber (Glud & Blackburn 2002).

It has been demonstrated that central stirring devices (paddles, magnetic bars) on benthic chambers create a radial flow velocity gradient with high flow velocity at the periphery and low velocity at the center (Glud et al. 1995), which may be enhanced in a chamber covering a high area of seafloor. In this work, centrifugal pumps have been selected and two water outlet systems have been compared in order to achieve and maintain the most possible homogeneous velocity flow throughout the chamber area. The stirring mechanism, consisting of three centrifugal pumps with three slotted PVC tubes as water outlet system, has succeeded in generating quite constant hydrodynamic conditions in most of the chamber. Water mixing within the chamber water phase is achieved in less than 4 minutes and the stirring system has been able to prevent gradient formation in the overlying water, fulfilling the main function of a chamber stirring system (Glud et al. 1995) which ensures that the measurements performed during the incubation represent an average condition of the water inside the chamber.

The selected stirring device produces a rotary flow with average tangential velocities (5 cm above bottom) ranging from 2 to 5 cm s^{-1} depending on the voltage applied to the pumps. These values are of the same order of magnitude as others reported in the literature for several near-shore coastal environments near the studied sites (e.g. Kagan et al. 2001, Ruiz-Villarreal et al. 2002), but lower than current velocities found in energetic coastal systems (e.g. Piedracoba et al. 2005). However, it must be taken into account that these reported values represent free-stream velocities, which exhibit a logarithmic decrease near the seabed due to frictional effects (Ogston et al. 2005), and therefore are expected to be lower at 5 cm above the bottom.

At high oxygen fluxes, the sediment oxygen consumption has been found to be dependent on the water flow dynamics above the sediment (Boynton et al. 1981, Jorgensen & Des Marais 1990), and consequently on the DBL thickness (e.g. Jorgensen & Revsbech 1985, Arega & Lee 2005). Jorgensen & Des Marais (1990) showed that diffusion through the DBL on a microbial mat constituted an important rate limitation on the oxygen flux, and that DBL thickness decreased from 590 to 160 µm when the flow velocity increased from 0.3 to 7.7 cm s^{-1}, which raised the oxygen uptake from 56 mmol m^{-2} day^{-1} to 135 mmol m^{-2} day^{-1}. On the other hand, Tengberg et al. (2004, 2005) studied the hydrodynamics inside various radically different benthic chambers and concluded that the chamber design and the hydrodynamic setting did not significantly influence the benthic fluxes of oxygen and nutrients measured in homogenized macrofauna-free non-permeable sediments. However, Tengberg et al. (2004) argued that in sediments with high oxygen uptakes (> 11 mmol m^{-2} d^{-1}), the impedance imposed by the DBL could be higher, and therefore, there could possibly be more differences among the fluxes measured with the different chambers. Therefore in coastal active sediments, where oxygen uptake is often very high (e.g. Lopez et al. 1995, Berelson et al. 1998, Forja et al. 2004, Ortega et al. 2005) and where macrofauna normally play an important role in benthic exchange (Forja & Gómez-Parra 1998, Glud et al. 2003), the effect of overlying hydrodynamics on benthic fluxes is probably higher. Recently, Glud et al. (2007) demonstrated that, though DBL thickness has only a modest effect on the annual O_2 uptake, it can strongly affect benthic O_2 concentration and O_2 uptake in a time scale of a few hours. Hence, a detailed characterization of the DBL thickness inside the chamber seems to be crucial for estimating benthic fluxes, especially if working in active coastal environments with high oxygen demands and affected by wave or tide action.

Considering the good correlation ($R^2 = 0.98$) obtained between the pump rates and the average DBL thickness, a range from 2 to 6 V would generate mean DBL thicknesses inside the chamber ranging from 175 µm to 645 µm. These values are consistent with DBL thicknesses reported *in situ* in coastal environments (Gundersen & Jørgensen 1991, Glud et al. 2003), as well as with laboratory DBL thickness measurements for several benthic chambers (Buchholtz-ten Brink et al. 1989, Glud et al. 1995, Broström & Nilsson 1999, Tengberg et al. 2005). Therefore, voltage regulation over the centrifugal pumps allows our benthic chamber to match a range of coastal hydrodynamic conditions.

5. Comments and recommendations

In this manuscript, we have reported the design, development and testing of a novel benthic chamber for use in shallow coastal areas. The stirring system has been shown to be reliable and able to reproduce a range of flow regimes as well as DBL thicknesses. However, fluxes can be highly variable in natural ecosystems, especially in areas where the influence of waves and tidal currents reaches the seafloor. In those cases, a steady flow inside the chamber may not reproduce this natural variability and associated fluxes. Additionally, even if the flow inside the chamber is well defined, the presence of biogenic structures (mounds or pits) or bedforms (ripples) at the sediment surface may significantly alter the effective DBL thickness distribution compared to the laboratory-derived values for a flat bottom. Special care must be taken when working with sediments with any significant degree of permeability, as the stirring of the water phase may generate artificial pressure gradients inside the chamber, enhancing pore-water advection and, thus, benthic fluxes (Janssen et al. 2005).

Due to the shallowness of coastal environments, benthic primary production may be significant at some sites, even where only small amounts of light reach the sediment surface

(Jahnke et al. 2000) and, consequently, opaque chambers are unable to integrate net benthic metabolism and to determine benthic photosynthetic production. Moreover, the latter may alter heterotrophic processes by modifying the sediment redox status (Risgaard-Petersen et al. 1994). However, the PVC chamber body may be replaced with a transparent one for studying net metabolism in sediments where light reaches the bottom.

To conclude, the equipment has power to operate autonomously for approximately 12 hours. Whether this length of time is sufficient for accurate benthic flux measurements depends on the magnitude of the fluxes in the study area and the sensitivity of analytical methods employed to measure chamber water parameters. Our initial field measurements show typical fluxes from coastal sediments that can be resolved within this time.

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References

Aller RC (1980) Diagenetic processes near sediment-water interface of Long Island Sound. I. Decomposition and nutrient element geochemistry (S, N, P). Adv Geophys 22:237–350

Aller JY, Aller RC (1986) Evidence for localized enhancement of biological associated with tube and burrow structures in deep-sea sediments at the HEEBLE site, western North Atlantic. Deep Sea Res Part Oceanogr Res Pap 33:755–790

Archer D, Emerson S, Smith CR (1989) Direct measurement of the diffusive sublayer at the deep sea floor using oxygen microelectrodes. Nature 340:623–626

Arega F, Lee J (2005) Diffusional Mass Transfer at Sediment–Water Interface of Cylindrical Sediment Oxygen Demand Chamber. J Environ Eng 131:755–766

Berelson WM, Hammond DE (1986) The calibration of a new free-vehicle benthic flux chamber for use in the deep sea. Deep Sea Res Part Oceanogr Res Pap 33:1439–1454

Berelson WM, Heggie D, Longmore A, Kilgore T, Nicholson G, Skyring G (1998) Benthic Nutrient Recycling in Port Phillip Bay, Australia. Estuar Coast Shelf Sci 46:917–934

Berner RA (1980) Early Diagenesis: A Theoretical Approach. Princeton University Press

Black KS, Fones GR, Peppe OC, Kennedy HA, Bentaleb I (2001) An autonomous benthic lander: preliminary observations from the UK BENBO thematic programme. Cont Shelf Res 21:859–877

Boudreau BP, Guinasso NL (1982) The influence of a diffusive sublayer on accretion, dissolution, and diagenesis at the sea floor. In: Fanning KA, Manheim FT (eds) The dynamic environment of the ocean floor. Lexington Books, Toronto, p 115–145

Boudreau BP, Jorgensen BB (2001) The Benthic boundary layer: transport processes and biogeochemistry (BP Boudreau and BB Jorgensen, Eds.). Oxford University Press

Boynton WR, Kemp WM, Osborne CG, Kaumeyer KR, Jenkins MC (1981) Influence of water circulation rate on in situ measurements of benthic community respiration. Mar Biol 65:185–190

Broström G, Nilsson J (1999) A theoretical investigation of the diffusive boundary layer in benthic flux chamber experiments. J Sea Res 42:179–189

Buchholtz-ten Brink MR, Gust G, Chavis D (1989) Calibration and performance of a stirred benthic chamber. Deep Sea Res Part Oceanogr Res Pap 36:1083–1101

Ferguson A, Eyre B, Gay J, Emtage N, Brooks L (2007) Benthic metabolism and nitrogen cycling in a sub-tropical coastal embayment : spatial and seasonal variation and controlling factors. Aquat Microb Ecol 48:175–195

Forja JM, Gómez-Parra A (1998) Measuring nutrient fluxes across the sediment-water interface using benthic chambers. Mar Ecol Prog Ser 164:95–105

Forja JM, Ortega T, DelValls TA, Gómez-Parra A (2004) Benthic fluxes of inorganic carbon in shallow coastal ecosystems of the Iberian Peninsula. Mar Chem 85:141–156

Glud RN, Berg P, Fossing H, Jorgensen BB (2007) Effect of the diffusive boundary layer on benthic mineralization and O2 distribution: A theoretical model analysis. Limnol Oceanogr 52:547–557

Glud RN, Blackburn N (2002) The effects of chamber size on benthic oxygen uptake measurements: A simulation study. Ophelia 56:23–31

Glud RN, Gundersen JK, Revsbech NP, Jorgensen BB, Hüttel M (1995) Calibration and performance of the stirred flux chamber from the benthic lander Elinor. Deep Sea Res Part Oceanogr Res Pap 42:1029–1042

Glud RN, Gundersen JK, Roy H, Jorgensen BB (2003) Seasonal dynamics of benthic O2 uptake in a semienclosed bay: Importance of diffusion and faunal activity. Limnol Oceanogr 48:1265–1276

Grasshoff K, Ehrhardt M, Kremling K (1983) Methods of seawater analyses. Verlag Chemie, Weinheim

Gundersen JK, Jorgensen BB (1991) Fine-scale in situ measurements of oxygen distribution in marine sediments. Kiel Meeresforsch 8:376–380

Hammond DE, Cummins KM, McManus J, Berelson WM, Smith G, Spagnoli F (2004) Methods for measuring benthic nutrient flux on the California Margin: Comparing shipboard core incubations to in situ lander results. Limnol Oceanogr Methods 2:146–159

Hartman B, Hammond DE (1984) Gas exchange rates across the sediment-water and air-water interfaces in south San Francisco Bay. J Geophys Res Oceans 89:3593–3603

Jahnke RA, Christiansen MB (1989) A free-vehicle benthic chamber instrument for sea floor studies. Deep Sea Res Part Oceanogr Res Pap 36:625–637

Jahnke RA, Nelson JR, Marinelli RL, Eckman JE (2000) Benthic flux of biogenic elements on the Southeastern US continental shelf: influence of pore water advective transport and benthic microalgae. Cont Shelf Res 20:109–127

Janssen F, Faerber P, Huettel M, Meyer V, Witte U (2005) Pore-water advection and solute fluxes in permeable marine sediments(I): Calibration and performance of the novel benthic chamber system Sandy. Limnol Oceanogr 50:768–778

Jorgensen BB, Boudreau BP (2001) Diagenesis and sediment-water exchange. In: Boudreau BP, Jorgensen BB (eds) The benthic boundary layer: transport processes and biogeochemistry. Oxford University Press

Jorgensen BB, Marais DJ Des (1990) The diffusive boundary layer of sediments: Oxygen microgradients over a microbial mat. Limnol Oceanogr 35:1343–1355

Jorgensen BB, Revsbech NP (1985) Diffusive boundary layers and the oxygen uptake of sediments and detritus. Limnol Oceanogr 30:111–122

Kagan BA, Tejedor L, Álvarez O, Izquierdo A, Tejedor B, Mañanes R (2001) Weak wave–tide interaction formulation and its application to Cádiz bay. Cont Shelf Res 21:697–725

López P, Vidal M, Lluch X, Morgui J (1995) Sediment metabolism in a transitional continental - marine area: The Albufera of Majorca (Balearic Islands, Spain). Mar Freshw Res 46:45–53

Ogston AS, Sternberg RW, Nittrouer CA (2005) Recent advances in fine-grained sediment-transport processes on the continental shelf. In: Robinson AR, Brink KH (eds) The Global Coastal Ocean: Multiscale Interdisciplinary Processes. Harvard University Press

Ortega T, Ponce R, Forja JM, Gómez-Parra A (2005) Fluxes of dissolved inorganic carbon in three estuarine systems of the Cantabrian Sea (north of Spain). J Mar Syst 53:125–142

Ortega T, Ponce R, Forja JM, Gómez-Parra A (2008) Benthic fluxes of dissolved inorganic carbon in the Tinto–Odiel system (SW of Spain). Cont Shelf Res 28:458–469

Pamatmat MM, Banse K (1969) Oxygen consumption by the seabed. II. In situ measurements to a depth of 180 m. Limnol Oceanogr 14:250–259

Piedracoba S, Souto C, Gilcoto M, Pardo PC (2005) Hydrography and dynamics of the Ría de Ribadeo (NW Spain), a wave driven estuary. Estuar Coast Shelf Sci 65:726–738

Reimers CE, Fischer KM, Merewether R, Smith KL, Jahnke RA (1986) Oxygen microprofiles measured in situ in deep ocean sediments. Nature 320:741–744

Risgaard-Petersen N, Rysgaard S, Nielsen LP, Revsbech NP (1994) Diurnal variation of denitrification and nitrification in sediments colonized by benthic microphytes. Limnol Oceanogr 39:573–579

Rowe GT, Clifford CH, Smith KL, Hamilton PL (1975) Benthic nutrient regeneration and its coupling to primary productivity in coastal waters. Nature 255:215–217

Ruiz-Villarreal M, Montero P, Taboada JJ, Prego R, Leitão PC, Pérez-Villar V (2002) Hydrodynamic Model Study of the Ria de Pontevedra Under Estuarine Conditions. Estuar Coast Shelf Sci 54:101–113

Santschi PH, Bower P, Nyffeler UP, Azevedo A, Broecker WS (1983) Estimates of the resistance to chemical transport posed by the deep-sea boundary layer. Limnol Oceanogr 28:899–912

Sayles FL (1981) The composition and diagenesis of interstitial solutions—II. Fluxes and diagenesis at the water-sediment interface in the high latitude North and South Atlantic. Geochim Cosmochim Acta 45:1061–1086

Tengberg A, Bovee F De, Hall P, Berelson W, Chadwick D, Ciceri G, Crassous P, Devol A, Emerson S, Gage J, Glud R, Graziottini F, Gundersen J, Hammond D, Helder W, Hinga K, Holby O, Jahnke R, Khripounoff A, Lieberman S, Nuppenau V, Pfannkuche O, Reimers C, Rowe G, Sahami A, Sayles F, Schurter M, Smallman D, Wehrli B, Wilde P De (1995) Benthic chamber and profiling landers in oceanography — A review of design, technical solutions and functioning. Prog Oceanogr 35:253–294

Tengberg A, Hall POJ, Andersson U, Lindén B, Styrenius O, Boland G, Bovee F de, Carlsson B, Ceradini S, Devol A, Duineveld G, Friemann J-U, Glud RN, Khripounoff A, Leather J, Linke P, Lund-Hansen L, Rowe G, Santschi P, Wilde P de, Witte U (2005) Intercalibration of benthic flux chambers: II. Hydrodynamic characterization and flux comparisons of 14 different designs. Mar Chem 94:147–173

Tengberg A, Stahl H, Gust G, Müller V, Arning U, Andersson H, Hall POJ (2004) Intercalibration of benthic flux chambers I. Accuracy of flux measurements and influence of chamber hydrodynamics. Prog Oceanogr 60:1–28

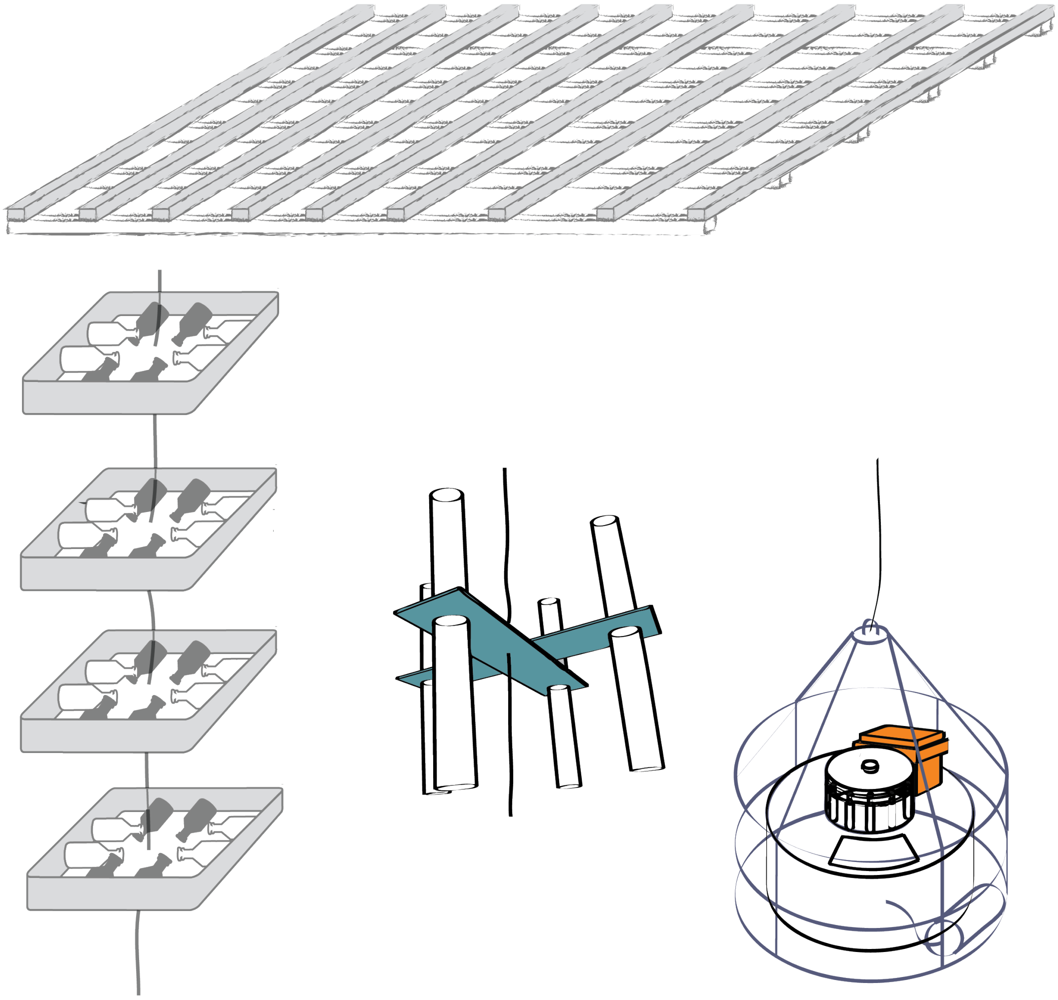
Vilas F, Bernabeu AM, Méndez G (2005) Sediment distribution pattern in the Rias Baixas (NW Spain): main facies and hydrodynamic dependence. J Mar Syst 54:261–276

Viollier E, Rabouille C, Apitz SE, Breuer E, Chaillou G, Dedieu K, Furukawa Y, Grenz C, Hall P, Janssen F, Morford JL, Poggiale J-C, Roberts S, Shimmield T, Taillefert M, Tengberg A, Wenzhöfer F, Witte U (2003) Benthic biogeochemistry: state of the art technologies and guidelines for the future of in situ survey. J Exp Mar Biol Ecol 285–286:5–31

Weiss RF, Price BA (1980) Nitrous oxide solubility in water and seawater. Mar Chem 8:347–359

Wiesenburg DA, Guinasso NL (1979) Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J Chem Eng Data 24:356–360

BENTHIC OXYGEN AND NUTRIENT FLUXES IN A COASTAL UPWELLING SYSTEM (RÍA DE VIGO, NW IBERIAN PENINSULA): SEASONAL TRENDS AND REGULATING FACTORS



Capítulo III

Alonso-Pérez, F. & Castro, C.G. 2014. Benthic oxygen and nutrient fluxes in a coastal upwelling system (Ría de Vigo, NW Iberian Peninsula): seasonal trends and regulating factors. *Marine Ecology Progress Series 511, 17-32*.

Abstract

Benthic oxygen and nutrient fluxes play a key role in the biogeochemical cycles of carbon and nutrients in coastal regions. However, there are no previous studies focused on benthic fluxes in the NW Iberian coastal upwelling system on an annual basis. The present work analyses the seasonal trends of benthic oxygen and nutrient fluxes as well as the main factors that control them in the Ría de Vigo. Between April 2004 and January 2005, 16 oceanographic cruises were carried out to measure water column properties, vertical fluxes of particulate organic matter by means of sediment traps, and oxygen and nutrient fluxes using a benthic chamber. Rates of sediment oxygen consumption (18 to 50 mmol m^{-2} d^{-1}), phosphate (0.08 to 0.34 mmol $m^{-2}d^{-1}$), silicate (1.7 to 10 mmol $m^{-2}d^{-1}$), ammonium (1.1 to 4.9 mmol m^{-2} d^{-1}) and nitrate (-0.95 to 0.78 mmol m^{-2} d^{-1}) ranged near the upper limit of benthic fluxes found in similar coastal areas. Nitrogen fluxes were dominated by ammonium fluxes (83 %). Benthic fluxes of oxygen, ammonium, phosphate and dissolved silicate were significantly lower during winter but did not show differences during spring, summer or autumn. The strong mutual correlations among fluxes points to the importance of aerobic respiration in the remineralization of organic matter. The amount and quality of organic matter appears to be an influencing factor on the benthic fluxes but it seems that changes in temperature, modulated by upwelling/downwelling pulses, trigger and control the benthic fluxes on the short time scale. The study assesses the importance of benthic fluxes to the potential primary production of the system as remineralized benthic nitrogen and phosphorous may account up to 41 % and 61 %, respectively, of the nutrient inputs from upwelled and continental runoff waters.

Resumen

Los flujos bentónicos de oxígeno y nutrientes tienen un papel importante en los ciclos biogeoquímicos de carbono y nutrientes de las zonas costeras. Sin embargo, en el sistema costero de afloramiento del noroeste Ibérico no existen estudios previos de flujos bentónicos que engloben un año de estudio. En este trabajo se analizan las variaciones estacionales de los flujos bentónicos de oxígeno y nutrientes así como los principales factores que los controlan en la Ría de Vigo. Entre los meses de abril de 2004 y enero de 2005, se realizaron un total de 16 campañas oceanográficas, en las que se midieron las propiedades de la columna de agua, los flujos verticales de materia orgánica particulada por medio de trampas de sedimento y los flujos bentónicos de oxígeno y nutrientes mediante una cámara bentónica. Las tasas de consumo de oxígeno por parte del sedimento (18 a 50 mmol m^{-2} d^{-1}), de fosfato (0.08 a 0.34 mmol $m^{-2}d^{-1}$), silicato (1.7 a 10 mmol $m^{-2}d^{-1}$), amonio (1.1 a 4.9 mmol m^{-2} d^{-1}) y nitrato (-0.95 a 0.78 mmol m^{-2} d^{-1}) se encuentran en el rango superior para flujos bentónicos obtenidos en zonas costeras similares. Los flujos bentónicos de amonio tienen un papel predominante en los flujos totales de nitrógeno (83 %). Los flujos de oxígeno, amonio, fosfato y silicato fueron significativamente inferiores en invierno pero no mostraron diferencias significativas durante las estaciones de primavera, verano y otoño. Las fuertes correlaciones entre estos flujos señalan a que la respiración aeróbica juega un papel importante en la remineralización de la materia orgánica. Tanto la cantidad como la calidad de la materia orgánica son factores importantes que controlan los flujos bentónicos, pero parece que los cambios de temperatura del agua de fondo, modulados por los pulsos de afloramiento / hundimiento , desencadenan y controlan los flujos bentónicos a cortas escalas de tiempo. El estudio evalúa además, la importancia de los flujos bentónicos sobre la producción primaria potencial en el sistema, obteniendo que el nitrógeno y el fósforo inorgánicos remineralizado en el sedimento puede representar hasta un 41 % y un 60 %, respectivamente, de la entrada de nutrientes al sistema provenientes de la suma de aguas afloradas y aguas continentales.

1. Introduction

Covering only 10 % of the total ocean surface (Wollast 1998), ocean margins support an important fraction of global primary production (10-50 %) and up to 83 % of carbon remineralization occurs in coastal sediments (Middelburg et al. 1993). Benthic and pelagic processes are generally tightly coupled in shallow marine environments where sediment nutrient regeneration is fueled by organic matter deposited in the sediments and previously produced in the water column (Nixon 1981). Conversely, benthic remineralization of nutrients within shallow coastal systems may sustain high proportions of the water column primary production (Boynton et al. 1980, Grenz et al. 2010), which may supply up to 75% of phytoplankton nutrient requirements (Billen 1978). These processes are enhanced within coastal upwelling systems where higher rates of primary production promote higher vertical organic matter fluxes (Varela et al. 2004, Thunell et al. 2007) so that higher amounts of organic carbon are available for remineralization in the sediments (Jahnke 1996).

Benthic remineralization processes have shown to be influenced by several factors. Temperature has been identified as the main factor controlling the seasonal variation of benthic fluxes in temperate estuaries (Cowan et al. 1996) as it affects porewater solute transport (Jahnke 2005) as well as metabolic activities of most organisms (Lomas et al. 2002). Another important factor is the supply and quality of organic matter to the sediment (Nixon 1981, Ståhl et al. 2004, Farías et al. 2004). Inputs of organic matter to the benthic environment may be based on primary production, primary production plus allochthonous organic matter and/or organic matter deposition rates (Hopkinson & Smith 2005). The redox status of the sediment and the overlying water column affects remineralization processes such as nitrification and denitrification (Sundby et al. 1992). Bottom water dissolved oxygen has also been reported as a factor controlling benthic flux rates (Caffrey et al. 2010), while nutrient concentrations of the overlying water may influence diffusion gradients and hence, flux direction (Boynton & Kemp 1985). Finally, feeding, bioturbation and burrowing of benthic macrofauna influence rates of organic matter inputs to the sediment, the rates and pathways of organic matter mineralization and thus, the amount of regenerated dissolved nutrients (Aller 1988, Kristensen 1988, Christensen et al. 2000).

The Rías Baixas (NW Iberian Peninsula, see Fig.1) are four flooded tectonic valleys that act as an extension of the adjacent continental shelf. Their hydrographic regime is highly influenced by upwelling/downwelling dynamics, mainly controlled by the along shore wind over the continental shelf (Rosón et al. 1995, Figueiras et al. 2002). The upwelling of nutrient-rich subsurface Eastern North Atlantic Central Waters (ENACW) favours the high primary production of the region (Fraga 1981). Several studies have shown that the nutrient content of ENACW is increased over the continental shelf (Álvarez-Salgado et al. 1997), with maximum values inside the Rías (Prego et al. 1999), probably due to intense benthic remineralization processes. In fact, measurements of magnetical properties of the Rías Baixas sediments point to a strong early diagenesis, which gains intensity towards the Ría interior (Emiroğlu et al. 2004, Mohamed et al. 2011). On the other hand, Álvarez-Salgado et al. (1996) and Rosón et al. (1999), using a 2-D non-stationary box model for the Ría de Arousa, concluded that 83 % of the carbon fixed in this Ría during the upwelling period is exported to the adjacent continental shelf and the other 17 % settles on the sediment. Later on Gago et al. (2003), applying a similar box model for the Ría de Vigo, estimated a much higher fraction of organic material settling onto the sediments (~62%). Although these previous works presented an estimate of the percentage of organic material deposited onto the sediments in the Rías, they were not able to distinguish between the remineralized and buried fractions of the organic matter. The only studies of directly measured diffusive benthic nutrient fluxes refer to the continental shelf off the NW Iberian coast (Epping et al. 2002) and inside the Ría de Pontevedra (Dale & Prego 2002). Recently, (Alonso-Pérez et al. 2010) have measured the total nutrient benthic fluxes under a mussel raft in the Ría de Vigo during an upwelling event. In this context, the present work aims to quantify, for the first time in this coastal upwelling system, the benthic oxygen and nutrient fluxes over the course of one year, to study their main controlling factors and to evaluate the importance of the fluxes in the potential productivity of the system.

2. Material and Methods

2.1 Study Area

The study site is located in the Ría de Vigo, a temperate coastal embayment and one of the four V-shaped Rías Baixas of the NW Iberian Peninsula. The Ría is oriented NE-SW, widens seawards, and is partially enclosed by the Cíes Islands (Fig. 1). From May to October, prevailing northerly winds cause the upwelling of cold nutrient-rich subsurface ENACW, which enters the Ría. During upwelling conditions, primary production is increased (Fraga 1981), as is the potential export of biogenic carbon to the sediment and the adjacent shelf (Álvarez-Salgado et al. 2001). During the other half of the year, downwelling conditions,

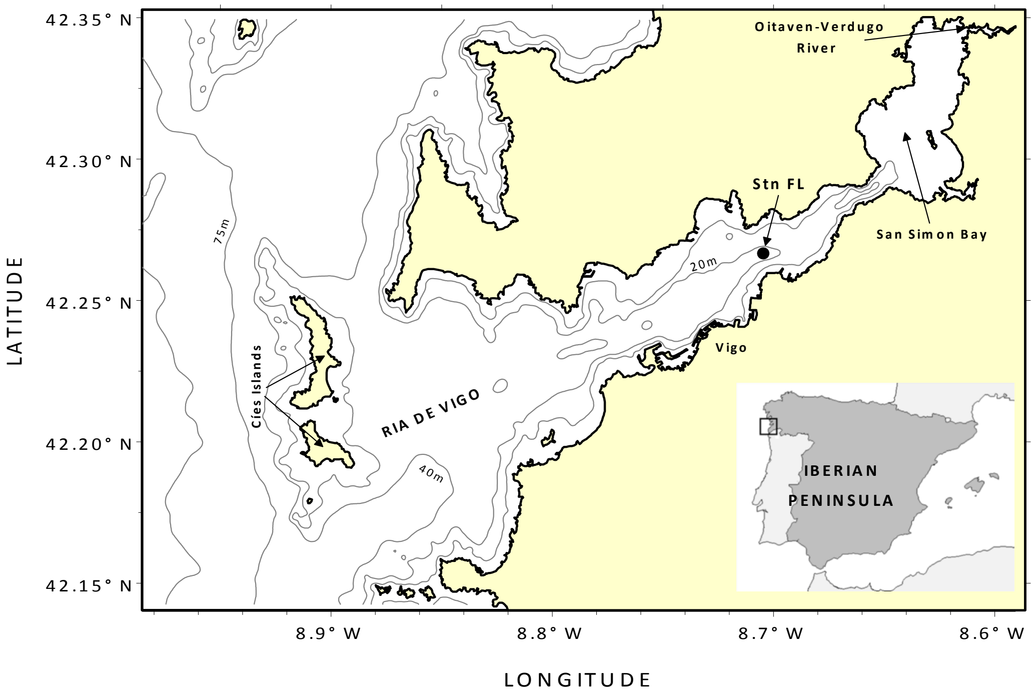


Figure 1. Ría de Vigo, NW Iberian Peninsula (inset), showing bathymetry and the location of the sampling station, Stn FL (●).

associated with prevailing southerly winds, are favoured.

2.2 Sampling strategy and water sampling

In the framework of the Spanish project FLUVBE (Coupling of benthic and pelagic fluxes in the Ría de Vigo), 16 oceanographic cruises were carried out at station FL, located in the inner part of the Ría de Vigo (Fig. 1). The sampling strategy of the cruises, which covered the period between April 2004 and January 2005, was intended to capture the predominant oceanographic conditions in the study area; i.e. spring bloom (April), summer upwelling-stratification (July), autumn bloom (October) and winter mixing (January). During each period, the station was visited twice a week during a 15 days period. One day cruises were carried out on board R/V Mytilus; vertical profiles of temperature and dissolved oxygen were obtained with a SBE911plus CTD. Bottle casts (rosette sampler with 10-L PVC Niskin bottles) were run to obtain water samples for dissolved oxygen, dissolved inorganic nutrients, suspended particulate organic carbon and nitrogen concentrations (POC and PON, respectively). Dissolved oxygen was determined by Winkler potentiometric titration. The estimated analytical error (SE) was ±1 µmol kg^{-1}. Nutrient samples were determined by segmented flow analysis with Alpkem autoanalyzers following Hansen & Grasshoff (1983) with some improvements (Mouriño & Fraga 1985). The analytical errors were ± 0.02 µmol kg^{-1} for nitrite, ± 0.05 µmol kg^{-1} for nitrate, ammonium and silicate and ± 0.01 µmol kg^{-1} for phosphate. Total dissolved inorganic nitrogen (DIN) is the sum of NO_3^--N, NO_2^--N and NH_4^+-N. For analysis of POC and PON, 250 mL of seawater were filtered on pre-weighted, pre-combusted (4 h, 450 °C) Whatman GF/F filters. Filters were vacuum dried and frozen (-20 °C) before analysis. A Perkin Elmer 2400 CHN analyzer was used for measurements of POC and PON, using an acetanilide standard daily. The precision of the method is ± 3.6 mg C m^{-3} and ± 1.4 mg N m^{-3}.

The upwelling index was estimated using the component $-Q_x$ of the Ekman transport following Bakun (1973) method:

$$-Q_x = (\rho_{air}\, C_D\, |V|\, V_Y)/(f\, \rho_{sw})$$

where ρ_{air} is the density of air (1.22 kg m^{-3} at 15°C), C_D is an empirical dimensionless drag coefficient (1.4 x 10^{-3} according to Hidy (1972)), f is the Coriolis parameter (9.946 x 10^{-5} at 43°N), ρ_{sw} is the density of seawater (1025 kg m^{-3}) and |V| and V_Y, are the average daily modulus and northerly component of the geostrophic winds centred at 43°N, 11°W, respectively. Average daily geostrophic winds were estimated from surface atmospheric pressure charts. Positive values of $-Q_x$ indicate upwelling and correspond to predominance of northerly winds.

2.3 Vertical particle fluxes

Vertical particle fluxes were estimated using a homemade multitrap collector system. It was composed by 4 PVC trap baffled cylinders of 28 cm^2 collecting area and aspect ratio of 10.8. Sediment traps were deployed at Stn FL at approximately 16 m depth (~5 m above sea bottom) for a 24 h period, filled with brine solution (5 PSU in excess) without the addition of any preservatives. A subsample of 200 mL of the material collected in each cylinder was used for analysis of POC and PON. Filters were vacuum dried and frozen (-20 °C) before analysis. Samples for POC and PON were determined as previously described for suspended organic matter in the previous section. Biogenic silica concentrations ($bSiO_2$) were determined by filtering 200 mL subsample onto a 0.6 µm polycarbonate filter under gentle vacuum, followed by a 30 min digestion with 0.2 M NaOH at 95 °C (Brzezinski & Nelson 1989). Silicic acid concentrations of the digested samples were determined using standard autoanalyzer methods as described for nutrient analysis in the ‘Sampling strategy and water sampling’ subsection (above this section).

In order to determine phytoplankton derived carbon settled in the traps (C_{Phyto}), a fraction of 100 mL preserved in Lugol´s iodine was employed for microplankton determination. Depending on the chl *a* concentration, a volume ranging from 10 to 50 mL was sedimented in composite sedimentation chambers and observed through an inverted microscope. The phytoplankton organisms were counted and identified to species level. Dimensions were taken to calculate cell biovolumes after approximation to the nearest geometrical shape

(Hillebrand et al. 1999) and cell carbon was calculated following Strathmann (1967) for diatoms and dinoflagellates, Verity et al. (1992) for other flagellates (> 20 µm) and Putt & Stoecker (1989) for ciliates. Unfortunately, subsamples for $bSiO_2$ and C_{Phyto} were not available for the spring period.

2.4 Benthic fluxes

Fluxes of oxygen and dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate) at the sediment-water interface were measured *in situ* by means of a benthic chamber (Ferrón et al. 2008), placed by a diver directly on the sediment surface at the FL station. The equipment consisted of a PVC opaque cylindrical chamber, which incubated 140 L of overlying seawater, and covered 0.64 m^2 of sediment surface. Three centrifugal pumps stirred the incubated water by means of a stepper motor, at adjustable stirring rates. Inside the chamber, sensors for temperature (SBE 39), turbidity (Seapoint Turbidity Meter) and dissolved oxygen (SBE 43) gave a continuous recording of these variables during the incubation time (approx. 8 hours). Data was monitored in real time using a two-way GSM communication system located at the mooring buoy. Discrete samples were withdrawn from the chamber at prefixed times with a multiple water KC Denmark sampler provided with 12 syringes of 50 ml capacity. Samples for dissolved inorganic nutrients were determined as described for water column measurements in ‘Sampling strategy and water sampling’.

2.5 Statistical data processing

Benthic fluxes of oxygen and nutrients were estimated by empirical linear fittings based on changes in concentration over time. Uncertainties of the fluxes account for the fit of the data to a linear function and the propagation of random errors. In order to test seasonal statistical difference of the benthic fluxes, Student *t*-test of the means were performed (Statistica, StatSoft 6.0). Correlation coefficient r between benthic fluxes and selected vertical fluxes and bottom water variables was calculated and presented as a correlation matrix. A forward stepwise regression model was applied to determine how much variability of the benthic fluxes may be described by different environmental parameters including seabed properties, upwelling index and vertical fluxes (Statistica, StatSoft 6.0). Only variables with statistical significance ($p < 0.1$) were included in the results. Seasonal and annual averages are presented as ± SD.

3. Results

3.1 Hydrography

An exhaustive analysis of the hydrographic conditions during the study year is explained in detail by Villacieros-Robineau et al. (2013). Here, we briefly describe the hydrographic situation during the four seasonal studies. The spring period was characterized by a transition from downwelling to upwelling conditions, reflected by $-Q_x$ values, which varied from negative to positive values (Fig. 2). Upwelling produced the entry of cold, NO_3^- rich and relative low O_2 ENACW. During this upwelling episode increased primary production in surface waters was associated with high suspended POC concentrations (240 mg m^{-3}) and high values of dissolved oxygen (up to 280 µmol kg^{-1}). The summer period was characterized by constant but not very intense upwelling conditions ($-Q_x$ = 518 ± 501 m^3 s^{-1} km^{-1}). Nutrients were consumed in surface waters by primary producers, generating a high standing stock of suspended organic matter (POC > 400 mg m^{-3}) and higher dissolved oxygen concentration, which decreased with depth as a result of higher proportions of ENACW and remineralization processes. During autumn, a strong negative peak of the $-Q_x$ (-4000 m^3 s^{-1} km^{-1}) just before the second sampling day, interrupted previous upwelling conditions. After that, there was a homogenization of the water column, at a constant temperature of 15 °C, low nitrate and suspended POC concentrations (< 4 µmol kg^{-1} and < 150 mg m^{-3}, respectively). The winter period showed a strong mixing in the water column, marked by low temperatures (< 13 °C), high nitrate concentrations (7-8 µmol kg^{-1}) and low suspended POC concentrations (< 150 mg m^{-3}).

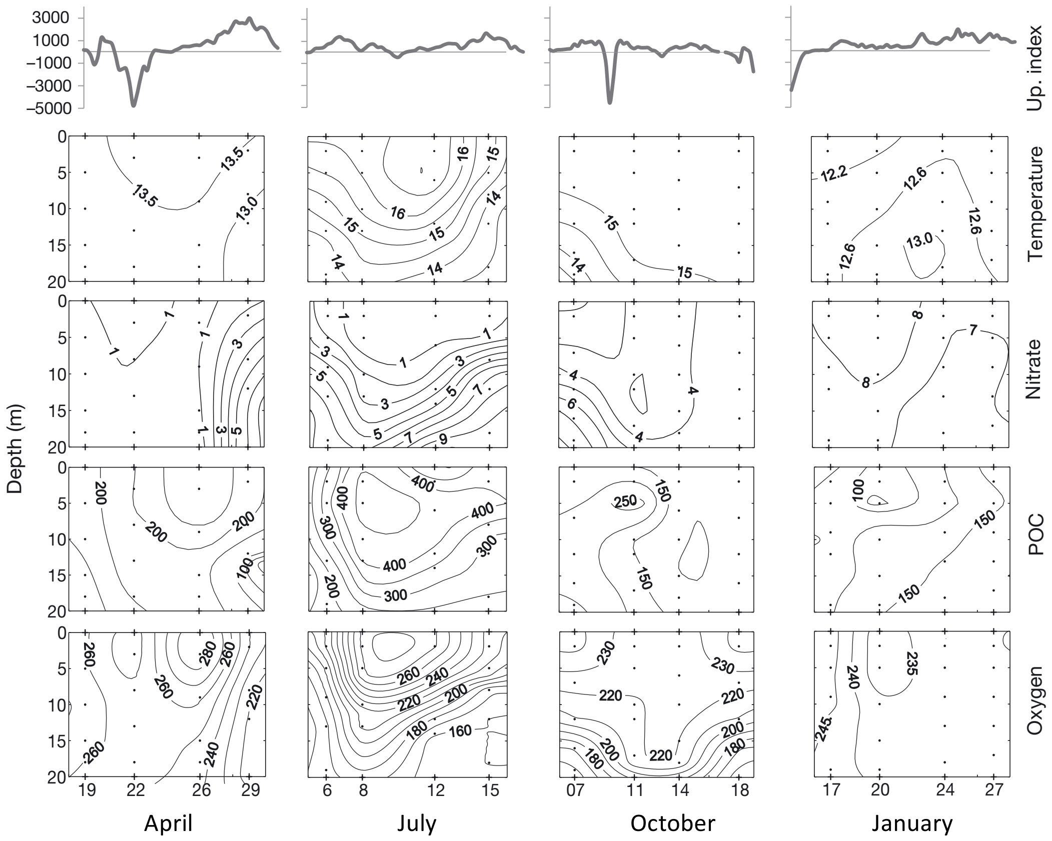


Figure 2. Time series of depth profiles for upwelling index (m^3 s^{-1} km^{-1}), temperature (°C), nitrate concentration (μmol kg^{-1}), particulate organic carbon (POC, mg m^{-3}) and dissolved oxygen (μmol kg^{-1}). Dots represent sampling depths.

3.2 Vertical Fluxes

For the spring period, POC vertical fluxes varied almost twofold, ranging between 586 and 1295 mg C m^{-2} d^{-1} (Fig. 3). However, the C:N ratio of the settling material did not vary among the sampling days (7.3 ± 1.6) except on the last one, when it reached 9.3. In general, the low C:N ratio of the material collected in the sediment traps pointed to the arrival of relatively fresh organic matter to the sea bottom. During summer, higher POC vertical fluxes were recorded at both ends of the sampling period, when upwelled waters occurred. In contrast, C_{Phyto} (Fig. 3) increased to a maximum value of 546 mg C m^{-2} d^{-1} on July 12, followed by a decrease to a still elevated value of 300 mg C m^{-2} d^{-1}. These elevated vertical fluxes of fresh

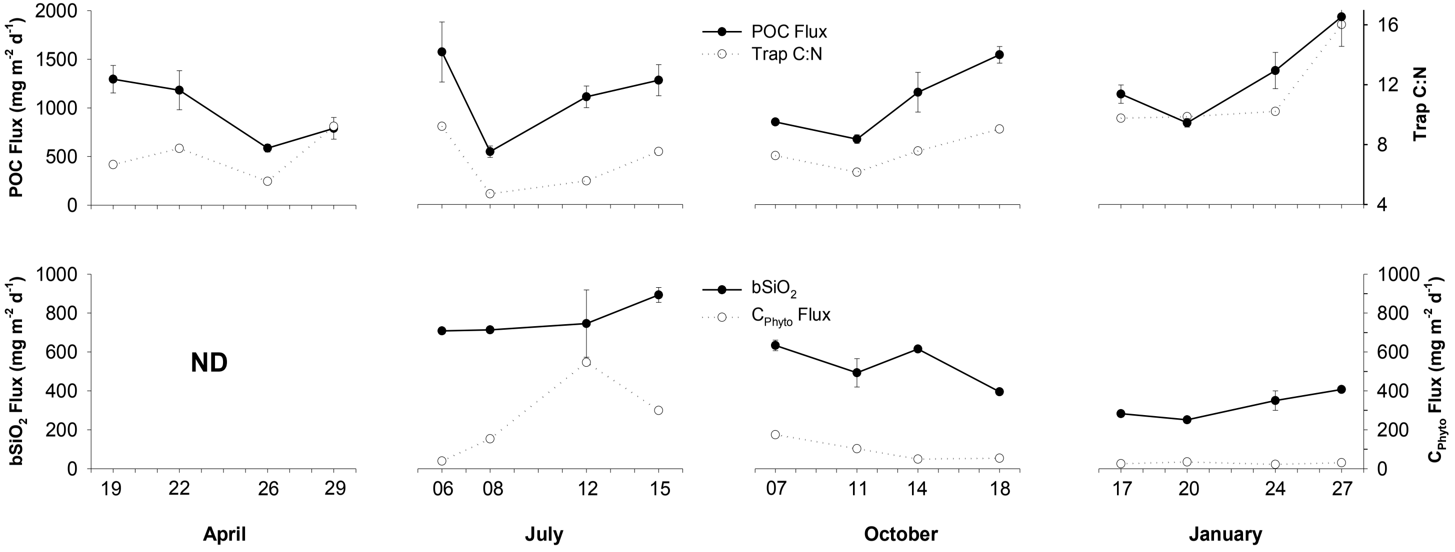


Figure 3. Seasonal vertical fluxes of particulate organic carbon (POC), C:N ratio (M:M) of the material collected in the sediment traps, carbon derived from phytoplankton (C_{Phyto}) and biogenic silica ($bSiO_2$). ND: no data for spring C_{Phyto} and $bSiO_2$. Error bars represented SD.

C_{Phyto} led to a decrease in the C:N ratio during this period. In addition, measured $bSiO_2$ fluxes were also the highest for the study year as a result of the dominance of diatoms in the phytoplankton registered in the trap material (Zúñiga et al. 2011). Downwelling and relaxation provoked the increase of the settling material during autumn, with C:N ratios increasing and C_{phyto} decreasing as the period progressed. The $bSiO_2$ fluxes were lower than during summer (534 ± 112 mg Si $m^{-2}d^{-1}$), showing a decreasing tendency during the autumn samplings. During winter, the strong water column mixing resulted in relatively high amounts of POC captured in the sediment traps, probably resulting from resuspension and river inputs. The trap material was characterized by high C:N ratios and very low values of C_{phyto} (28 ± 5 mg C m^{-2} d^{-1}) and $bSiO_2$ (323 ± 70 mg Si m^{-2} d^{-1}).

3.3 Benthic fluxes

Following the oxidative decomposition and remineralization of organic matter in the sediments, benthic oxygen fluxes were negative, averaging -34 ± 10 mmol $m^{-2}d^{-1}$ for the whole study year. As an example, the decrease in oxygen concentration during benthic chamber incubation on 15th July 2004 is presented in Fig. 4. Benthic fluxes of ammonium, phosphate and silicate were always towards the water column (Fig. 5, Table 1), increasing their concentrations during the incubation period (Fig. 4). Benthic fluxes of nitrate were taken up by the sediment during summer and autumn. In the other two seasons, daily fluxes were in the same range as for autumn, despite a transition from release to uptake during spring and conversely during winter. In fact, average nitrate fluxes for these two periods were not significantly different from zero.

During spring, relatively high and constant benthic oxygen fluxes during the first 3 sampling days (-43.7 ± 2.3 mmol m^{-2} d^{-1}, Fig. 5) were followed by an abrupt decrease in the oxygen uptake by the sediment (-28 mmol m^{-2} d^{-1}) on 29 April 2004 as upwelled ENACW entered the Ría. The earlier water was replaced by colder (12.7 °C) and less oxygenated waters (215 µmol kg^{-1}), which appears to slow down the benthic oxygen fluxes. The same pattern is also observed for the benthic fluxes of phosphate, silicate and ammonium, which decreased in magnitude at the end of the period when the upwelling occurred. Benthic nitrate fluxes reversed from being released (0.43 mmol m^{-2} d^{-1}) to being taken up (-0.21 mmol m^{-2} d^{-1}) by the sediments.

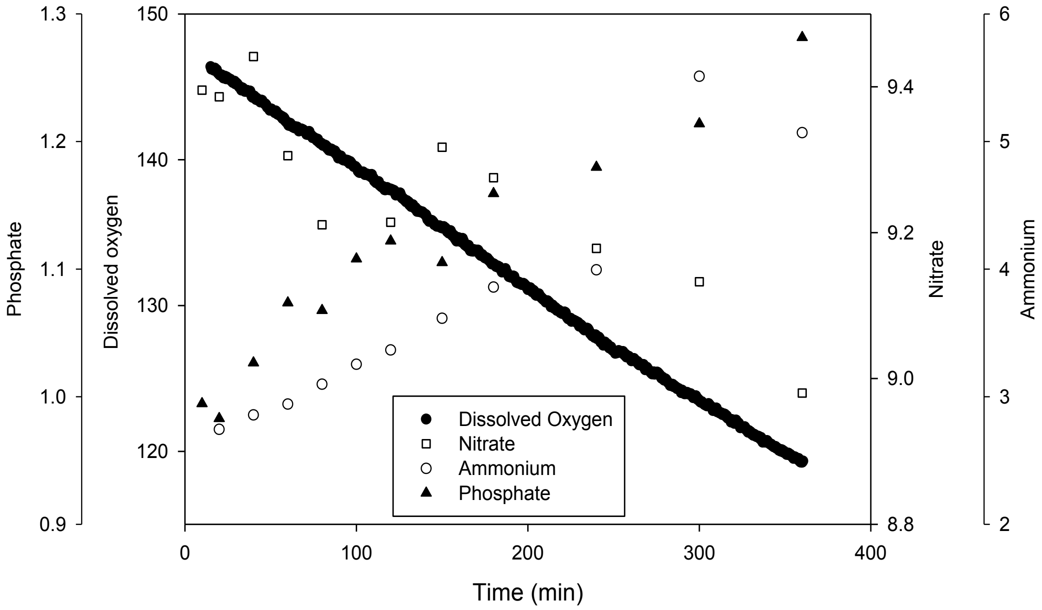


Figure 4. Example of the evolution in the concentration (in µmol kg^{-1}) of dissolved oxygen, nitrate, ammonium and phosphate during chamber incubation (15th July 2004).

Benthic fluxes responded to the gravitational stability of the water column during summer. Oxygen uptake by the sediments is almost constant for the whole period (-34.6 ± 3.2 mmol m^{-2} d^{-1}), concomitant with constant sea bottom temperature (13.22 ± 0.08 °C). Ammonium and silicate also show relatively small variations in the benthic fluxes during the summer period (2.4 ± 0.3 mmol m^{-2} d^{-1} and 5.8 ± 1.1 mmol m^{-2} d^{-1}, respectively). However, they appear to covary with the concentration of dissolved oxygen in sea bottom waters (Fig 5). Nitrate fluxes were consistently negative throughout the period (-0.7 ± 0.3 mmol m^{-2} d^{-1}) coinciding with the lowest concentrations of dissolved oxygen of sea-bottom waters of the whole year (162 ± 7 µmol kg^{-1}).

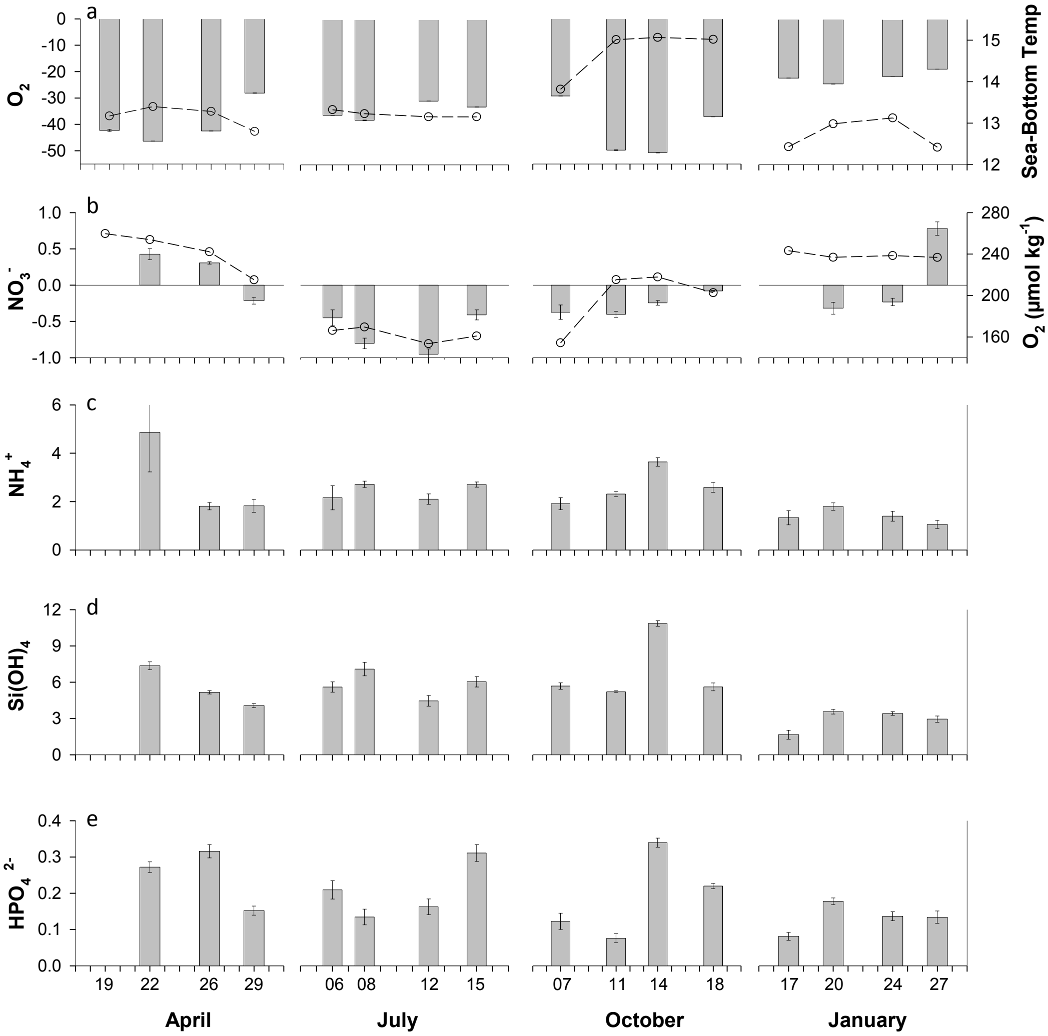


Figure 5. Seasonal (a) benthic flux of oxygen along with sea-botom temperature (dashed line, right axis), (b) benthic flux of nitrate along with sea-bottom oxygen (dashed line, right axis), as well as bethic fluxes of (c) ammonium, (d) silicate and (e) phosphate. Fluxes are in mmol m^{-2} d^{-1}. Error bars are based on the propagation of random errors from measured benthic fluxes.

During autumn, an abrupt change in the hydrographic conditions appears to have had a strong influence in the benthic fluxes. On 10th October 2004, downwelling provoked the replacement of previous cold waters (13.6 °C) by warmer (15.1 °C) and more oxygenated sea-surface waters (154 to 215 µmol kg^{-1}). Benthic oxygen uptake by the sediment responded to this change with an increase from -29 to -50 mmol m^{-2} d^{-1} (Fig. 5). The same pattern is observed for ammonium, silicate and phosphate fluxes, which attained maximum benthic fluxes on 14th October (3.6, 10.9 and 0.34 mmol m^{-2} d^{-1}, respectively). Nitrate fluxes were negative for all the period, though its magnitude tends to decrease. The lowest values of benthic oxygen fluxes were recorded during winter (-21.8 ± 2.3 mmol m^{-2} d^{-1}) as was the case for the benthic fluxes of ammonium (1.4 ± 0.7 mmol m^{-2} d^{-1}) phosphate (0.13 ± 0.04 mmol m^{-2} d^{-1}) and silicate (2.9 ± 0.9 mmol m^{-2} d^{-1}).

Table 1. Seasonal benthic fluxes (mean ± SD, in mmol m^{-2} d^{-1}) of oxygen, nitrate, ammonium, silicate and phosphate.

	Apr	Jul	Oct	Jan
O_2	-39.8 ± 8.0	-34.6 ± 3.2	-41.7 ± 10.4	-21.8 ± 2.3
NO_3^-	0.2 ± 0.3	-0.7 ± 0.3	-0.3 ± 0.1	0.1 ± 0.5
NH_4^+	2.8 ± 1.8	2.4 ± 0.3	2.6 ± 0.7	1.4 ± 0.7
$Si(OH)_4$	5.5 ± 1.7	5.8 ± 1.1	6.8 ± 2.7	2.9 ± 0.9
HPO_4^{2-}	0.25 ± 0.08	0.20 ± 0.08	0.19 ± 0.12	0.13 ± 0.04

Seasonally averaged benthic fluxes of oxygen showed no significant differences for spring, summer and autumn periods, with values ranging between -35 mmol m^{-2} d^{-1} and -42 mmol m^{-2} d^{-1} (Table 1). However, oxygen uptake during winter (-21.8 mmol m^{-2} d^{-1}) was significantly lower than the three other periods (spring: $p < 0.05$; summer: $p < 0.01$; autumn: $p < 0.01$, Table 2). Benthic fluxes of nutrients, silicate, ammonium and phosphate followed the same trend as oxygen, with lowest values during winter and no significant differences between the first three periods. Benthic silicate fluxes ranged between 5.5 mmol m^{-2} d^{-1} and 6.8 mmol m^{-2} d^{-1} from April to October and decreased significantly (Table 2) to 2.9 mmol m^{-2} d^{-1} during winter. Ammonium benthic fluxes were reduced from 2.4 – 2.8 mmol m^{-2} d^{-1} (spring, summer and autumn) to 1.4 mmol m^{-2} d^{-1} during winter. In the case of phosphate, we also obtained lower values of benthic fluxes during winter (0.13 mmol m^{-2} d^{-1}) than for the rest of the seasons (0.19 - 0.25 mmol m^{-2} d^{-1}) though, the difference was only significant between winter and spring ($p < 0.1$). Negative nitrate fluxes during summer and autumn were significantly different from nitrate fluxes in April (summer: $p < 0.05$; autumn: $p < 0.1$) and nitrate uptake by the sediment was higher during summer than autumn ($p < 0.05$).

Table 2. Statistical significances in the seasonal variability of benthic fluxes (see Table 1), according to Student's *t*-test. p-values (above the diagonal) are given if significant (p<0.1); ns: not significant.

Flux		Apr	Jul	Oct	Jan
O_2	Apr	-	ns	ns	<0.05
	Jul		-	ns	<0.01
	Oct			-	<0.01
	Jan				-
NO_3^-	Apr	-	<0.05	<0.1	ns
	Jul		-	<0.05	<0.05
	Oct			-	ns
	Jan				-
NH_4^+	Apr	-	ns	ns	ns
	Jul		-	ns	<0.01
	Oct			-	<0.05
	Jan				-
$Si(OH)_4$	Apr	-	ns	ns	P<0.05
	Jul		-	ns	P<0.01
	Oct			-	P<0.05
	Jan				-
HPO_4^{2-}	Apr	-	ns	ns	<0.1
	Jul		-	ns	ns
	Oct			-	ns
	Jan				-

Table 3 shows that sediment oxygen uptake was strongly negatively correlated with benthic fluxes of ammonium, phosphate and silicate ($p < 0.01$) to the water column, as a result of the organic matter decomposition and remineralization; the more nutrient fluxes the more oxygen uptake by the sediment. Benthic oxygen fluxes also correlated negatively with sea bottom temperature ($r = -0.707$, $p < 0.01$) and positively with sea bottom nitrate concentration ($r = 0.700$, $p < 0.01$). No significant correlation was found between upwelling index and the oxygen and nutrient benthic fluxes. Vertical fluxes of C_{phyto} and vertical $bSiO_2$ fluxes correlated negatively with the benthic oxygen fluxes. In terms of nutrient fluxes, except for nitrate, they correlated with each other positively and were strongly affected by temperature and vertical fluxes of $bSiO_2$ as well. Parameters related with the quality of settling material (C:N and C_{Phyto}) seem to affect the benthic fluxes of ammonium and silicate.

Table 3. Correlation matrix between benthic fluxes and selected vertical fluxes and bottom water variables. Benthic fluxes (oxygen, nitrate, ammonium, phosphate and silicate) are in mmol m^{-2} d^{-1}. C_{Phyto}: phytoplankton-derived carbon; POC: particulate organic carbon; $bSiO_2$: biogenic silica; Temp: temperature. *p < 0.05, **p < 0.01, all others, p < 0.10. ns: not significant.

		F_O_2	$F\_NO_3^-$	$F\_NH_4^+$	$F\_HPO_4^{2-}$	$F\_Si(OH)_4$
Benthic Fluxes	F_O_2	1				
	$F\_NO_3^-$	ns	1			
	$F\_NH_4^+$	-0.793^{**}	ns	1		
	$F\_HPO_4^{2-}$	-0.723^{**}	ns	0.610^{*}	1	
	$F\_Si(OH)_4$	-0.801^{**}	ns	0.926^{**}	0.723^{**}	1
Vert. Fluxes	Trap C:N	0.570^{*}	ns	-0.640^{*}	ns	ns
	Trap Cphyto	-0.555	ns	0.716^{**}	ns	0.622^{*}
	Trap $bSiO_2$	-0.546	-0.571	0.608^{*}	0.561	0.619^{*}
	Trap POC	ns	ns	ns	ns	ns
Bottom Water	Temp	-0.707^{**}	ns	0.717^{**}	0.553^{*}	0.644^{**}
	O_2	ns	0.738^{**}	ns	ns	ns
	NO_3^-	0.700^{**}	-0.507	ns	ns	ns
	NO_2^-	ns	-0.681^{**}	ns	ns	ns
	HPO_4^{2-}	ns	-0.650^{**}	ns	ns	ns
	$Si(OH)_4$	ns	-0.589^{**}	ns	ns	ns

The only nutrient not significantly affected by sea bottom water temperature was nitrate. However, this nutrient was highly correlated with sea bottom water dissolved oxygen ($r = 0.738$; $p < 0.01$) and with sea bottom concentration of nitrite ($r = -0.681$; $p < 0.01$) phosphate ($r = -0.650$; $p < 0.\ 01$) and silicate ($r = -0.589$; $P < 0.01$).

4. Discussion

4.1 Comparison with other coastal systems

Results analysed here represent the first study of oxygen and nutrient benthic fluxes on a seasonal scale for the NW Iberian coast, which is the only upwelling system in Europe. Rates of oxygen and nutrient fluxes between the sediment and the overlying water column are at the upper limits of benthic rates reported for similar coastal areas (Devol & Christensen 1993, Hammond et al. 1999, Hopkinson et al. 2001, Ferrón et al. 2009a) and much higher than deeper sediments like the Mid-Atlantic continental slope (Jahnke & Jahnke 2000). The average sediment oxygen demand in the present study (-34 mmol O_2 m^{-2} d^{-1}) is double the average value of benthic community respiration (-17 mmol O_2 m^{-2} d^{-1}) for the European coastal zone (Gazeau et al. 2004) and coincides with the mean global respiration for estuarine benthic systems (-34 mmol O_2 m^{-2} d^{-1}) obtained by Hopkinson & Smith (2005).

Although nitrate fluxes were consistently negative during summer and autumn, sediments were a net source of inorganic N as DIN was dominated by ammonium fluxes, averaging 83 % of the total DIN fluxes. This pattern is very common in coastal benthic N fluxes (Hopkinson et al. 2001) but there have been cases where NO_3^- flux exceeded NH_4^+ fluxes (Billen 1978, Devol & Christensen 1993), where there was no net flux of DIN (Berelson et al. 2003) or even where there was net DIN uptake (Berelson et al. 1996). In contrast with the ammonium fluxes, which were positive and directed towards the water column for the Ría de Vigo, Farías et al. (2004) in the upwelling system off Central Chile found a larger range of fluxes, ranging from -14 to 10 mmol m^{-2} d^{-1}. These authors suggest that maximum ammonium uptake was probably caused either by ammonium assimilation from bacteria or by anammox processes. Off Washington State, Devol & Christensen (1993) measured positive ammonium fluxes up to 1.54 mmol m^{-2} d^{-1}, although combined inorganic nitrogen flux was always negative because benthic nitrogen cycling was dominated by denitrification. For our study site, we do not expect to find a prevalence of anaerobic processes as described for these coastal upwelling systems, mainly due to presence of well ventilated upwelled ENACW (O_2 > 200 µmol kg^{-1}; Castro et al. 2000) and thus we suggest that ammonium effluxes are mainly driven by aerobic respiration, as explained in the next section.

In terms of benthic phosphate fluxes, the literature reveals high variability, ranging from sites where P is taken up by the sediment (Fisher et al. 1982) to sites where P is mainly released to the overlying water column (Hammond et al. 1999, Ferrón et al. 2009b), at rates as high as 2 mmol m^{-2} d^{-1} in Port Philip Bay, Australia (Berelson et al. 1998). Benthic phosphate flux in the Ría de Vigo averaged 0.2 ± 0.09 mmol m^{-2} d^{-1} and was always released from the sediment. This value is similar to the highest fluxes obtained by Berelson et al. (2013) and Hopkinson et al. (2001) on the Oregon / California shelf and in Massachusets Bay, respectively. Benthic silicate fluxes ranged from 1.7 to 10.9 mmol m^{-2} d^{-1}, lowest during winter and highest during autumn. These fluxes are in the range obtained by Berelson et al. (2013) and higher than those found on the coast of SW Spain (Ferrón et al. 2009b) where silicate fluxes did not exceed 3 mmol m^{-2} d^{-1} during an annual study. Rates were similar to those found by Hammond et al. (1999) in the Adriatic Sea and in the lower range of fluxes obtained in Port Phillip Bay, Australia (Berelson et al. 1998).

4.2 Factors controlling benthic fluxes in the Ría de Vigo

4.2.1 Benthic oxygen fluxes

Seabed temperature and dissolved oxygen have been reported as the most relevant factors influencing benthic oxygen and nutrient fluxes (Cowan et al. 1996). Moreover, sediments located in coastal upwelling areas, like our study region, receive larger amounts of organic matter (Jahnke 1996) and thus factors such as primary production and concentration of labile organic matter in the sediments may have major influence on these fluxes (Farías et al. 2004). While it seems that sea-bottom dissolved oxygen has no clear influence on the benthic oxygen fluxes (Fig. 6a), it is evident that temperature significantly affected the magnitude of benthic fluxes despite the restricted range of seabed temperature (12.4 to 15.1 °C). Benthic oxygen uptake becomes higher as temperature increases ($r = -0.707$; $p < 0.01$, Table 3). Hopkinson & Smith (2005) reported that a large percentage of the variance of

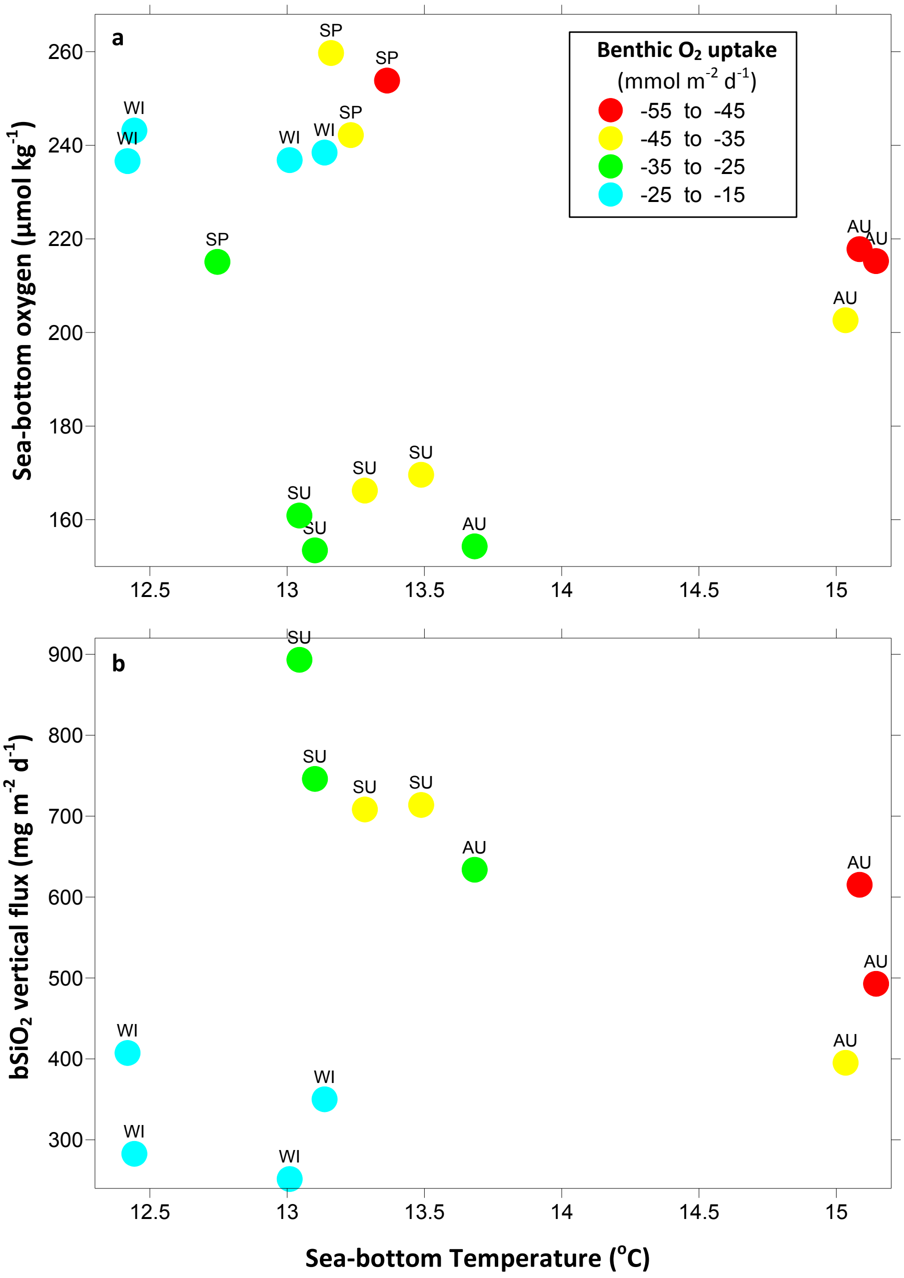


Figure 6. Seasonal bethic oxygen fluxes depending on (a) seasonal bottom dissolved oxygen and temperature, and (b) vertical fluxes of biogenic silica ($bSiO_2$) and sea-bottom temperature. SP: spring, SU: summer, AU: autumn, WI: winter.

benthic fluxes is explained by seasonal temperature change. However, in the Ría de Vigo, sea bottom temperature is not controlled by atmospheric temperature but by the upwelling/downwelling processes driven by along-shore wind over the adjacent shelf (Nogueira et al. 1997). The entrance of cold upwelled ENACW in the Ría reduces seabed temperature while downwelling processes introduce oceanic warm surface waters towards the bottom (Nogueira et al. 1997). This is probably the reason that there were no significant seasonal differences in benthic oxygen fluxes among the spring, summer and autumn periods, i.e. the benthic oxygen fluxes are mainly modulated by the presence/absence of cold upwelled water.

Benthic oxygen fluxes were separated into three groups based on bottom temperature and dissolved oxygen (Fig. 6a). The major group, characterized by low temperatures (12.4-13.5 °C) and high content in dissolved oxygen (215-260 µmol kg^{-1}), includes data from winter and spring periods. However, the magnitude of benthic oxygen fluxes was significantly higher during spring. Though bottom waters had high levels of dissolved oxygen during winter, as a result of vertical mixing, net community production was lowest during this period (0.22 g C m^{-2} d^{-1}, Arbones et al. 2008) and so, settling of fresh organic material was low (28 ± 8 mg C_{Phyto} m^{-2} d^{-1}). Besides, the winter C:N ratio of the settling material was the highest of the whole study (11 ± 3) and vertical fluxes of $bSiO_2$ the lowest (< 400 mg m^{-2} d^{-1}). Therefore, low values of sediment oxygen uptake obtained during winter appear to be caused by the combination of low sea bottom temperatures and low levels of fresh organic compounds arriving to the sediment. In contrast, the spring period, while having similar values of sea bottom temperature and dissolved oxygen as the winter time, was characterized by higher levels of net community production (1 g C m^{-2} d^{-1}, Arbones et al. 2008) and lower C:N ratio of the material settled in the traps (7.3 ± 1.3), reflecting fresher organic material available for remineralization. The result was higher benthic oxygen fluxes in spring than winter, which explains the correlation between the benthic oxygen fluxes and the quality of the settling material (C:N and C_{Phyto}; Table 3). Summer data and the first sampling day of autumn present similar benthic oxygen fluxes under similar hydrographic conditions, and consequently they are grouped together by low temperatures (13-13.6 °C) and low dissolved oxygen (< 170 µmol kg^{-1}, Fig. 6a) at the bottom, due to the entrance of more remineralized ENACW upwelled waters as the upwelling season progresses (Álvarez-Salgado et al. 1997). The most favourable scenario for the highest sediment oxygen uptake appeared in autumn, after a strong downwelling and subsequent relaxation in the water column. The arrival of surface warmer (> 15 °C) and well oxygenated waters to the bottom (205-220 µmol kg^{-1}) favours decomposition of the organic matter and so, the sediment oxygen uptake.

A stepwise regression analysis indicates that seabed temperature in our study region explains as much as 74 % of the variability in benthic oxygen fluxes (Table 4). If we consider as well the $bSiO_2$ vertical fluxes, the variability of the benthic oxygen fluxes explained is raised to 87%. In contrast with similar studies in other regions (Cowan et al. 1996), sea-

Table 4. Stepwise regression between benthic fluxes (oxygen, nitrate, ammonium, silicate and phosphate) and main variables affecting benthic fluxes. There is no multicollinearity among predictor variables. T: temperature; $bSiO_2$: biogenic silica.

Flux	Variable	Cummulative R^2	R^2 change	p
O_2	Bottom T	0.742	0.742	<0.001
	Trap $bSiO_2$	0.866	0.122	0.019
NO_3^-	Bottom O_2	0.544	0.544	0.002
NH_4^+	Bottom T	0.505	0.505	0.009
	Trap $bSiO_2$	0.756	0.251	0.014
HPO_4^{2-}	Bottom T	0.390	0.390	0.039
	Trap $bSiO_2$	0.584	0.194	0.089
$Si(OH)_4$	Bottom T	0.456	0.456	0.016
	Trap $bSiO_2$	0.723	0.267	0.016

bottom oxygen concentration does not have a clear influence on the benthic oxygen fluxes, and is not a limiting factor. Thus sediment oxygen uptake in the Ría de Vigo is highly influenced by sea bottom temperature, mainly modulated by upwelling / downwelling processes, and to some extent by the amount and quality of the settled organic material. The presence of labile organic matter in the sediments is essential for regenerating processes, but physical factors appear to trigger these processes in the short term. In this sense, (Boynton et al. 1991) shows a delay in degradation of deposited material until temperature increases in late spring. We have also observed a similar pattern in our study region in a plot of sea bottom temperature *vs* $bSiO_2$ flux (Fig. 6b). Major vertical $bSiO_2$ fluxes occur during summer stratification and the first sampling day of autumn, but it is just after the autumn downwelling, when sea bottom temperature increased, that sediment oxygen uptake increased as well. Another key factor is macrofauna activity mediating bioturbation and bioirrigation (Hammond et al. 1985, Aller 1994, Welsh 2003). Median grain size (MGS) for the FL station was 12.3 ± 1.8 µm, indicating this sample site lies in the range of muddy sediments. Previous studies in the Ría de Vigo (Cacabelos et al. 2009, Rodil et al. 2009) showed that sediments with similar MGS (10 -13 µm) were dominated by surface and subsurface deposit feeders. Deposit feeders obtain their nutritional intake mainly from sedimented organic matter (Heip et al. 1995) and would mainly favour aerobic processes and oxidized sediment conditions as they enhance oxygen transfer to the sediment burrow irrigation (Welsh 2003). Unfortunately, we lack information to determine seasonal influence of macrofaunal activitities on the benthic fluxes. Further studies are necessary to address this important issue.

4.2.2 Benthic nutrient fluxes

The benthic fluxes of ammonium, silicate and phosphate showed a strong correlation with the benthic oxygen fluxes (Table 3), pointing to similar biogeochemical processes. Benthic fluxes of ammonium dominated dissolved inorganic nitrogen (DIN) fluxes during the entire study (83 ± 10 %) and were in all cases from the sediment to the water column, leading to a net positive efflux of DIN. Blackburn & Henridsen (1983) estimated that about 10-70 % of DIN effluxes to the water column were due to ammonium excretion by macrofauna. In the

Ría de Vigo, benthic fluxes of ammonium were influenced by seabed temperature and the quality of the settling material. Fluxes were lowest during winter, when vertical fluxes of $bSiO_2$ and organic carbon derived from phytoplankton were minimum and C:N ratio of this material highest, indicating less labile organic matter (Fig. 7a).

Dale & Prego (2002) suggested that the mixing of bottom waters during upwelling was an important factor for the large diffusive NH_4^+ fluxes they obtained in the Ría de Pontevedra. However, during the present study it was noticed that ammonium benthic fluxes had their maximum values after two downwelling events, for spring and autumn (4.9 and 3.6 mmol m^{-2} d^{-1}, respectively). In fact, Villacieros-Robineau et al. (2013) found that the most energetic periods of bottom shear stress and thus, of most probable surface sediment resuspension occurred during downwelling conditions and strong southerly swells. Moncoiffé et al. (2000) have previously described for the Ría de Vigo that N-assimilative processes dominate during the upwelling and N-regeneration processes in the water column predominate during downwelling conditions. However, both processes may be coupled during moderate upwelling events when an efficient consumption of upwelled N nutrients occur (Álvarez-Salgado & Gilcoto 2004). Therefore, the benthic ammonium fluxes seem to account for an important amount of the observed N-regenerated inside the Ría de Vigo during downwelling periods. Since the concentration of ammonium in the oceanic ENACW that upwells in the Ría from the continental shelf is < 0.5 µmol kg^{-1} (Álvarez-Salgado et al. 1997, Castro et al. 2000), the high ammonium levels inside the Ría are mostly regenerated *in situ*. Álvarez-Salgado et al. (2010), by means of a 2D non-stationary box model for the Ría de Arousa during the upwelling season, indirectly estimated an extra flux of DIN of 2.5 mmol m^{-2} d^{-1} due to *in situ* pelagic and benthic nitrogen regeneration processes. This additional input enriched the nitrogen content of upwelled waters by 18%. Results from the present study obtained benthic DIN fluxes of 2 mmol m^{-2} d^{-1} which represent ~80 % of this extra DIN pointing to the importance of benthic remineralization processes in the Ría.

Benthic fluxes of nitrate showed a different behaviour from the rest of the benthic nutrient and oxygen fluxes, with no correlation with any of them. Nitrate fluxes were constantly

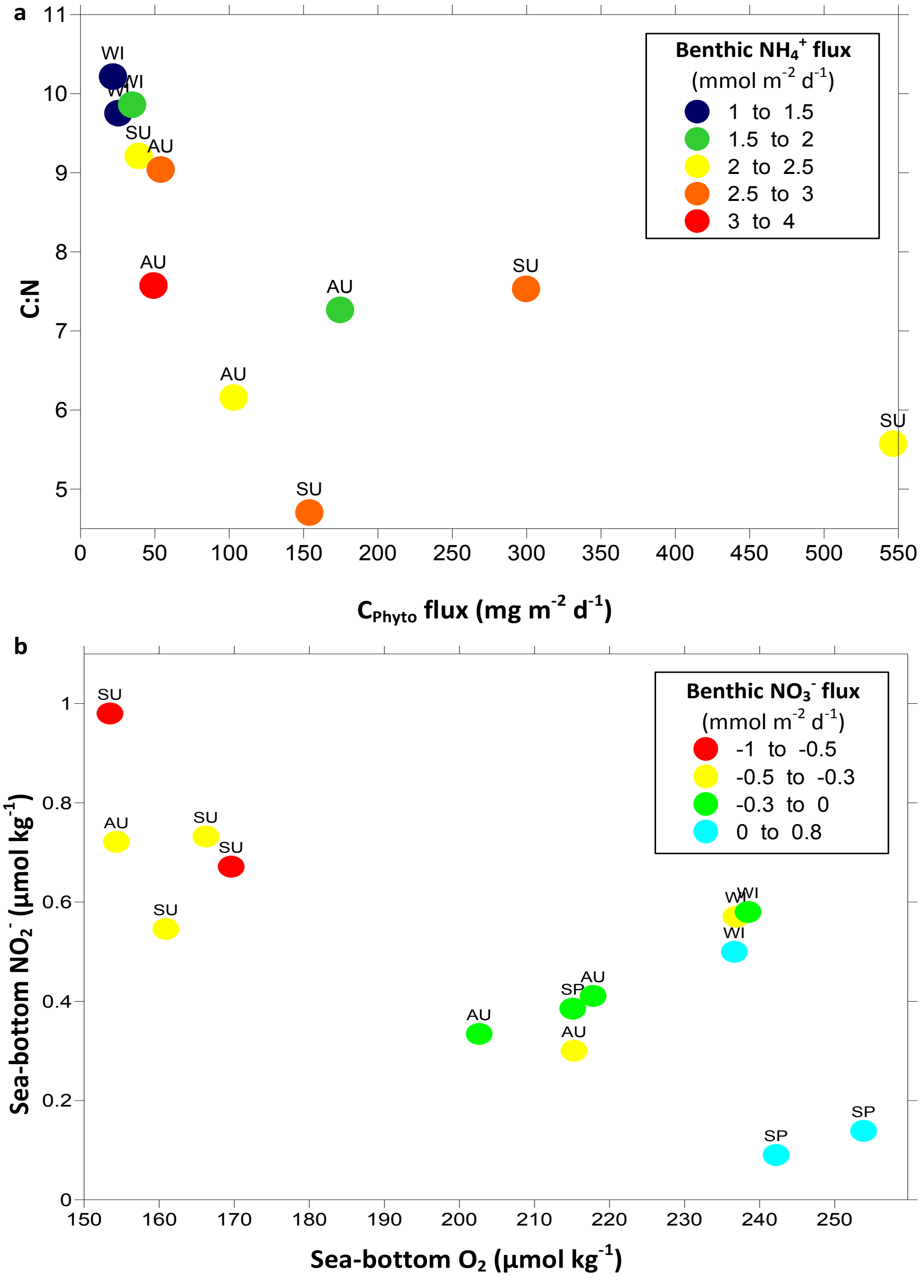


Figure 7. Seasonal benthic fluxes of (a) ammonium depending on C:N ratio from trap material and vertical flux of phytoplankton carbon (C_{Phyto}), and (b) benthic nitrate fluxes depending on sea-bottom nitrite concentration and sea-bottom dissolved oxygen. SP: spring, SU: summer, AU: autumn, WI: winter.

towards the sediment during summer and autumn periods (Fig. 5). They appeared to be strongly and positively influenced by sea-bottom concentration of dissolved oxygen and negatively correlated to initial concentrations of dissolved nutrients: nitrite, phosphate, silicate and to a minor extent nitrate. Dissolved oxygen concentration explained 54 % of the variability of the nitrate benthic fluxes (Table 4). The influence of dissolved oxygen and nitrite concentrations is clearly shown in Fig. 7b. Nitrate tends to be taken up by sediments when dissolved oxygen in the overlying water is low and nitrite concentration is high. This process is particularly evident when hydrodynamic changes occur (i.e. spring and autumn cruises). Fennel et al. (2009) found an increase in total denitrification with increasing bottom-water nitrate concentrations as well as an increase in the rate of direct denitrification. In this sense, the entrance of upwelled waters into the Ría, conveying high levels of both N-nutrients (nitrate and nitrite) probably enhances denitrification processes and thus may be responsible of the consistent benthic nitrate fluxes towards the sediment during the upwelling periods. Following the findings of Fennel et al. (2009), nitrate enriched upwelled waters seems to favour direct denitrification with respect to coupled nitrification-denitrification, though both processes may occur.

In terms of total DIN, dominance of ammonium fluxes may indicate that probably not all the ammonium generated by ammonification is rapidly oxidised to nitrate by nitrification processes. Although part of the ammonium effluxes might be provided also by other metabolic processes such as dissimilatory nitrate reduction to ammonium (Giblin et al. 2013), sulphate reduction or Mn / Fe reduction, the good correlation of ammonium fluxes with sediment oxygen consumption (r: 0.79) and the well oxygenated bottom waters in the Ría de Vigo suggest that ammonification is probably the main process behind the observed ammonium effluxes.

The main factors controlling sediment phosphate dynamics in the Ría de Vigo were water temperature at the seabed and vertical $bSiO_2$ fluxes. Temperature alone explained 39 % of the benthic flux variability (Table 4) and together with vertical $bSiO_2$ fluxes, raises the explained variability to 58%. Vertical fluxes of $bSiO_2$ are directly related to the arrival of fresh phytoplankton material to the surface sediment, as diatoms dominated the phytoplankton community in the sediment traps (Zúñiga et al. 2011). All these data suggest that phosphate fluxes are enhanced by the increasing rates of organic matter decomposition as sea bottom temperature increases and by the presence of fresh organic matter settling on the sediment.

Although previous studies showed positive correlations between benthic phosphate fluxes and bottom oxygen concentration (e.g. Fernandez 1995) as well as negative correlations with salinity (Cowan et al. 1996), the present study did not show such relationships. The magnitude of the benthic fluxes are also influenced by the sediment redox state and so, several studies have shown that release of phosphate in oxygenated sediments is reduced or even that phosphate is taken up by sediments (Sundby et al. 1986, Skoog et al. 1996, Viktorsson et al. 2012) due to phosphate adsorption to iron and manganese oxyhydroxides within the sediment. On the other hand, phosphate may be released to the water column if the metal is reduced under anoxic conditions (Sundby et al. 1992). Thus, in spite of expecting phosphorus adsorption in surface sediments due to the oxic conditions of bottom waters in the Ría de Vigo, we have always observed a positive flux of phosphate towards the overlying waters, suggesting that phosphorus adsorption does not seem to be a dominant process in these sediments. Additionally, a value of 114 for the $-\Delta O_2$: ΔP benthic flux ratio indicates that adsorption/desorption processes might be slightly balanced towards desorption and there might be an additional O_2 consumption for reoxidation of reduced inorganic forms produced by anaerobic respiration in the sediments. Mohamed et al. (2011), analysing the magnetic properties of sediments from the Ría de Vigo, found that the suboxic part of the sediment, characterized by a progressive reduction of magnetic iron oxides, increasing sulphate reduction, lies closer to the surface towards the inner parts of the Ría de Vigo, being about 1 cm below the surface sediment close to our study site (Santos-Echeandia et al. 2009). Based on this vertical zonation, we could expect little phosphate retention in the upper part of the sediment due to iron oxide reduction. Thus, we conclude that oxygenated overlying water would favour the aerobic mineralization of recent organic matter arriving to the sediment, releasing phosphate to the water column. Morever, the proximity of reducing conditions to the upper millimeters of the sediment would prevent phosphate retention and also may enhance phosphate efflux through the reduction of Mn and Fe oxides which, on the other hand, would favour reoxidation of reduced inorganic compounds with an additional oxygen consumption.

Benthic silicate fluxes were mainly controlled by sea-bottom water temperature and the amount of $bSiO_2$ settled into the sediment traps. Dissolution rates of silica exponentially increases with temperature as it is a physically rather than biologically driven process (Conley & Malone 1992). Hurd & Birdwhistell (1983) found a 50-fold increase in the opal dissolution velocity between 0°C and 25 °C. Only temperature explained 46 % of the variability in the silicate fluxes (Table 4), which is very close to the value of 48 % obtained by Cowan et al. (1996), and taking into account the $bSiO_2$ vertical flux, the explained variability raises up to 72 %. Moreover, any process removing organic matter from the opal surfaces, like microbial degradation or grazing, exposes silica directly to seawater, enhancing its dissolution rate (Bidle & Azam 1999) and therefore the benthic silicate fluxes. The high correlation of silicate benthic fluxes with benthic fluxes of oxygen and ammonia support this idea.

Evaluating the importance of benthic fluxes on the biogeochemical cycles of the nutrients in the Ría de Vigo, we estimated that on annual basis, benthic remineralization provides 1300 t N yr^{-1} and 255 t P yr^{-1} of inorganic nitrogen and inorganic phosphorous, respectively. In these calculations, we have assumed the same benthic rates for all the surface sediment of the Ría de Vigo (117 km^2, not taking into account the innermost part of the Ría, San Simón Bay, Fig. 1). On the other hand, (Prego 1993, 1994) obtained an average influx of inorganic nitrogen and phosphate into the Ría from upwelled waters of 3000 t N yr^{-1}, and 350 t P yr^{-1} by means of a box model. Reported inputs of inorganic nitrogen from continental runoff are 160 t N yr^{-1} (Gago et al. 2005) and in the range of 8 t P yr^{-1} (Gago et al. 2005) to 80 t P yr^{-1} (Prego 1993) for phosphate. Based on all these data, we estimate that benthic fluxes account for ~ 43 % of the nitrogen provided from upwelled waters and ~ 41 % of the total inorganic nitrogen entering the Ría from outside waters. Regarding phosphate, sediment remineralization would contribute to ~ 61 % of the total phosphate that the Ría receives and ~ 72 % of the upwelled phosphate.

5. Conclusions

Muddy sediments of the Ría de Vigo play an important role in the degradation of organic material supplied from the water column, and so in the supply of inorganic nutrients back to the water column. Apart from winter, benthic fluxes did not show seasonal differences; instead, benthic fluxes in the Ría de Vigo appeared to be highly influenced by sea-bottom temperature, which is modulated to some extent by upwelling/downwelling oceanographic pulses. Benthic fluxes tend to respond on a short time scale to these processes. The amount and quality of the organic matter deposited on the sediments have also been shown to control the dynamics of benthic fluxes in the Ría de Vigo. The high correlation between benthic fluxes of phosphate, silicate and ammonium and the sediment oxygen uptake pointed to the importance of the aerobic respiration processes in the remineralization. In contrast, nitrate benthic fluxes acted in a different way; they were highly influenced by seabed concentration of dissolved oxygen and the N-nutrients, nitrite and nitrate. Denitrification seems to be a key process on the uptake of nitrate by the sediments. There is a clear need for further studies of properties of the sediment such as labile organic matter content and benthic macrofauna, which may also be important factors controlling the magnitude of benthic fluxes, as has been found in other coastal studies.

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References

Aller RC (1988) Benthic fauna and biogeochemical processes in marine sediments: the role of burrow structures. In: Blackburn TH, Sorensen J (eds) Nitrogen cycling in coastal marine environments. John Wiley & Sons, Chichester, p 301–338

Aller RC (1994) Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. Chem Geol 114:331–345

Alonso-Pérez F, Ysebaert T, Castro CG (2010) Effects of suspended mussel culture on benthic–pelagic coupling in a coastal upwelling system (Ría de Vigo, NW Iberian Peninsula). J Exp Mar Biol Ecol 382:96–107

Álvarez-Salgado XA, Borges AV, Figueiras FG, Chou L (2010) Iberian margin: the Rías. In: Liu K, Atkinson L, Quiñones R, Talaue-McManus L (eds) Carbon and Nutrient Fluxes in Continental Margins. Springer, Berlin, p 103–120

Álvarez-Salgado XA, Castro CG, Pérez FF, Fraga F (1997) Nutrient mineralization patterns in shelf waters of the Western Iberian upwelling. Cont Shelf Res 17:1247–1270

Álvarez-Salgado XA, Doval MD, Borges AV, Joint I, Frankignoulle M, Woodward EMS, Figueiras FG (2001) Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian Upwelling System. Prog Oceanogr 51:321–337

Álvarez-Salgado XA, Gilcoto M (2004) Inferring nitrification rates with an inverse method in a coastal upwelling system, Ría de Vigo (NW Spain). Mar Ecol Prog Ser 276:3–17

Álvarez-Salgado XA, Rosón G, Pérez FF, Figueiras FG, Ríos AF (1996) Nitrogen cycling in an estuarine upwelling system, the Ría de Arousa (NW Spain). II. Spatial differences in the short-time-scale evolution of fluxes and net budgets. Mar Ecol Prog Ser 135:275–288

Arbones B, Castro CG, Alonso-Pérez F, Figueiras FG (2008) Phytoplankton size structure and water column metabolic balance in a coastal upwelling system: the Ría de Vigo, NW Iberia. Aquat Microb Ecol 50:169–179

Bakun A (1973) Coastal upwelling indices, west coast of North America, 1946-71. US Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, WA

Berelson WM, Heggie D, Longmore A, Kilgore T, Nicholson G, Skyring G (1998) Benthic Nutrient Recycling in Port Phillip Bay, Australia. Estuar Coast Shelf Sci 46:917–934

Berelson W, McManus J, Coale K, Johnson K, Burdige D, Kilgore T, Colodner D, Chavez F, Kudela R, Boucher J (2003) A time series of benthic flux measurements from Monterey Bay, CA. Cont Shelf Res 23:457–481

Berelson WM, McManus J, Coale KH, Johnson KS, Kilgore T, Burdige D, Pilskaln C (1996) Biogenic matter diagenesis on the sea floor: A comparison between two continental margin transects. J Mar Res 54:731–762

Berelson WM, McManus J, Severmann S, Reimers CE (2013) Benthic flux of oxygen and nutrients across Oregon/California shelf sediments. Cont Shelf Res 55:66–75

Bidle KD, Azam F (1999) Accelerated dissolution of diatom silica by marine bacterial assemblages. Nature 397:508–512

Billen G (1978) A budget of nitrogen recycling in North Sea sediments off the Belgian coast. Estuar Coast Mar Sci 7:127–146

Blackburn TH, Henridsen K (1983) Nitrogen Cycling in Different Types of Sediments from Danish Waters. Limnol Ocean 28:477–493

Boynton WR, Kemp WM (1985) Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Mar Ecol Prog Ser 23:45–55

Boynton WR, Kemp WM, Barnes JM, Matteson LL, Watts JL, Stammerjohn SE, Jasinski DA, Rohland FM (1991) Mary-land Chesapeak Bay water quality monitoring program; ecosystem processes component level 1 interpretive report no 8 (interpretive no [UMCEES] CBL ref no 91-110). Chesapeak Biological Laboratory, Salomons MD, University of Maryland, Center for Environmental Science, Solomons, MD

Boynton WR, Kemp W, Osbourne C (1980) Nutrient fluxes across the sediment-water interface in the turbid zone of a coastal plain estuary. In: Estuarine perspectives, Kennedy V. John Wiley & Sons, New York, p 93–109

Brzezinski MA, Nelson DM (1989) Seasonal changes in the silicon cycle within a Gulf Stream warm-core ring. Deep Sea Res Part Oceanogr Res Pap 36:1009–1030

Cacabelos E, Domínguez M, Troncoso JS (2009) Trophic structure of soft-bottom macrobenthos in an inlet in north-western Spain. J Mar Biol Assoc U K 89:439–447

Caffrey JM, Hollibaugh JT, Bano N, Haskins J (2010) Effects of upwelling on short-term variability in microbial and biogeochemical processes in estuarine sediments from Elkhorn Slough, California, USA. Aquat Microb Ecol 58:261–271

Castro CG, Pérez FF, Álvarez-Salgado XA, Fraga F (2000) Coupling between the thermohaline, chemical and biological fields during two contrasting upwelling events off the NW Iberian Peninsula. Cont Shelf Res 20:189–210

Christensen B, Vedel A, Kristensen E (2000) Carbon and nitrogen fluxes in sediment inhabited by suspension-feeding (Nereis diversicolor) and non-suspension-feeding (N. virens) polychaetes. Mar Ecol Prog Ser 192:203–217

Conley DJ, Malone TC (1992) Annual cycle of dissolved silicate in Chesapeake Bay: implications for the production and fate of phytoplankton biomass. Mar Ecol Prog Ser 81:121–128

Cowan JLW, Pennock JR, Boynton WR (1996) Seasonal and interannual patterns of sediment-water nutrient and oxygen fluxes in Mobile Bay, Alabama (USA): regulating factors and ecological significance. Mar Ecol Prog Ser 141:229–245

Dale AW, Prego R (2002) Physico-biogeochemical controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system. Mar Ecol Prog Ser 235:15–28

Devol AH, Christensen JP (1993) Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific. J Mar Res 51:345–372

Emiroğlu S, Rey D, Petersen N (2004) Magnetic properties of sediment in the Ría de Arousa (Spain): dissolution of iron oxides and formation of iron sulphides. Phys Chem Earth Parts ABC 29:947–959

Epping E, Zee C van der, Soetaert K, Helder W (2002) On the oxidation and burial of organic carbon in sediments of the Iberian margin and Nazaré Canyon (NE Atlantic). Prog Oceanogr 52:399–431

Farías L, Graco M, Ulloa O (2004) Temporal variability of nitrogen cycling in continental-shelf sediments of the upwelling ecosystem off central Chile. Deep Sea Res Part II Top Stud Oceanogr 51:2491–2505

Fennel K, Brady D, DiToro D, Fulweiler RW, Gardner WS, Giblin A, McCarthy MJ, Rao A, Seitzinger S, Thouvenot-Korppoo M, Tobias C (2009) Modeling denitrification in aquatic sediments. Biogeochemistry 93:159–178

Fernandez F (1995) Nitrogen and phosphorous fluxes across the sediment water interface during summer oxic and hypoxic/anoxic periods in Mobile Bay, Alabama, MSc Thesis. University of South Alabama, Mobile, AL

Ferrón S, Alonso-Pérez F, Anfuso E, Murillo FJ, Ortega T, Castro CG, Forja JM (2009b) Benthic nutrient recycling on the northeastern shelf of the Gulf of Cádiz (SW Iberian Peninsula). Mar Ecol Prog Ser 390:79–95

Ferrón S, Alonso-Pérez F, Castro CG, Ortega T, Pérez FF, Ríos AF, Gómez-Parra A, Forja JM (2008) Hydrodynamic characterization and performance of an autonomous benthic chamber for use in coastal systems. Limnol Oceanogr Methods 6:558–571

Ferrón S, Alonso-Pérez F, Ortega T, Forja JM (2009a) Benthic respiration on the northeastern shelf of the Gulf of Cádiz (SW Iberian Peninsula). Mar Ecol Prog Ser 392:69–80

Figueiras FG, Labarta U, Reiriz MJF (2002) Coastal upwelling, primary production and mussel growth in the Rías Baixas of Galicia. Hydrobiologia 484:121–131

Fisher TR, Carlson PR, Barber RT (1982) Sediment nutrient regeneration in three North Carolina estuaries. Estuar Coast Shelf Sci 14:101–116

Fraga F (1981) Upwelling off the Galician Coast, Northwest Spain. In: Richards FA (ed) Coastal Upwelling. American Geophysical Union, Washington D.C., p 176–182

Gago J, Álvarez-Salgado XA, Gilcoto M, Pérez FF (2003) Assessing the contrasting fate of dissolved and suspended organic carbon in a coastal upwelling system (’Ría de Vigo’, NW Iberian Peninsula). Estuar Coast Shelf Sci 56:271–279

Gago J, Álvarez-Salgado XA, Nieto-Cid M, Brea S, Piedracoba S (2005) Continental inputs of C, N, P and Si species to the Ría de Vigo (NW Spain). Estuar Coast Shelf Sci 65:74–82

Gazeau F, Smith SV, Gentili B, Frankignoulle M, Gattuso J-P (2004) The European coastal zone: characterization and first assessment of ecosystem metabolism. Estuar Coast Shelf Sci 60:673–694

Giblin A, Tobias C, Song B, Weston N, Banta G, Rivera-Monroy V (2013) The Importance of Dissimilatory Nitrate Reduction to Ammonium (DNRA) in the Nitrogen Cycle of Coastal Ecosystems. Oceanography 26:124–131

Grenz C, Denis L, Pringault O, Fichez R (2010) Spatial and seasonal variability of sediment oxygen consumption and nutrient fluxes at the sediment water interface in a sub-tropical lagoon (New Caledonia). Mar Pollut Bull 61:399–412

Hammond DE, Fuller C, Harmon D, Hartman B, Korosec M, Miller LG, Rea R, Warren S, Berelson W, Hager SW (1985) Benthic fluxes in San Francisco Bay. In: Cloern JE, Nichols FH (eds) Temporal Dynamics of an Estuary: San Francisco Bay. Springer Netherlands, Dordrecht, p 69–90

Hammond DE, Giordani P, Berelson WM, Poletti R (1999) Diagenesis of carbon and nutrients and benthic exchange in sediments of the Northern Adriatic Sea. Mar Chem 66:53–79

Hansen HP, Grasshoff K (1983) Automated chemical analysis. In: Grasshoff K, Enrardt M, Kermling K (eds) Methods of Seawater Analysis. Verlag Chemie, Weinheim, p 347–395

Heip CHR, Goosen NK, Herman PMJ, Kromkamp J, Middelburg JJ, Soetaert K (1995) Production and consumption of biological particles in temperate tidal estuaries. Oceanogr Mar Biol Annu Rev 33:1–149

Hidy GM (1972) A View of Recent Air-Sea Interaction Research. Bull Am Meteorol Soc 53:1083–1102

Hillebrand H, Dürselen C-D, Kirschtel D, Pollingher U, Zohary T (1999) Biovolume Calculation for Pelagic and Benthic Microalgae. J Phycol 35:403–424

Hopkinson CS, Giblin AE, Tucker J (2001) Benthic metabolism and nutrient regeneration on the continental shelf of Eastern Massachusetts, USA. Mar Ecol Prog Ser 224:1–19

Hopkinson CS, Smith EM (2005) Estuarine respiration: an overview of benthic, pelagic, and whole system respiration. In: Williams PJL (ed) Respiration in aquatic ecosystems. Oxford University Press, Oxford, New York, p 122–146

Hurd DC, Birdwhistell S (1983) On producing a more general model for biogenic silica dissolution. Am J Sci 283:1–28

Jahnke RA (1996) The global ocean flux of particulate organic carbon: Areal distribution and magnitude. Glob Biogeochem Cycles 10:71–88

Jahnke RA (2005) Transport processes and organic matter cycling in coastal sediments. In: Robinson AR, Brink KH (eds) The global coastal ocean. The sea: ideas and observations on progress in the study of the seas. Harvard University Press, Cambridge, p 163–191

Jahnke RA, Jahnke DB (2000) Rates of C, N, P and Si recycling and denitrification at the US Mid-Atlantic continental slope depocenter. Deep Sea Res Part Oceanogr Res Pap 47:1405–1428

Kristensen E (1988) Benthic fauna and biogeochemical processes in marine sediments. In: Blackburn TH, Sorensen J (eds) Nitrogen Cycling in Coastal Marine Environments. Wiley & Sons, Chichester, p 275–299

Lomas MW, Glibert PM, Shiah F-K, Smith EM (2002) Microbial processes and temperature in Chesapeake Bay: current relationships and potential impacts of regional warming. Glob Change Biol 8:51–70

Middelburg JJ, Vlug T, Jaco F, Nat WA van der (1993) Organic matter mineralization in marine systems. Glob Planet Change 8:47–58

Mohamed KJ, Rey D, Rubio B, Dekkers MJ, Roberts AP, Vilas F (2011) Onshore-offshore gradient in reductive early diagenesis in coastal marine sediments of the Ria de Vigo, Northwest Iberian Peninsula. Cont Shelf Res 31:433–447

Moncoiffé G, Álvarez-Salgado XA, Figueiras FG, Savidge G (2000) Seasonal and short-time-scale dynamics of microplankton community production and respiration in an inshore upwelling system. Mar Ecol Prog Ser 196:111–126

Mouriño C, Fraga F (1985) Determinación de nitratos en agua de mar. Investig Pesq 49:81–96

Nixon SW (1981) Remineralization and Nutrient Cycling in Coastal Marine Ecosystems. In: Neilson BJ, Cronin LE (eds) Estuaries and Nutrients. Humana Press, Clifton, New Jersey, p 111–138

Nogueira E, Pérez FF, Ríos AF (1997) Seasonal Patterns and Long-term Trends in an Estuarine Upwelling Ecosystem (Ría de Vigo, NW Spain). Estuar Coast Shelf Sci 44:285–300

Prego R (1993) Biogeochemical Pathways of Phosphate in a Galician Ria (North-western Iberian Peninsula). Estuar Coast Shelf Sci 37:437–451

Prego R (1994) Nitrogen interchanges generated by biogeochemical processes in a Galician Ria. Mar Chem 45:167–176

Prego R, Barciela M del C, Varela M (1999) Nutrient dynamics in the Galician coastal area (Northwestern Iberian Peninsula): Do the Rias Bajas receive more nutrient salts than the Rias Altas? Cont Shelf Res 19:317–334

Putt M, Stoecker DK (1989) An experimentally determined carbon: volume ratio for marine oligotrichous ciliates from estuarine and coastal waters. Limnol Oceanogr 34:1097–1103

Rodil IF, Lastra M, López J (2009) Spatial variability of benthic macrofauna in the Ria of Vigo (NW Spain): Effect of sediment type and food availability. Mar Biol Res 5:572–584

Rosón G, Álvarez-Salgado XA, Pérez FF (1999) Carbon cycling in a large coastal embayment, affected by wind-driven upwelling: short-time-scale variability and spatial differences. Mar Ecol Prog Ser 176:215–230

Rosón G, Pérez FF, Álvarez-Salgado XA, Figueiras FG (1995) Variation of Both Thermohaline and Chemical Properties in an Estuarine Upwelling Ecosystem: Ria de Arousa; I. Time Evolution. Estuar Coast Shelf Sci 41:195–213

Santos-Echeandia J, Prego R, Cobelo-García A, Millward GE (2009) Porewater geochemistry in a Galician Ria (NW Iberian Peninsula): Implications for benthic fluxes of dissolved trace elements (Co, Cu, Ni, Pb, V, Zn). Mar Chem 117:77–87

Skoog A, Hall POJ, Hulth S, Paxéus N, Der Loeff MR Van, Westerlund S (1996) Early diagenetic production and sediment-water exchange of fluorescent dissolved organic matter in the coastal environment. Geochim Cosmochim Acta 60:3619–3629

Ståhl H, Tengberg A, Brunnegård J, Bjørnbom E, Forbes TL, Josefson AB, Kaberi HG, Karle Hassellöv IM, Olsgard F, Roos P, Hall POJ (2004) Factors influencing organic carbon recycling and burial in Skagerrak sediments. J Mar Res 62:867–907

Strathmann RR (1967) Estimating the Organic Carbon Content of Phytoplankton from Cell Volume or Plasma Volume. Limnol Oceanogr 12:411–418

Sundby B, Anderson LG, Hall POJ, Iverfeldt Å, Loeff MMR van der, Westerlund SFG (1986) The effect of oxygen on release and uptake of cobalt, manganese, iron and phosphate at the sediment-water interface. Geochim Cosmochim Acta 50:1281–1288

Sundby B, Gobeil C, Silverberg N, Mucci A (1992) The phosphorous cycle in coastal marine sediments. Limnol Oceanogr 37:1129–1145

Thunell R, Benitez-Nelson C, Varela R, Astor Y, Muller-Karger F (2007) Particulate organic carbon fluxes along upwelling-dominated continental margins: Rates and mechanisms. Glob Biogeochem Cycles 21:GB1022

Varela M, Prego R, Pazos Y (2004) Vertical biogenic particle flux in a western Galician Ria (NW Iberian Peninsula). Mar Ecol Prog Ser 269:17–32

Verity PG, Robertson CY, Tronzo CR, Andrews MG, Nelson JR, Sieracki ME (1992) Relationships between cell volume and the carbon and nitrogen content of marine photosynthetic nanoplankton. Limnol Oceanogr 37:1434–1446

Viktorsson L, Almroth-Rosell E, Tengberg A, Vankevich R, Neelov I, Isaev A, Kravtsov V, Hall POJ (2012) Benthic Phosphorus Dynamics in the Gulf of Finland, Baltic Sea. Aquat Geochem 18:543–564

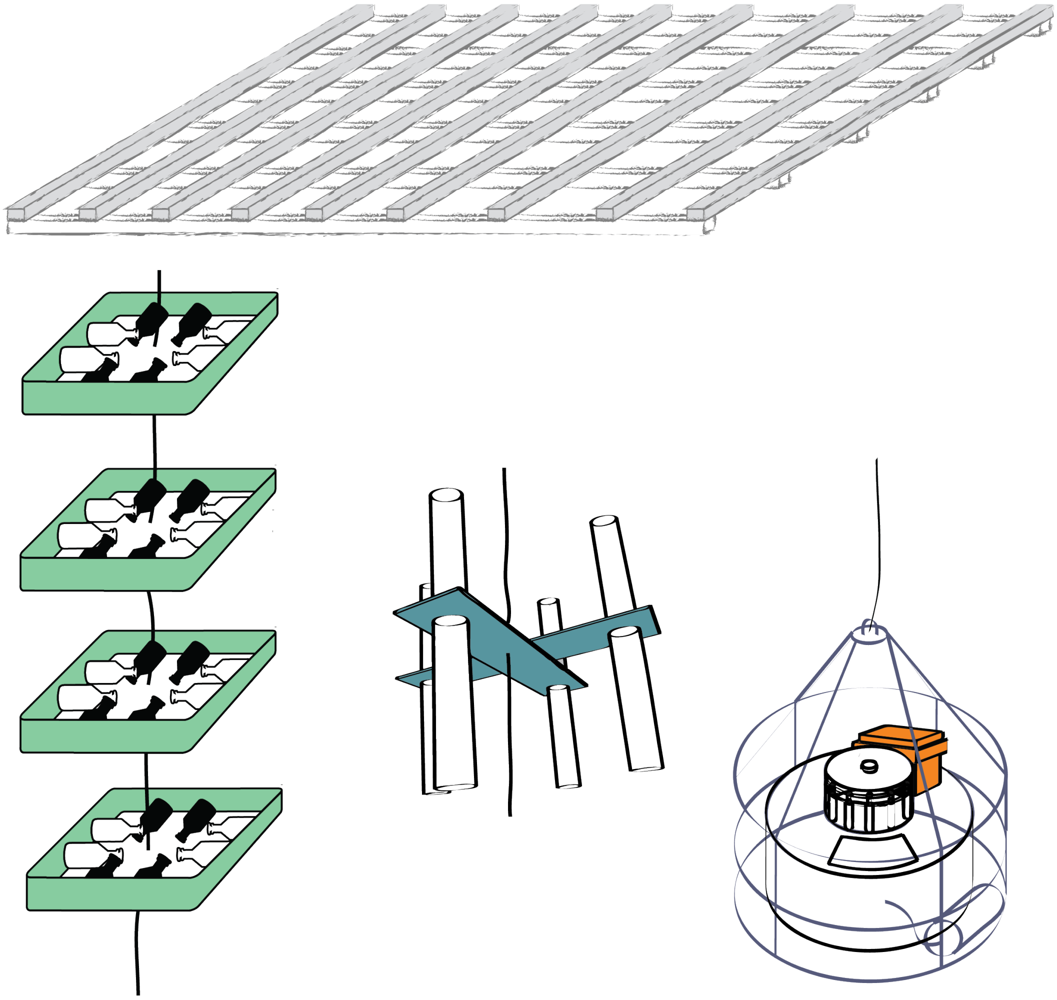
Villacieros-Robineau N, Herrera JL, Castro CG, Piedracoba S, Rosón G (2013) Hydrodynamic characterization of the bottom boundary layer in a coastal upwelling system (Ría de Vigo, NW Spain). Cont Shelf Res 68:67–79

Welsh DT (2003) It's a dirty job but someone has to do it: The role of marine benthic macrofauna in organic matter turnover and nutrient recycling to the water column. Chem Ecol 19:321–342

Wollast R (1998) Evaluation and comparisson of the global carbon cycling in the coastal zone and in the open ocean. In: Brink KH, Robinson AR (eds) The Sea, Brink, K.H. Wiley & Sons, New York, p 213–252

Zúñiga D, Alonso-Pérez F, Castro CG, Arbones B, Figueiras FG (2011) Seasonal contribution of living phytoplankton carbon to vertical fluxes in a coastal upwelling system (Ría de Vigo, NW Spain). Cont Shelf Res 31:414–424

Benthic fluxes, net ecosystem metabolism and seafood harvest: completing the organic carbon balance in the Ría de Vigo (NW Spain)



Capítulo IV

Alonso-Pérez, F., Zúñiga, D., Arbones, B., Figueiras, F.G., Castro, C.G., 2015. Benthic fluxes, net ecosystem metabolism and seafood harvest: completing the organic carbon balance in the Ría de Vigo (NW Spain). *Estuarine, Coastal and Shelf Science (in review).*

Abstract

Simultaneous direct measurements of primary production, pelagic and benthic respiration and vertical fluxes allowed, for the first time, the evaluation of the carbon metabolism in the Ría de Vigo (NW Spain) on seasonal and annual scales. With this aim, a total of 16 oceanographic cruises covering the main oceanographic conditions were carried out between April 2004 and January 2005. In addition, a 2D carbon budget, including extraction from mussel culture and fisheries activities, is proposed. The pelagic system was net autotrophic during the spring and summer periods and autotrophic or almost in balance during autumn and winter. Vertical fluxes of organic carbon were higher than net community production (NCP) during autumn and winter periods, probably due to resuspension processes and inputs of organic matter from continental runoff. Benthic remineralization is an important process in the Ría de Vigo, which gains significance during autumn and winter when benthic respiration accounts for 40% and 45% of the total respiration, respectively. The Ría de Vigo is net autotrophic on annual basis (317 ± 113 g C m^{-2} yr^{-1}) even though the benthic metabolism reduces the NCP by 23%. Total annual carbon seafood harvest amounted 3% of the net ecosystem metabolism and it is dominated by mussel culture (89%). However, based on mean energy transfer efficiency between trophic levels of 10%, it is estimated that mussel culture and reported fish catches require up to 38% of the NCP. The organic carbon produced *in situ* at the Ría de Vigo and available for export to the adjacent shelf and/or to be buried in the sediment represents ¼ of the gross primary production and it is favoured during summer upwelling.

Resumen

Medidas directas de producción primaria, respiración pelágica y bentónica así como medidas de flujos verticales, permitieron, por vez primera, la evaluación del metabolismo de carbono en la Ría de Vigo, a escala estacional y anual. Con este objetivo, se realizaron un total de 16 campañas oceanográficas entre Abril 2004 y Enero 2005, cubriendo las principales condiciones oceanográficas en este área de estudio. Además de ello, se propuso un balance de carbono 2D, incluyendo la extracción de mejillón proveniente de cultivo de batea y la correspondiente a las actividades pesqueras. El sistema pelágico fue netamente autotrófico durante los períodos de primavera y verano, y autotrófico o prácticamente en balance durante otoño e invierno. Los flujos verticales de carbono orgánico fueron superiores a la producción neta del ecosistema (NCP) durante los períodos de otoño e invierno, debido probablemente a procesos de resuspensión y contribución de materia orgánica proveniente de aguas continentales. La remineralización bentónica es un proceso importante en la Ría de Vigo, ganando relevancia durante los períodos de otoño e invierno en los que la respiración bentónica representa un 40% y un 45% de la respiración total del sistema, respectivamente. La Ría de Vigo es netamente autotrófica a escala anual (317 ± 113 g C m^{-2} yr^{-1}) incluso a pesar de que el metabolismo bentónico reduce el NCP en un 23%. El carbono orgánico anual extraído de la pesca y del cultivo de mejillón supone un 3% del metabolismo neto del ecosistema, dónde la extracción de mejillón de cultivo representa el 89% del total extraído. Sin embargo, si nos basamos en la eficiencia en la transferencia de energía entre niveles tróficos del 10%, se estima que el conjunto de cultivo de mejillón y las actividades pesqueras, requieren hasta un 38% del NCP. El carbono orgánico producido *in situ* en la Ría de Vigo y disponible para ser exportado a la plataforma adyacente o ser enterrado en el sedimento, representa una cuarta parte de la producción primaria bruta y es favorecido durante el afloramiento estival.

1. Introduction

Coastal zones contribute disproportionately large amounts of production and respiration in relation to their areas covered over the global ocean (Wollast 1998). In these regions, production (P) and respiration (R) processes are magnified due to the influence of hydrodynamic events, such as upwelling and continental inputs, combined with the proximity of the sediment remineralizing environment (Zeldis 2004). To provide a better understanding of the functioning of these biogeochemically active regions, studies of ecosystem metabolism are necessary. Net ecosystem metabolism (NEM) represents the balance between primary production and total respiration in an ecosystem and can be measured as the summation of anabolic and catabolic rates of all the organisms in the system (Kemp et al. 1997), where catabolic rates represent the sum of the respiratory processes (Testa et al. 2012). The term net community production (NCP) is often used when just the microbial pelagic community metabolism is being measured (Staehr et al. 2012). The balance between net autotrophy and heterotrophy will depend on the nature of exogenous inputs (Caffrey et al. 1998) and so, coastal systems receiving high inorganic nutrient inputs tend to be net autotrophic (P>R) while those ones with high organic inputs tend to be net heterotrophic (R>P). Measurements of ecosystem metabolism indicate the trophic status of the ecosystem (Odum 1956), as well as they give an idea of how the system processes nutrients and organic matter (Smith & Hollibaugh 1997). This information is essential to nourish food web models and to partition biogeochemical processes among the different aerobic and anaerobic pathways (Hopkinson et al. 1999). Among the different methods used to calculate NEM, direct rate measurements allow partitioning of production and respiration processes into shares of different habitats (Testa et al. 2012), i.e. they have the advantage of estimating the relative contribution to total ecosystem metabolism by pelagic and benthic components (Staehr et al. 2012).

Several factors can regulate the trophic status in a coastal system such as inputs of inorganic nutrients, exchange rate with the adjacent seaward region and loading rates of organic carbon. Organic matter produced by phytoplankton not respired in the water column may be transferred to higher trophic levels, transported offshore, exported vertically towards the sediment and mineralized or buried in the sediment. High *in situ* primary production in many coastal systems provides the substrate of autochthonous organic matter that contributes to secondary production either directly or indirectly (Hyndes et al. 2014) and is then, available to higher trophic levels such as predators and scavengers. Therefore, primary production is an important factor on the production of marine fishes as it supports food to fisheries harvest (Pauly & Christensen 1995, Kemp et al. 1997). Harvest and migration of marine organisms may represent potentially significant losses in the organic carbon budget of a coastal ecosystem (Houde & Rutherford 1993) and so, overharvesting of marine organisms reduces the abundance of consumers and so it reduces the carbon transfer towards higher trophic levels (Hyndes et al. 2014).

The Galician Rías Baixas (NW Iberian Peninsula; Fig. 1) comprise four V-shaped coastal inlets located in the unique coastal upwelling system of Europe. In this region, the upwelling of subsurface cold and nutrient rich Eastern North Atlantic Central Waters (ENACW) promote high phytoplankton abundance able to support the highest mussel production (*Mytilus galloprovincialis* Lamark) in Europe. This activity renders a total estimated production of 250 x 10^6 kg yr^{-1} (Figueiras et al. 2002). The Ría de Vigo sustains 478 suspended mussel rafts and provides approx. 15 % of the total mussel production of the Rías Baixas. Studies dealing with the biogeochemical fluxes and net budgets of organic carbon in the Rías Baixas have been mainly derived from stationary box models of inorganic nutrients (Prego 1993, 1994), which then developed to non-stationary box models (Álvarez-Salgado et al. 1996, Rosón et al. 1999, Gilcoto et al. 2001, Dale & Prego 2002). Later on, Piedracoba et al. (2008) included direct measurements of vertical fluxes and water column production/respiration experiments incubated at laboratory. These studies have inferred that mineralization of the organic matter in the sediments of the rías must have a major importance in the net ecosystem metabolism, but up to date none of them have measured *in situ* benthic fluxes.

The first goal of this manuscript is to explore the importance of benthic respiration in the Ría de Vigo and to evaluate in what extent it determines the trophic status of the ecosystem. With this aim, benthic respiration was analyzed in relation to *in situ* and simultaneously measured primary production, pelagic respiration rates (Arbones et al. 2008) and vertical export of particles (Zúñiga et al. 2011) during four seasonal campaigns carried out in the framework of the FLUVBE project (Coupling of benthic and pelagic fluxes in the Ría de Vigo). Bringing together all these measurements, the main objective of the manuscript was to determine the Net Ecosystem Metabolism in the Ría de Vigo on seasonal and annual basis. From here, an annual carbon budget including potential carbon inputs from continental sources and losses from the system in the form of mussel harvest, wild catch fisheries and shellfishing has been built. In this way, this manuscript presents an integrative view of the

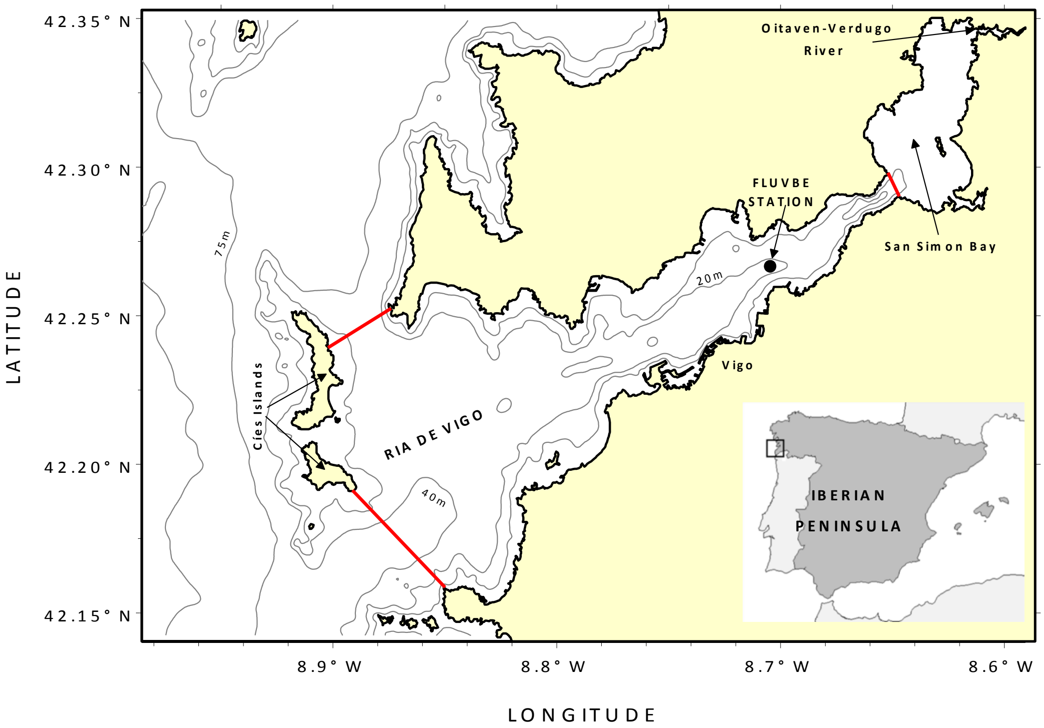


Figure 1. Map of the Ría de Vigo, showing the location of the station FLUVBE (●) and boundary limits (red solid lines) used for the calculations of carbon budget.

ecosystem carbon trade off, increasing our general knowledge of coastal system responses to different combination of environmental changes (Hobbie 2000, Rhoten et al. 2009, Carpenter et al. 2009, Kemp & Boynton 2012).

2. Methods

2.1. Study area

The study site was located in the Ría de Vigo, a temperate coastal embayment and one of the four Rías Baixas of the NW Iberian Peninsula. The Ría is oriented NE-SW, widens seawards, and is partially enclosed by the Cíes Islands (Fig. 1). From May to October, prevailing northerly winds cause the upwelling of cold nutrient-rich subsurface ENACW, which enter into the Ría. During upwelling conditions, primary production is increased (Fraga 1981), as it is the potential export of biogenic carbon to the sediment and the adjacent shelf (Álvarez-Salgado et al. 2001). During the other half of the year, downwelling conditions, associated with prevailing southerly winds, are favoured.

2.2. Sampling strategy and water sampling

In the framework of the Spanish project FLUVBE, 16 oceanographic cruises were carried out at FLUVBE station, located in the main channel of the Ría de Vigo (Fig. 1). The sampling strategy of the cruises, which covered the period between April 2004 and January 2005, was intended to capture the predominant oceanographic conditions in the study area; i.e. spring bloom (April), summer upwelling-stratification (July), autumn bloom (October) and winter mixing (January). During each period, the station was visited twice a week during a 15 days period. Arbones et al. (2008) explained in detail the measurements that are briefly described below. Measurements of plankton community gross primary production (GPP), NCP, and dark community respiration (DCR) were determined by 24h *in situ* light-dark bottle oxygen incubations at 4 depths in the photic layer and 1 depth in the aphotic zone of the water column. Samples were taken with 10 L PVC Niskin bottles mounted on a rosette with a SBE 911 CTD. At each of the 4 photic depths, 4 light and 4 dark bottles were placed in a specially constructed plexiglass holder. For the aphotic depth, only 4 dark samples were incubated. A further set of 4 replicates at each depth was fixed at time 0. Dissolved oxygen was determined by an automated Winkler titration system. Net *in vitro* changes in the light and dark bottles gave NCP and DCR, respectively. Production and respiration rates were calculated as follows: NCP = ΔO_2 in light bottles in relation with the initial oxygen concentration; DCR = ΔO_2 in dark bottles in relation with the initial oxygen concentration; GPP = NCP + DCR. In order to convert oxygen production and oxygen consumption to carbon units a photosynthetic quotient and an O_2/TCO_2 ratio for pelagic respiration of 1.4 were assumed following Fraga et al. (1998).

The upwelling index was estimated using the component $-Q_x$ of the Ekman transport following Bakun's (1973) method:

$$-Q_x = (\rho_{air}\ C_D\ |V|\ V_Y)/(f\ \rho_{sw})$$

where ρ_{air} is the density of air (1.22 kg m^{-3} at 15°C), C_D is an empirical dimensionless drag coefficient (1.4×10^{-3} according to Hidy 1972), f is the Coriolis parameter (9.946×10^{-5} at 43°N), ρ_{sw} is the density of seawater (1025 kg m^{-3}) and $|V|$ and V_Y, are the average daily modulus and northerly component of the geostrophic winds centred at 43°N, 11°W, respectively. Average daily geostrophic winds were estimated from surface atmospheric pressure charts. Positive values of $-Q_x$ indicate upwelling and correspond to predominance of northerly winds.

Continental runoff into the Ría de Vigo is dominated by the discharge from the river Oitavén-Verdugo at the inner part of the Ría (Fig. 1). Its flow is a combination of regulated and natural flow. Daily flows were provided by the company in charge of the management of urban waters. The Eiras reservoir controlled 23 ± 12 % of the total flow during the study year. The natural component of the flow per unit area was calculated following Ríos et al. (1992).

2.3. Vertical Fluxes

Vertical particle fluxes towards the sediment were estimated using a homemade multitrap collector system. It was composed by 4 PVC trap baffled cylinders of 28 cm^2 collecting area and aspect ratio of 10.8. Sediment traps were deployed at FLUVBE site at approximately 16 m depth (approx. 5 meters above sea bottom) for a 24 hour period, filled with filtered seawater with additional 5 PSU in excess per liter and without the addition of any preservatives. A subsample of 200 mL of the material collected in each cylinder was used for analysis of particulate organic carbon (POC). Filters were vacuum dried and frozen (-20 °C) before analysis. Samples were vapored with HCl (32%) for 24 h to eliminate inorganic carbon. A Perkin Elmer 2400 CHN analyzer was used for measurements of POC, using an acetanilide standard daily. The precision of the method is ± 3.6 mg C m^{-3}.

In order to determine phytoplankton derived carbon settled in the traps (C_{Phyto}), a fraction of 100 mL preserved in Lugol´s iodine was employed for microplankton determination. Depending on the chl *a* concentration, a volume ranging from 10 to 50 mL was sedimented in a composite sedimentation chamber and observed through an inverted microscope. The phytoplankton organisms were counted and identified to species level. Dimensions were taken to calculate cell biovolumes after approximation to the nearest geometrical shape (Hillebrand et al. 1999) and cell carbon was calculated following Strathmann (1967) for diatoms and dinoflagellates, Verity et al. (1992) for other flagellates (> 20 µm) and Putt & Stoecker (1989) for ciliates. Unfortunately, subsamples for C_{Phyto} were not available for the spring period.

2.4. Benthic fluxes

Fluxes of dissolved oxygen, total alkalinity and pH at the sediment-water interface were measured *in situ* by means of a benthic chamber, placed by a diver directly on the sediment surface. The equipment consisted of a PVC opaque cylindrical chamber, which incubated 140 L of overlying seawater, and covered 0.64 m^2 of sediment surface. Inside the chamber, sensors for temperature (SBE39), turbidity (Seapoint Turbidity Meter) and dissolved oxygen

(SBE43) gave a continuous recording of these variables during the incubation time (approx. 8 h) (Ferrón et al. 2008). Discrete samples were withdrawn from the chamber at prefixed times with a multiple water KC Denmark sampler provided with 12 syringes of 50 ml capacity.

Total alkalinity was determined by potentiometric titration with HCl to a final pH of 4.4 (Pérez & Fraga 1987) and adapted for small sampling volume of 5 mL. The measurements of pH were analyzed spectrophotometrically following Clayton & Byrne (1993). Total CO_2 was estimated from pH and total alkalinity using the carbonic system equations with the carbonic and boric acid dissociations constants of Lueker et al. (2000). Benthic fluxes were estimated by empirical linear fittings based on changes in concentration over time. Alkalinity fluxes were corrected for the influence of ammonium and nitrate fluxes by adding the fluxes of NO_3^- and subtracting the NH_4^+ fluxes. Assuming that calculated TCO_2 fluxes account for organic carbon remineralization and net dissolution of $CaCO_3$, it can establish an upper limit of the amount of carbon oxidized as the calculated TCO_2. As Ca^{2+} fluxes were not measured, an estimate of the maximum dissolution of $CaCO_3$ was calculated as ½ alkalinity fluxes following Berelson et al. (1998). Consequently, the lower limit of the carbon oxidation was obtained subtracting maximum $CaCO_3$ dissolution rates from measured TCO_2 fluxes. Based on these assumptions, carbon oxidation rates (Cox_{avg}) were calculated as the average between the upper and lower limit. Uncertainties of the fluxes account for the fit of the data to a linear function and the propagation of random errors.

3. Results & Discussion

3.1. Hydrographic conditions, pelagic production and respiration rates

The seasonal sampling for the study year captured the most relevant hydrodynamic conditions for this coastal upwelling system, as explained in detail by Villacieros-Robineau et al. (2013). Here, the main hydrographic features of each seasonal period are described. During the spring period there was a transition from downwelling to upwelling as observed

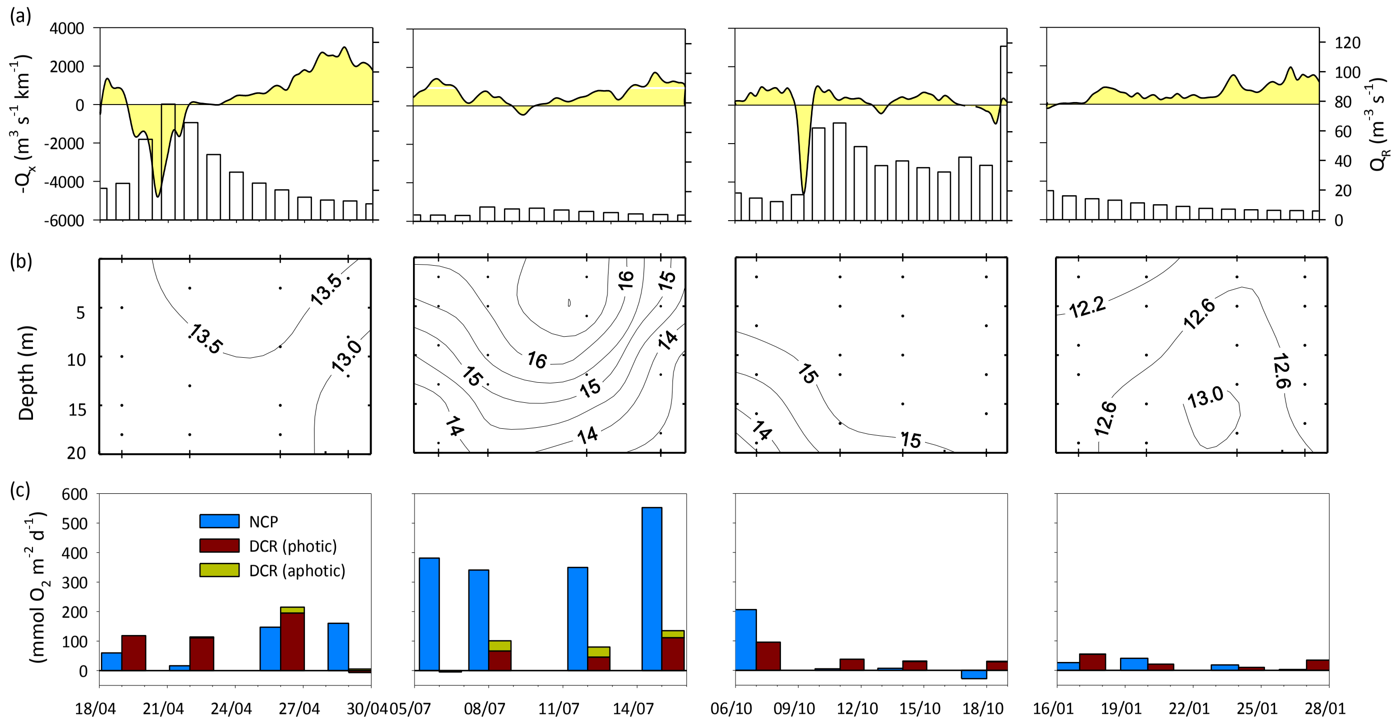


Figure 2. Time series of upwelling index (-Q$_x$, solid line) and daily averaged runoff (Q$_R$, bars) (a), temperature (°C) (b), Net Community Production (NCP) and Dark Community Respiration (DCR) both in the photic layer and aphotic layer (c).

by $-Q_x$ values and temporal evolution of temperature (Fig. 2). There was also a shift in the continental runoff, with the highest values associated with downwelling-favouring southerly winds. Biological properties responded to this transition situation with an increase of the NCP as upwelling waters entered. The summer period was characterized by constant upwelling conditions and low values of continental runoff (< 20 m^{-3} s^{-1}). Pelagic autotrophy dominated during this period as NCP reached the highest values for the whole year (> 300 mmol O_2 m^{-2} d^{-1}), pointing to *in situ* produced organic carbon potentially available to be exported to the continental shelf, to the sediment or to higher trophic levels. Under upwelling conditions, outwelling of waters from the Ría are favoured (Álvarez-Salgado et al. 2000), and consequently the offshore export of organic matter is enhanced (Fraga 1981, Álvarez-Salgado et al. 1997). The autumn period started with upwelling conditions though a strong downwelling pulse ($-Q_x < -4000$ m^3 s^{-1} km^{-1}) between the 1st and 2nd sampling days, homogenized the water column, bringing warmer waters (>15 °C) towards sea bottom. Continental runoff increased after the downwelling pulse and maintained high values until the end of the period (> 40 m^3 s^{-1}). NCP and respiration decreased after the downwelling pulse, and the water column was basically in metabolic balance for these last days. Finally, during the winter period, there was a thermal inversion associated with the winter cooling and NCP reached its minimum as expected (Cermeño et al. 2006).

There was a clear seasonal pattern for both NCP and DCR in the water column with maximum values during summer and spring periods, when phytoplankton community was dominated by large cells (> 20 µm). The pelagic system of the Ría de Vigo was net autotrophic during the spring and summer seasons and autotrophic or almost in balance during the winter and autumn periods (Arbones et al. 2008).

3.2 Vertical fluxes of organic carbon

The annual vertical fluxes of organic carbon, which averaged 1.08 ± 0.15 g C m^{-2} d^{-1}, were of the same order as previous values reported for the Galician coast (Bode et al. 1998, Varela et al. 2004, Piedracoba et al. 2008) and did not show any significant seasonal variations ($p > 0.1$) (Fig. 3). However, there was a seasonal variability on the fluxes of phytoplankton derived carbon (C_{Phyto}) with maximum values during summer upwelling (0.26 ± 0.21 g C m^{-2} d^{-1}, Fig. 3.) decreasing in autumn and reaching minimum values during winter (0.03 ± 0.01 g C m^{-2} d^{-1}). Therefore, the average percentage of phytoplankton carbon flux over the total organic carbon varied seasonally, decreasing from 26 % during summer to 9 % during autumn and finally 2 % during winter. According to Zúñiga et al. (2011), the seasonality in the C_{Phyto} fluxes towards the sediment is influenced by the phytoplankton community structure of the water column.

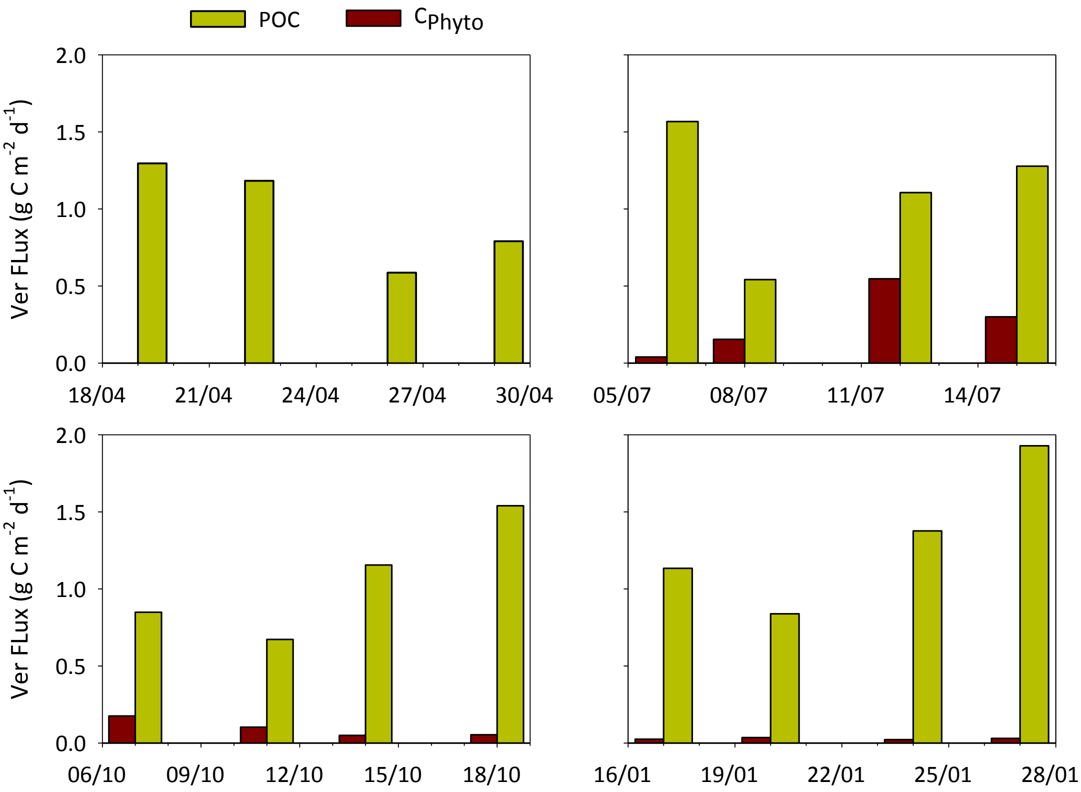


Figure 3. Seasonal vertical fluxes of particulate organic carbon (POC) and carbon derived from phytoplankton (C_{Phyto}). No data for spring C_{Phyto}. Units in g C m^{-2} d^{-1}.

Based on the data from primary production, vertical fluxes and pelagic respiration, a 1D carbon budget for each season was built (Fig. 4). During spring, half of the GPP (52 %) is respired in the photic zone, a value comparable to the 43 % obtained by Moncoiffé et al. (2000) during the upwelling season. Organic carbon vertical fluxes are of the same order of magnitude as the NCP, which means that vertical export is favoured over offshore transport.

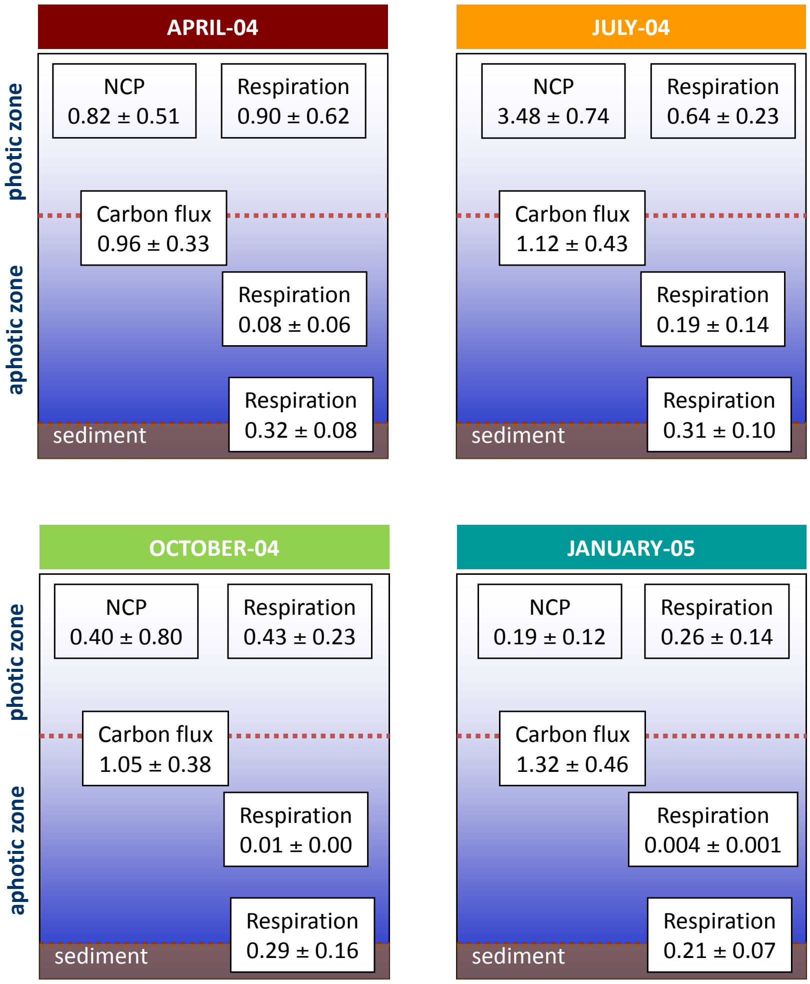


Figure 4. Seasonal carbon budgets. Benthic respiration obtained from alkalinity and pH benthic fluxes (Cox_{avg}). Units in g C m^{-2} d^{-1}. Errors presented as the SD of the mean for each season. Pelagic respiration and NCP were converted to carbon units using a R_C= 1.4 (Fraga et al. 1998)

The fact that the spring period comprised a transition from downwelling to upwelling, constrained on average the export to the adjacent shelf, being a situation similar to a weak upwelling scenario as described by Torres-López et al. (2005). The summer upwelling period is characterized by the highest GPP (4.12 g C m^{-2} d^{-1}) of the year, from which the photic zone is able to respire just 15 %. Vertical organic carbon fluxes represented 32 % of the integrated NCP. These values were very similar to those obtained during an upwelling/relaxation cycle in the Ría de Vigo (30 %, Piedracoba et al. 2008), and close to the 14-26 % obtained by Olli et al. (2001) on the shelf of the Iberian upwelling system. Approximately 70 % of the NCP is available to be transferred to higher trophic levels or exported to the adjacent continental shelf. This last process is favoured by the positive circulation of the Ría during the upwelling season. During autumn and winter, vertical fluxes of organic carbon exceeded by far NCP (2.7 and 7 fold higher, respectively), suggesting that there are additional sources of organic carbon to the fluxes others than *in situ* primary production, as advection, resuspension processes or organic matter from continental runoff. Villacieros-Robineau et al. (2013), studying the hydrodynamics of the bottom boundary layer in the Ría de Vigo by means of a downwards looking Acoustic Doppler Current Profiler, found that bottom shear stress was strong enough for the autumn period to cause the resuspension of sea surface sediments. The presence of allochthonous material in the settling particles explained the lower contribution of C_{Phyto} to the vertical organic carbon fluxes during autum and winter compared to the summer period. Furthermore, higher C:N ratios of the material for winter than the other seasons (11.3 ± 3 and 7.2 ± 0.4 respectively, Alonso-Pérez & Castro 2014) reflected less labile organic matter, more characteristic from continental runoff (Kemp et al. 1997) or resuspended material.

On annual average, vertical organic carbon flux represented approx. 91 % of the integrated NCP. Although these data might contrast with Prego (1993), who found that the Ría de Vigo exports offshore 1/3 of the annual net community production, it has to be taken into account that during autumn and winter a major proportion of organic carbon is from allochthonous origin and not produced inside the Ría.

3.3 Benthic fluxes

Benthic respiration may be measured either as oxygen consumption or carbon dioxide production, and so most researchers measure one of both parameters and assume a BRQ (benthic respiration quotient) = 1 and Redfield C:N:P stoichiometry for the organic matter (Hopkinson & Smith 2005). However, BRQ of benthic systems varies widely across studies and dissolved inorganic carbon flux may exceed oxygen consumption when organic matter is mainly anaerobically degraded, reaching values of BRQ as high as 2.15 in Tomales Bay (Dollar et al. 1991). In the present study, both oxygen taken up and inorganic carbon production were measured. Benthic fluxes of Cox_{avg} showed a similar trend to oxygen uptake (Fig. 5) being the two variables highly correlated (r: -0.78, $p < 0.01$, n= 15), with no

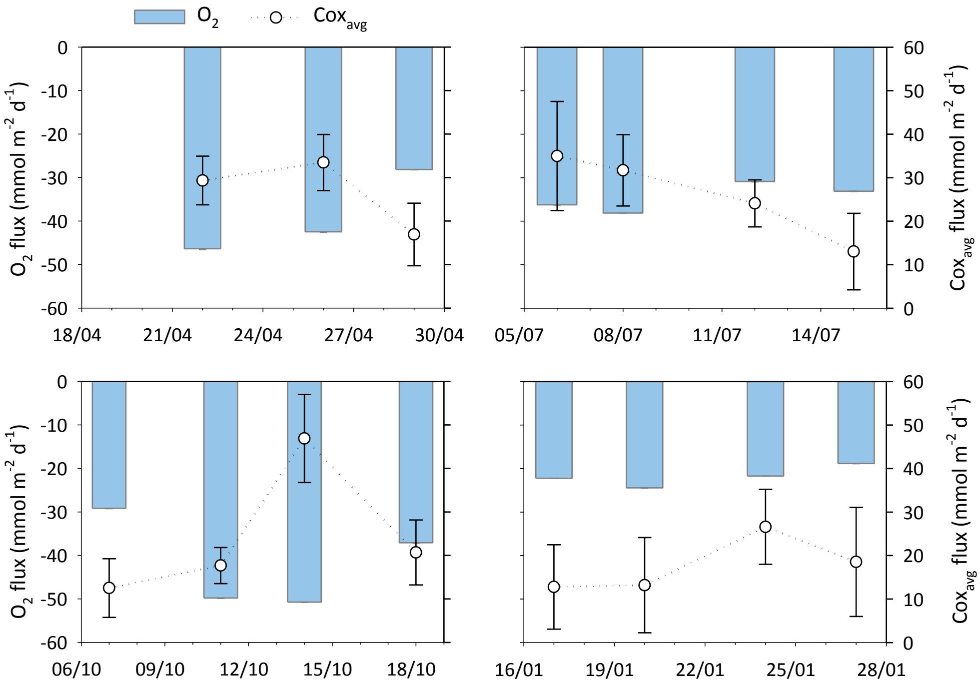


Figure 5. Sediment oxygen uptake (vertical bars) and benthic carbon oxidation fluxes (Cox_{avg}, open circles). Fluxes are in mmol m^{-2} d^{-1}. Error bars are based on the propagation of random errors from measured benthic fluxes.

significant differences among spring, summer and autumn but significantly lower during winter. Thus, it is suggested that benthic inorganic carbon fluxes at the Ría de Vigo are also influenced by the upwelling/downwelling events and the arrival of labile organic matter to the sediment as it was previously found for the oxygen fluxes (Alonso-Pérez & Castro 2014). Likewise, averaged BRQ was 0.76 ± 0.23 which can be considered low compared to values reported by Hopkinson & Smith (2005) from different estuaries worldwide, and values obtained by Forja et al. (2004) at 5 different coastal sites in the Iberian Peninsula (1.1 to 3.1). These low BRQ values point to the preference of aerobic catabolic processes in the degradation of organic matter at the sediment surface.

Taking into account the vertical fluxes, 26 % of the organic carbon is remineralized in the sediment and only 7 % in the aphotic layer of the water column (Fig. 4). This benthic share was similar to the average of 24 % compiled by Hopkinson & Smith (2005) for different estuaries worldwide. The percentage of the vertical fluxes remineralized in the sediment is higher during spring, summer and autumn (approx. 30 %) and descends to 16 % during winter (Fig. 4), when benthic fluxes were lower and the highest values of relatively refractory material were registered in the sediment trap. Respiration at the aphotic water column reaches its maximum (17 % of the vertical fluxes) during summer upwelling coinciding with the highest contribution of C_{Phyto} to the vertical fluxes, though it remains low during the whole year. In contrast, Piedracoba et al. (2008) obtained a contribution of 61% of the aphotic respiration at the Ría de Vigo during upwelling conditions, based on P/R oxygen measurements incubated at laboratory.

Overall, benthic respiration appears to be an important metabolic process in the Ría de Vigo, averaging 34 % of the total respiration, which includes it in the upper range for estuaries (23 % to 37 %, Hopkinson & Smith 2005). There is a dominance of pelagic respiration during spring and summer periods (75 % and 73 %, respectively) while benthic mineralization gains importance during autumn and winter periods, reaching values of 40 % and 44 % of the total respiration, respectively.

3.4 NEM: importance of benthic fluxes, mussel culture and fisheries

The unique opportunity of simultaneous measurements of production and pelagic and benthic respiration allowed to establish an assessment of Net Ecosystem Metabolism (GPP – total respiration) for the Ría de Vigo on seasonal and annual scales. On a seasonal scale, the proportion of NEM over the calculated GPP reaches its maximum during summer (72%) and reduces to -6 % for the winter period (Fig. 4), with an annual average NEM sharing 49% of GPP. Smith & Hollibaugh (1993) in a study including 22 coastal ecosystems obtained an inverse relationship between GPP and NEM, where most productive systems had the most heterotrophic metabolism. This relationship was attributed to the fact that most of the nutrients delivered to these systems were derived from terrestrial organic matter. In contrast to coastal sites highly influenced by riverine inputs, NEM in the Ría de Vigo was positively correlated with *in situ* GPP (r: 0.98), due to the major contribution of inorganic nutrients advected into the Ría by upwelled waters (Fraga 1981). The seasonal variability of NEM also remarks the importance of the benthic respiration on the autotrophy of the ecosystem. As previously indicated, the pelagic domain of the Ría de Vigo is autotrophic or in balance (Arbones et al. 2008). When the benthic respiration is included to evaluate the trophic status of the system, averaged NEM for spring is still autotrophic, though not significant (0.43 ± 0.53 g C m^{-2} d^{-1}, $p > 0.05$), autumn NEM is in balance (0.09 ± 0.82 g C m^{-2} d^{-1}), and averaged NEM during winter is even negative (-0.03 ± 0.13 g C m^{-2} d^{-1}).

Based on data collected in this study and estimations from the literature, a 2D annual carbon budget for the Ría de Vigo has been built (Fig. 6), including the carbon extracted from the system by mussel culture, wild catch fisheries and shellfishing. Inputs and outputs of carbon from the system were normalized to the area of the Ría (117 km^2) as delimited in Fig. 1. Calculations were based on wet weight catches and wet weight: carbon ratios for each of the faunal groups using referenced data as shown in the first 3 columns of Table 1. Continental inputs were obtained from Evans et al. (2011).

The main feature of the budget is that the Ría de Vigo is net autotrophic on annual basis (317 ± 113 g C m^{-2} yr^{-1}) in contrast to the majority of estuaries that on average appear to be

Table 1. Summary of annual harvest for each faunal group, ratio Wet Weight (WW): Organic Carbon (C), Carbon extracted from the system (Carbon flux), trophic level (TL), primary production required to sustain catches (PPR) and percentage of net community production (NCP) represented by PPR, in mussel raft culture, fisheries and shellfishing at the Ría de Vigo. Data were averaged for the area covered by the Ría de Vigo (117 km^2), excluding San Simón Bay.

		Harvest Tn WW yr^{-1}	Ratio WW/C	Carbon flux g C m^{-2} yr^{-1}	TL	PPR g C m^{-2} yr^{-1}	% PPR/ NCP
Mussel Raft	Mussel	**34502**[a]	33.3[c]	**8.85**	2	**88.5**	**19.80**
Fisheries		**819**[b]		**0.76**		**76.1**	**17.03**
	Fish	528	8.7[d]	0.52	3	51.8	11.59
	Cephalopod	214	10.8[e]	0.17	3	16.9	3.78
	Crustacean	77	8.9[f]	0.07	3	7.4	1.66
Shellfishing		**1264**[b]		**0.35**		**3.5**	**0.80**
	Bivalves	992	33.3[g]	0.25	2	2.5	0.57
	Sea Urchin	192	66.2[h]	0.02	2	0.2	0.06
	Goose barnacle	80	8.9[f]	0.08	3	0.8	0.17
Total		**36585**		**9.96**		**168.1**	**37.63**

[a] Number of rafts: 474, annual production per raft: 72.18 Tn yr^{-1} (Labarta 1999)

[b] Annual wild catches in 2006 (Peleteiro et al. 2008)

[c] Pérez-Camacho & Gonzalez (1984)

[d] Czamanski et al. (2011)

[e] Clarke et al. (1994)

[f] Vinogradov (1953); Walve & Larsson (1999)

[g] Ansell (1974)

[h] Vinogradov (1953)

net heterotropic (Hopkinson & Smith 2005), including coastal sites affected by upwelling processes as Tomales Bay (Smith & Hollibaugh 1997). In fact, the annual NEM value of the Ría de Vigo appeared to be high compared with systems as Chesapeake bay (47 g C m^{-2} yr^{-1}, Kemp et al. 1997) and some Australian coastal sites (11-21 g C m^{-2} yr^{-1}, Eyre & McKee 2002, Ferguson & Eyre 2010). Our result is closer to the value of NCP obtained by Dale & Prego (2002) at the Ría de Pontevedra (210-314 g C m^{-2} yr^{-1}) using a non-stationary state mass balance. Another important highlight from the budget is that benthic remineralization in this coastal system (104 ± 20 g C m^{-2} yr^{-1}) reduces the autotrophy of the system (NCP) by 23%. Input of continental runoff of particulate organic carbon (4.1 g C m^{-2} yr^{-1}) represented

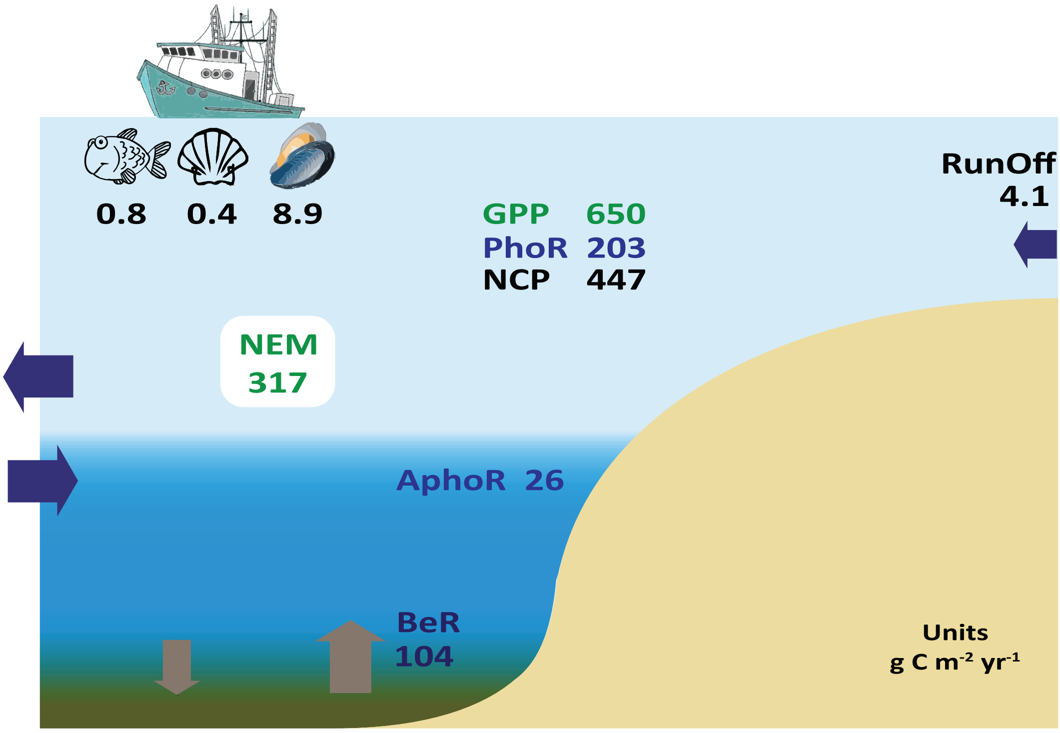


Figure 6. Annual carbon budget for the Ría de Vigo presented as a summary of mean annual carbon fluxes. Rates in g C m^{-2} yr^{-1}. Upper left corner represents the carbon extraction rate from wild catch fisheries, shellfishing and mussel harvest, respectively (see Table 1). NEM: net ecosystem metabolism. GPP: gross primary production. PhoR: photic respiration. NCP: net community production. AphoR: aphotic respiration. BeR: benthic respiration. Runoff: inputs from continental runoff obtained from Evans et al. (2011).

only about 1.3 % of the NEM, of which 2.8 g C m^{-2} yr^{-1} derived from sewage treatment plants (Evans et al. 2011). If dissolved organic carbon (DOC) is also considered from fluvial discharges, the input of continental runoff will reach 2.3% (Gago et al. 2005). Carbon extracted from mussel harvest (8.9 g C m^{-2} yr^{-1}) represented 89 % of the total annual harvest in the Ría de Vigo, followed by wild catch of fishes (0.8 g C m^{-2} yr^{-1}) and shellfishing (0.4 g C m^{-2} yr^{-1}). The result means that mussel may uptake approx. 2% of the NCP generated annually at the Ría de Vigo. Figueiras et al. (2002) already estimated that 12 % of the NCP was incorporated by mussel at the Ría de Arousa. Although the Ría de Arousa has a surface 1.3 times higher than in the Ría de Vigo, this percentage of NCP taken up by mussels does not differ substantially between both Rías if it is taken into account that the number of mussel rafts in the Ría de Arousa is 5 times higher than in the Ría de Vigo (Labarta 1999). Total harvest in the Ría de Vigo extracted 10 g C m^{-2} yr^{-1} from the Ría (Table 1), which comprised 3 % of the NEM. Kemp et al. (1997) obtained a carbon loss rate from fish wild catches in Chesapeake Bay very similar (8 g C m^{-2} yr^{-1}), but in this case it represented larger proportion of the NEM (17%). When analyzing the contribution of seafood harvest in terms of primary production required (PPR) to sustain these mussel culture and fisheries activities, this low 3% value shifts to a larger share of PPR. For doing this, it has to be taken into account that the energy transfer efficiency between trophic levels is ± 10 % and estimate PPR following Pauly & Christensen (1995):

$$PPR = C_i \times 10^{(TLi-1)}$$

C_i: Organic carbon from each species harvested

TL_i: Trophic Level of each species harvested

Mussel harvest at the Ría de Vigo requires approx. 20 % of the annual NCP, wild catch of fishes 17 % and shellfishing 0.8 % (Table 1). Total mussel culture and fishing requires 38 % of the NCP, surpassing the value of 25.1 % for upwelling areas and the 8.3 % for coastal/reef systems, obtained by Pauly & Christensen (1995).

If the PPR from fisheries and mussel culture harvest (168 g C m^{-2} yr^{-1}) is extracted to the NEM, the organic carbon produced *in situ* at the Ría de Vigo and available for export to the adjacent shelf or to be buried in the sediment is 149 g C m^{-2} yr^{-1}, which is approx. 1/4 of the GPP. This proportion is higher during spring and summer, when export/advection of organic material to the adjacent shelf is favoured by means of outwelling events and be an important food for the shelf benthic communities (López-Jamar et al. 1992).

Overall, this first assessment of the NEM of the Ría evidences the strong autotrophic state of this ecosystem. However, there are still important uncertainties that must be resolved to accurately evaluate the trophic state and complete the carbon budget in the Ría. The FLUVBE station was located in the central axis of the Ría, an area covered by muddy sediment, which is the most abundant sediment type in the Ría de Vigo (Vilas et al. 2005). Moreover, the Ría de Vigo is a coastal upwelling driven system which acts as an extension of the continental shelf and channels the 3D variability of the adjacent ocean into a 2D-circulation along the Ría main channel which, in last term, modulates the hydrodynamic and biogeochemical responses (Figueiras et al. 2002). Taking into account both circumstances, our study site can be considered representative of the subtidal regime in the Ría, though it has to be recognized that there are different specific benthic habitats in the Ría (López-Jamar & Cal 1990, Rodil et al. 2009, Casal et al. 2013) mainly driven by sea surface sediment type (Vilas et al. 2005). As a future remark, it has been shown that changes in atmospheric pressure fields and associated wind patterns may decrease the intensity of upwelling-induced ecosystem production along many coastal systems (Barth et al. 2007). For the NW Iberian coastal upwelling system, several studies demonstrated an interannual weakening of northerly winds (Pardo et al. 2011, Barton et al. 2013) which leads to a decrease in the occurrence and intensity of the upwelling of cold and nutrient-rich subsurface waters into the Rías. If continuing this trend, the potential upwelled waters entering into the Rías will be warmer and not so nutrient rich. These warmer temperatures will favour benthic fluxes but on the other hand a decrease on primary production is expected, ending up in less autotrophy of this coastal upwelling system.

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References

Alonso-Pérez F, Castro CG (2014) Benthic oxygen and nutrient fluxes in a coastal upwelling system (Ria de Vigo, NW Iberian Peninsula): seasonal trends and regulating factors. Mar Ecol Prog Ser 511:17–32

Álvarez-Salgado XA, Castro CG, Pérez FF, Fraga F (1997) Nutrient mineralization patterns in shelf waters of the Western Iberian upwelling. Cont Shelf Res 17:1247–1270

Álvarez-Salgado XA, Doval MD, Borges AV, Joint I, Frankignoulle M, Woodward EMS, Figueiras FG (2001) Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian Upwelling System. Prog Oceanogr 51:321–337

Álvarez-Salgado XA, Gago J, Míguez BM, Gilcoto M, Pérez FF (2000) Surface Waters of the NW Iberian Margin: Upwelling on the Shelf versus Outwelling of Upwelled Waters from the Rías Baixas. Estuar Coast Shelf Sci 51:821–837

Álvarez-Salgado XA, Rosón G, Pérez FF, Figueiras FG, Ríos AF (1996) Nitrogen cycling in an estuarine upwelling system, the Ría de Arousa (NW Spain). II. Spatial differences in the short-time-scale evolution of fluxes and net budgets. Mar Ecol Prog Ser 135:275–288

Arbones B, Castro CG, Alonso-Pérez F, Figueiras FG (2008) Phytoplankton size structure and water column metabolic balance in a coastal upwelling system: the Ría de Vigo, NW Iberia. Aquat Microb Ecol 50:169–179

Bakun A (1973) Coastal upwelling indices, west coast of North America, 1946-71. US Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, WA

Barth JA, Menge BA, Lubchenco J, Chan F, Bane JM, Kirincich AR, McManus MA, Nielsen KJ, Pierce SD, Washburn L (2007) Delayed upwelling alters nearshore coastal ocean ecosystems in the northern California current. Proc Natl Acad Sci 104:3719–3724

Barton ED, Field DB, Roy C (2013) Canary current upwelling: More or less? Prog Oceanogr 116:167–178

Berelson WM, Heggie D, Longmore A, Kilgore T, Nicholson G, Skyring G (1998) Benthic Nutrient Recycling in Port Phillip Bay, Australia. Estuar Coast Shelf Sci 46:917–934

Bode A, Varela M, Barquero S, Ossorio-Álvarez MT, González N (1998) Preliminary Studies on the Export of Organic Matter During Phytoplankton Blooms off La Coruña (Northwestern Spain). J Mar Biol Assoc U K 78:1–15

Caffrey J, Cloern J, Grenz C (1998) Changes in production and respiration during a spring phytoplankton bloom in San Francisco Bay, California, USA: implications for net ecosystem metabolism. Mar Ecol Prog Ser 172:1–12

Carpenter SR, Armbrust EV, Arzberger PW, Chapin FS, Elser JJ, Hackett EJ, Ives AR, Kareiva PM, Leibold MA, Lundberg P, Mangel M, Merchant N, Murdoch WW, Palmer MA, Peters DPC, Pickett STA, Smith KK, Wall DH, Zimmerman AS (2009) Accelerate Synthesis in Ecology and Environmental Sciences. BioScience 59:699–701

Casal G, Kutser T, Domínguez-Gómez JA, Sánchez-Carnero N, Freire J (2013) Assessment of the hyperspectral sensor CASI-2 for macroalgal discrimination on the Ría de Vigo coast (NW Spain) using field spectroscopy and modelled spectral libraries. Cont Shelf Res 55:129–140

Cermeño P, Marañón E, Pérez V, Serret P, Fernández E, Castro CG (2006) Phytoplankton size structure and primary production in a highly dynamic coastal ecosystem (Ría de Vigo, NW-Spain): Seasonal and short-time scale variability. Estuar Coast Shelf Sci 67:251–266

Clayton TD, Byrne RH (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Res Part Oceanogr Res Pap 40:2115–2129

Dale AW, Prego R (2002) Physico-biogeochemical controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system. Mar Ecol Prog Ser 235:15–28

Dollar SJ, Smith SV, Vink SM, Obrebski S, Hollibaugh JT (1991) Annual cycle of benthic nutrient fluxes in Tomales Bay, California, and contribution of the benthos to total ecosystem metabolism. Mar Ecol Prog Ser 79:115–125

Evans G, Prego R, Marshall JE (2011) Organic matter in ria sediments: Relevance of terrestial sources and temporal variations in rates of accumulation. Estuar Coast Shelf Sci 94:246–254

Eyre BD, McKee J (2002) Carbon, nitrogen and phosphorous budgets for a shallow subtropical coastal embayment (Moreton Bay, Australia). Limnol Oceanogr 47:1043–1055

Ferguson AJP, Eyre BD (2010) Carbon and Nitrogen Cycling in a Shallow Productive Sub-Tropical Coastal Embayment (Western Moreton Bay, Australia): The Importance of Pelagic–Benthic Coupling. Ecosystems 13:1127–1144

Ferrón S, Alonso-Pérez F, Castro CG, Ortega T, Pérez FF, Ríos AF, Gómez-Parra A, Forja JM (2008) Hydrodynamic characterization and performance of an autonomous benthic chamber for use in coastal systems. Limnol Oceanogr Methods 6:558–571

Figueiras FG, Labarta U, Reiriz MJF (2002) Coastal upwelling, primary production and mussel growth in the Rías Baixas of Galicia. Hydrobiologia 484:121–131

Forja JM, Ortega T, DelValls TA, Gómez-Parra A (2004) Benthic fluxes of inorganic carbon in shallow coastal ecosystems of the Iberian Peninsula. Mar Chem 85:141–156

Fraga F (1981) Upwelling off the Galician Coast, Northwest Spain. In: Richards FA (ed) Coastal Upwelling. American Geophysical Union, Washington D.C., p 176–182

Fraga F, Ríos AF, Pérez FF, Figueiras FG (1998) Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and mineralisation of organic matter in the sea. Sci Mar 62:161–168

Gago J, Álvarez-Salgado XA, Nieto-Cid M, Brea S, Piedracoba S (2005) Continental inputs of C, N, P and Si species to the Ría de Vigo (NW Spain). Estuar Coast Shelf Sci 65:74–82

Gilcoto M, Álvarez-Salgado XA, Pérez FF (2001) Computing optimum estuarine residual fluxes with a multiparameter inverse method (OERFIM): Application to the Ria de Vigo (NW Spain). J Geophys Res Oceans 106:31303–31318

Hidy GM (1972) A View of Recent Air-Sea Interaction Research. Bull Am Meteorol Soc 53:1083–1102

Hillebrand H, Dürselen C-D, Kirschtel D, Pollingher U, Zohary T (1999) Biovolume Calculation for Pelagic and Benthic Microalgae. J Phycol 35:403–424

Hobbie JE (2000) Estuarine Science: A Synthetic Approach to Research and Practice. Island Press

Hopkinson CS, Giblin AE, Tucker J, Garritt RH (1999) Benthic metabolism and nutrient cycling along an estuarine salinity gradient. Estuaries 22:863–881

Hopkinson CS, Smith EM (2005) Estuarine respiration: an overview of benthic, pelagic, and whole system respiration. In: Williams PJL (ed) Respiration in aquatic ecosystems. Oxford University Press, Oxford, New York, p 122–146

Houde ED, Rutherford ES (1993) Recent trends in estuarine fisheries: Predictions of fish production and yield. Estuaries 16:161–176

Hyndes GA, Nagelkerken I, McLeod RJ, Connolly RM, Lavery PS, Vanderklift MA (2014) Mechanisms and ecological role of carbon transfer within coastal seascapes. Biol Rev 89:232–254

Kemp WM, Boynton WR (2012) Synthesis in Estuarine and Coastal Ecological Research: What Is It, Why Is It Important, and How Do We Teach It? Estuaries Coasts 35:1–22

Kemp WM, Smith EM, Marvin-DiPasquale M, Boynton WR (1997) Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Mar Ecol Prog Ser 150:229–248

Labarta U (1999) La acuicultura en Galicia. A economía Galega. Instituto de desarrollo de Galicia. Universidade de Santiago-Fundación Caixa Galicia, Santiago de Compostela

López-Jamar E, Cal R (1990) El sistema bentónico de la Ría de Vigo: macroinfauna y microbiologia de los sedimentos. Boletin Inst Esp Oceanogr 6:49–60

López-Jamar E, Cal RM, González G, Hanson RB, Rey J, Santiago G, Tenore KR (1992) Upwelling and outwelling effects on the benthic regime of the continental shelf off Galicia, NW Spain. J Mar Res 50:465–488

Lueker TJ, Dickson AG, Keeling CD (2000) Ocean pCO_2 dissolved inorganic carbon, alkalinity and equations for K1 and K2 validation based on laboratory measurements of CO_2 in gas and seawater equilibrium. Mar Chem 70:105–119

Moncoiffé G, Álvarez-Salgado XA, Figueiras FG, Savidge G (2000) Seasonal and short-time-scale dynamics of microplankton community production and respiration in an inshore upwelling system. Mar Ecol Prog Ser 196:111–126

Odum HT (1956) Primary production in flowing waters. Limnol Oceanogr 1:102–117

Olli K, Wexels Riser C, Wassmann P, Ratkova T, Arashkevich E, Pasternak A (2001) Vertical flux of biogenic matter during a Lagrangian study off the NW Spanish continental margin. Prog Oceanogr 51:443–466

Pardo P, Padín X, Gilcoto M, Farina-Busto L, Pérez F (2011) Evolution of upwelling systems coupled to the long-term variability in sea surface temperature and Ekman transport. Clim Res 48:231–246

Pauly D, Christensen V (1995) Primary production required to sustain global fisheries. Nature 374:255–257

Pérez FF, Fraga F (1987) A precise and rapid analytical procedure for alkalinity determination. Mar Chem 21:169–182

Piedracoba S, Nieto-Cid M, Teixeira IG, Garrido JL, Álvarez-Salgado XA, Róson G, Castro CG, Pérez FF (2008) Physical-biological coupling in the coastal upwelling system of the Ría de Vigo (NW Spain). II: In vitro approach. Mar Ecol Prog Ser 353:41–53

Prego R (1993) Biogeochemical Pathways of Phosphate in a Galician Ria (North-western Iberian Peninsula). Estuar Coast Shelf Sci 37:437–451

Prego R (1994) Nitrogen interchanges generated by biogeochemical processes in a Galician Ria. Mar Chem 45:167–176

Putt M, Stoecker DK (1989) An experimentally determined carbon: volume ratio for marine oligotrichous ciliates from estuarine and coastal waters. Limnol Oceanogr 34:1097–1103

Rhoten D, O'Connor E, Hackett EJ (2009) The Act of Collaborative Creation and the Art of Integrative Creativity: Originality, Disciplinarity and Interdisciplinarity. Thesis Elev 96:83–108

Ríos AF, Nombela MÁ, Pérez FF, Rosón G, Fraga F (1992) Calculation of runoff to an estuary. Ria de Vigo. Sci Mar 56:29–33

Rodil IF, Lastra M, López J (2009) Spatial variability of benthic macrofauna in the Ria of Vigo (NW Spain): Effect of sediment type and food availability. Mar Biol Res 5:572–584

Rosón G, Álvarez-Salgado XA, Pérez FF (1999) Carbon cycling in a large coastal embayment, affected by wind-driven upwelling: short-time-scale variability and spatial differences. Mar Ecol Prog Ser 176:215–230

Smith SV, Hollibaugh JT (1993) Coastal metabolism and the oceanic organic carbon balance. Rev Geophys 31:75–89

Smith SV, Hollibaugh JT (1997) Annual cycle and interannual variability of ecosystem metabolism in a temperate climate embayment. Ecol Monogr 67:509–533

Staehr PA, Testa JM, Kemp WM, Cole JJ, Sand-Jensen K, Smith SV (2012) The metabolism of aquatic ecosystems: history, applications, and future challenges. Aquat Sci 74:15–29

Strathmann RR (1967) Estimating the Organic Carbon Content of Phytoplankton from Cell Volume or Plasma Volume. Limnol Oceanogr 12:411–418

Testa JM, Kemp WM, Hopkinson Jr CS, Smith SV (2012) Ecosystem metabolism. In: Day JW, Crump BC, Kemp WM, Yañez-Arancibia A (eds) Estuarine Ecology. John Wiley & Sons, p 381–416

Torres-López S, Álvarez-Salgado XA, Varela RA (2005) Offshore export versus in situ fractionated mineralization: a 1-D model of the fate of the primary production of the Rías Baixas (Galicia, NW Spain). J Mar Syst 54:175–193

Varela M, Prego R, Pazos Y (2004) Vertical biogenic particle flux in a western Galician Ria (NW Iberian Peninsula). Mar Ecol Prog Ser 269:17–32

Verity PG, Robertson CY, Tronzo CR, Andrews MG, Nelson JR, Sieracki ME (1992) Relationships between cell volume and the carbon and nitrogen content of marine photosynthetic nanoplankton. Limnol Oceanogr 37:1434–1446

Vilas F, Bernabeu AM, Méndez G (2005) Sediment distribution pattern in the Rias Baixas (NW Spain): main facies and hydrodynamic dependence. J Mar Syst 54:261–276

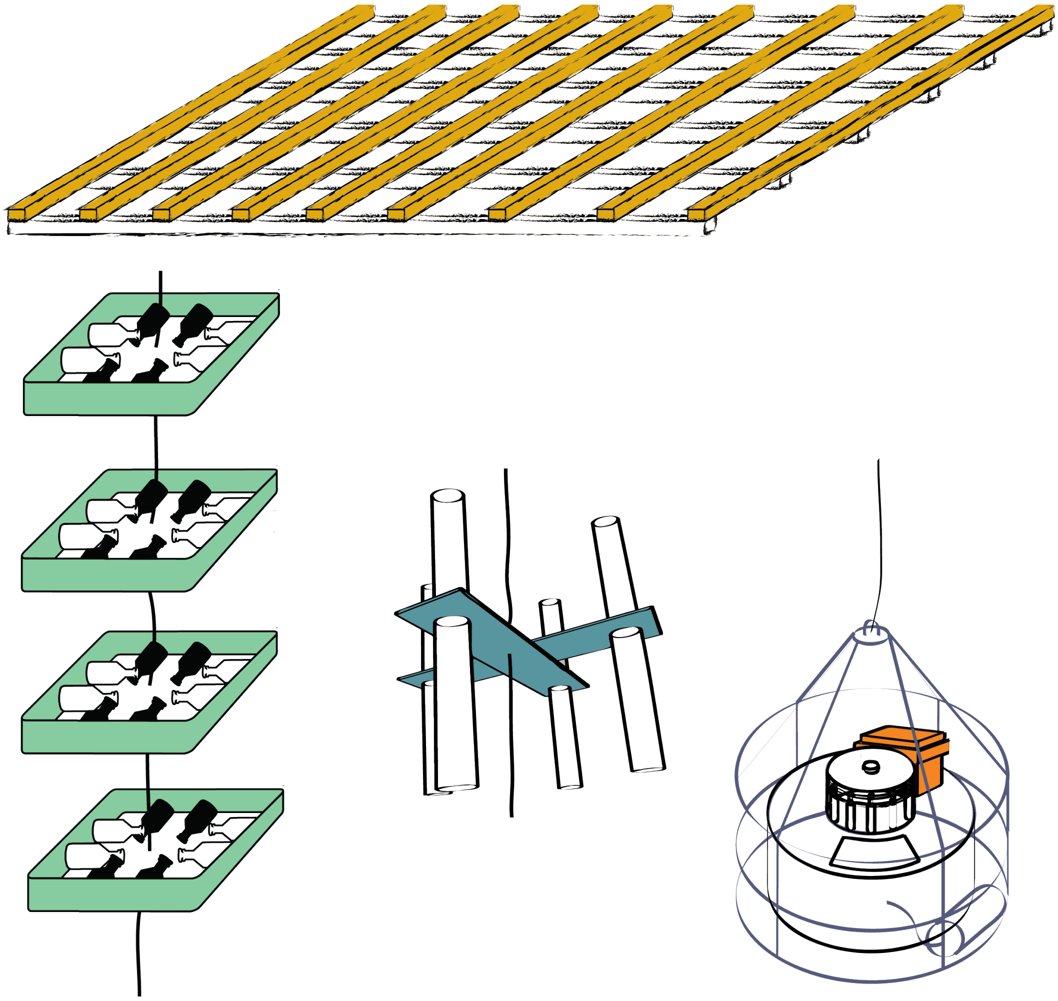
Villacieros-Robineau N, Herrera JL, Castro CG, Piedracoba S, Rosón G (2013) Hydrodynamic characterization of the bottom boundary layer in a coastal upwelling system (Ría de Vigo, NW Spain). Cont Shelf Res 68:67–79

Wollast R (1998) Evaluation and comparisson of the global carbon cycling in the coastal zone and in the open ocean. In: Brink KH, Robinson AR (eds) The Sea, Brink, K.H. Wiley & Sons, New York, p 213–252

Zeldis JR (2004) New and remineralised nutrient supply and ecosystem metabolism on the northeastern New Zealand continental shelf. Cont Shelf Res 24:563–581

Zúñiga D, Alonso-Pérez F, Castro CG, Arbones B, Figueiras FG (2011) Seasonal contribution of living phytoplankton carbon to vertical fluxes in a coastal upwelling system (Ría de Vigo, NW Spain). Cont Shelf Res 31:414–424

EFFECTS OF SUSPENDED MUSSEL CULTURE ON BENTHIC-PELAGIC COUPLING IN A COASTAL UPWELLING SYSTEM (RÍA DE VIGO, NW IBERIAN PENINSULA)



Capítulo V

Alonso-Pérez, F., Ysebaert, T. Castro, C.G. 2010. Effects of suspended mussel culture on benthic-pelagic coupling in a coastal upwelling system (Ría de Vigo, NW Iberian Peninsula). *Journal of Experimental Marine Biology and Ecology* 382, 96-107.

Abstract

The influence of suspended mussel culture on the benthic-pelagic coupling was evaluated in the Ría de Vigo, in the coastal upwelling system of the NW Iberian Peninsula, during the month of July 2004. Measurements of water column properties were carried out at three stations in the Ría de Vigo: under a mussel raft (1), and at two reference sites in the main channel (2) and in the inner part (3) of the Ría. Dissolved nutrients, dissolved oxygen and inorganic carbon benthic fluxes were measured by means of a benthic chamber at stations (1) and (3). Sediment traps were deployed at 6 locations to estimate vertical fluxes. The water column structure at the three study stations was very similar, characterized by upwelling conditions during the second week of July and a posterior stratification showing a strong thermocline, with a depth fluctuation mainly modulated by the shelf wind regime. Vertical particulate organic carbon (POC) fluxes underneath the mussel raft (3.2 g C m^{-2} d^{-1}) were 3 times higher than those obtained between rafts and 10 times higher than in the main channel reference site. Dissolved oxygen, ammonium, silicate and phosphate benthic fluxes were significantly higher under the raft than at the inner Ría reference site. A 1D carbon budget showed the importance of benthic metabolism under the raft (2.7 ± 0.6 g C m^{-2} d^{-1}), being higher than the organic carbon produced at the photic layer (1.3 ± 0.7 g C m^{-2} d^{-1}), as a result of higher organic loading compared to the inner Ría reference site. The results show for the first time the important role that suspended mussel cultures play in the benthic-pelagic coupling in this coastal upwelling ecosystem.

Resumen

Este trabajo estudió la influencia del cultivo de mejillón en suspensión sobre el acoplamiento pelágico-bentónico en la Ría de Vigo, la cual forma parte del sistema de afloramiento costero del NO de la península Ibérica, durante el mes de Julio de 2004. Se realizaron medidas de las propiedades de la columna de agua en tres estaciones posiciones en la Ría de Vigo: bajo una batea de mejillón (1), y en dos estaciones de referencia localizadas en el canal principal (2) y en la parte más interna de la ría (3). Se midieron los flujos bentónicos de nutrientes, oxígeno y carbono inorgánico disueltos por medio de una cámara bentónica en las estaciones (1) y (3). Para la estimación de flujos verticales se utilizaron trampas de sedimento en 6 posiciones en la ría. La estructura de la columna de agua en las estaciones (1 - 3) fue muy similar, caracterizada por condiciones de afloramiento durante la segunda semana de Julio y una posterior estratificación en la que se observó una fuerte termoclina, cuya profundidad fluctuó principalmente modulada por el régimen de viento. Los flujos verticales de carbono orgánico particulado (POC) bajo la batea de mejillón (3.2 g C m^{-2} d^{-1}) fueron 3 veces mayores que los flujos obtenidos entre bateas y 10 veces superiores a los obtenidos en la estación de referencia del canal central. Los flujos bentónicos de oxígeno disuelto, amonio, silicato y fosfato fueron significativamente superiores a los obtenidos en la estación de referencia en la parte interna de la Ría. Mediante un balance 1D de carbono se observó la importancia del metabolismo bentónico bajo la batea (2.7 ± 0.6 g C m^{-2} d^{-1}), siendo muy superior al carbono orgánico producido en la capa fótica (1.3 ± 0.7 g C m^{-2} d^{-1}), como resultado de una mayor descarga de materia orgánica en la batea. Estos resultados muestran por primera vez el papel importante que tiene el cultivo de mejillón en el acoplamiento pelágico-bentónico en este sistema de afloramiento costero.

1. Introduction

Intensive studies of shallow coastal ecosystems have in recent decades shown the complexity of the couplings between biogeochemical processes in the benthos and water column (Giordani et al. 2002, Trimmer et al. 2003, Lund-Hansen et al. 2004). Pelagic production in these systems may be stimulated by continental inputs (Kemp & Boynton 1984), nutrient regeneration at the sediment-water interface (Nixon 1981, Herbert 1999, Gibbs et al. 2005) and in coastal upwelling systems by nutrient enrichment from upwelled offshore waters (Wooster et al. 1976, Fraga 1981). The coupling between the benthic and pelagic realms works in both directions: sediment nutrient fluxes fuel primary production into the water column (Nixon et al. 1976) and cycles of production in the water column provide pulsed inputs of labile organic substrate for regeneration in the sediments (Hatcher et al. 1994). Thus, benthic-pelagic coupling appears to be a key feature in coastal ecosystems (Grenz et al. 2000) where the benthic system generally plays an important role in coastal nutrient regeneration (Balzer et al. 1983).

The appearance of an intensive bivalve culture, which introduces a large biomass of filter-feeders, may alter the biogeochemistry on the system. Dense bivalve populations may exert a strong “top-down” control on suspended particulate matter (including phytoplankton, detritus, auto- and heterotrophic picoplankton and microzooplankton) in coastal systems through their huge capacity to clear particles from the surrounding waters (Dame 1996). Contemporary studies to the present one in the Ría de Vigo, working on a single mussel raft scale, observed depletion of phytoplankton (Petersen et al. 2008) and zooplankton (Maar et al. 2008) resulted from the feeding activity of cultured mussels and associated epifaunal community. This feeding activity results in the packing of organic and inorganic material in their faeces and pseudofaeces (biodeposits) that rapidly settle to the seabed (Kautsky & Evans 1987).

Bivalve faeces and pseudofaeces are characterised by large bioavailability to microbial assemblages and by rapid degradation rates (Grenz et al. 1990). Biodeposition leads to an increase in microbial activity and an enhancement of nutrient regeneration at the sediment-water interface under the mussel rafts. Benthic remineralization processes will vary depending on suspension filter feeder population and the rate of mixing of oxygenated water down to the sediment surface. As a result, different chemical processes like denitrification (Kaspar et al. 1985) or sulphate reduction (Hatcher et al. 1994) may occur at the sediment-water interface under mussel cultures. In short, suspended mussel culture activities divert primary production and energy flow from planktonic food webs by producing faeces and pseudofaeces, and cause strong changes in the physical and chemical characteristics of the sediments, playing a key role in the benthic-pelagic coupling of the ecosystem.

Studies on the effects of mussel culture within the water system have been mainly focussed on its capability for increasing organic matter deposition to the sediment (Dahlbäck & Gunnarsson 1981, Hatcher et al. 1994, Hartstein & Stevens 2005) and enhancing the rate of nutrient recycling at the sediment-water interface (Dahlbäck & Gunnarsson 1981, Nizzoli et al. 2005). Few investigations exist reporting its influence on the water column inorganic and organic suspended matter (Souchu et al. 2001, La Rosa et al. 2002, Nizzoli et al. 2005) and the number of studies targeting the three processes simultaneously is even less. In the present work, we have performed direct measurements in order to examine the impacts of suspended mussel cultures on the biogeochemistry of the water column, water-sediment interface, and vertical fluxes of biogenic particles and finally, evaluate its effect on the benthic-pelagic coupling. Furthermore, most of the studies on the effects of mussel farming have been carried out in low energy tide-dominated areas (Hatcher et al. 1994, Christensen et al. 2003, Nizzoli et al. 2006, Giles et al. 2006). The present work represents the first study on the effects of mussel culture in a highly dynamic coastal upwelling system.

The NW Iberian coast is characterized by upwelling northerly winds from March to September. The rest of the year, winds are predominantly from the south and south-west, favouring the predominance of downwelling conditions. The extension and intensity of the seasonal upwelling and downwelling favourable periods varies strongly from year to year. One of the main features of this region is the Galician Rías Baixas, four large (> 2.5 km^3) and V-shaped coastal inlets. They are openly connected with the adjacent shelf and the interaction between coastal upwelling and the circulation patterns in the Rías Baixas promotes a massive response of phytoplankton productivity inside the Rías (~1.4 g C m^{-2} d^{-1} during upwelling season; Figueiras et al. 2002). This high primary production enables the culture of *Mytilus galloprovincialis* Lamark in the Rías, supporting the highest mussel production in Europe. Mussels are the major herbivore harvesting bursts of pelagic primary production associated with intermittent upwelling (Tenore et al. 1982). Nowadays, the number of suspended mussel rafts in the Rías Baixas is 3237, with an estimated annual mussel production per raft of 75×10^3 kg $raft^{-1}$ yr^{-1}, rendering a total estimated production 250×10^6 kg yr^{-1} of edible mussels, which represents enough biomass to have clear impact on the Rías as an entire ecosystem (Figueiras et al. 2002). Mussel production gives employment to 9000 people directly and 20000 indirectly, and hence it is an activity of great socio-economic importance for the region (Labarta et al. 2004).

Several studies of the Rías Baixas have reported that the organic load under the rafts area seems to be high enough to cause important effects on the sedimentary environment (Tenore et al. 1982, Macias et al. 1991, García-Gil 2003, Otero et al. 2006) and over the benthic community structure (López-Jamar 1978, Tenore et al. 1982, Ysebaert et al. 2009). However, very few studies report rates of biogenic vertical fluxes (Cabanas et al. 1980, Tenore et al. 1982) and none of them investigate the role played by the mussel culture on the benthic-pelagic coupling of the ecosystem.

In this context, the aim of this work was to study the impact of suspended mussel culture on the benthic-pelagic coupling in the Ría de Vigo by means of direct measurements of water column properties, biogenic sinking material and benthic fluxes. Even though the Galician Rías Baixas are the most important mussel farming producer of Europe, none study of these characteristics have been carried out in this system. This study was carried out in July 2004, in the framework of the EU-funded MaBenE project, which aimed to develop fully coupled ecological models for ecosystems dominated by filter feeders to optimise shellfish production in terms of yield as well as nature conservation.

2. Material and methods

2.1 Study site

The study site is located in the Ría de Vigo, one of the four Rías Baixas of the NW Iberian Peninsula (Fig. 1). The circulation in the Ría de Vigo follows a two-layered residual

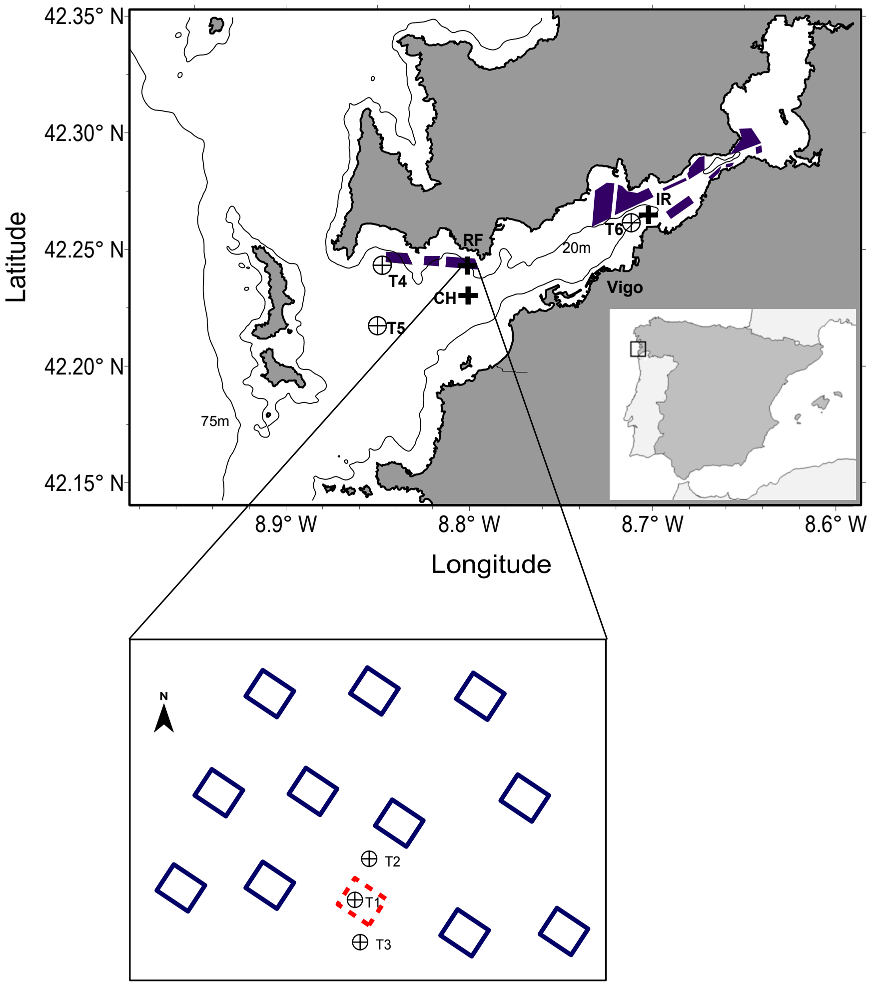


Figure 1. Map of the Ría de Vigo showing the location of the raft polygons, the 3 sampling stations (RF: Raft, CH: Channel and IR: Inner Ría), and the positions used for trap deployments T4, T5 and T6. Below, zoom in nearby the experimental raft (dotted square) showing the locations T1, T2 and T3 used for trap deployments.

circulation pattern, positive under upwelling (Prego & Fraga 1992) and negative under downwelling conditions (Piedracoba et al. 2005). Under upwelling conditions, nutrient-rich subsurface Eastern North Atlantic Central Waters (ENACW) enters the Rías by positive estuarine circulation. Conversely, downwelling conditions cause the slowdown or even reversal of the positive circulation pattern, with the inflow of nutrient-poor surface oceanic waters. A total of 478 mussel rafts are located inside the Ría de Vigo, occupying ~ 5 % of its surface. Nowadays, rafts are 500 m^2 with an average of 500 hanging ropes 12 m long each. In the Ría de Vigo rafts are organized in several polygons differing in size (DOGA 30/10/1989). Most of the rafts occur in the inner part of the Ría, but three polygons are located in its outer part (Fig. 1). The experimental raft for this study was situated in the outer part, located at the southeastern part of a polygon with a total of 68 rafts that were arranged in five parallel rows (100 m apart).

2.2 Water column characterization

During the MaBenE cruise (19th July to 29th July), daily water column observations were carried out on board R/V Mytilus at three stations in the Ría de Vigo: (1) the Raft station (RF), with the vessel attached to the experimental raft, (2) the Channel station (CH), in the main channel away from the mussel rafts and (3) the Inner ría station (IR), situated in the inner part of the Ría de Vigo (Fig. 1).

At each station, vertical profiles of temperature, salinity, photosynthetic active radiation (PAR), transmittance (Sea Tech, 25 cm wavelength) and fluorescence were obtained with a Seabird CTD probe with a Seatech fluorometer. Besides, at the IR station, in order to have a continuous recording of water temperature profile, an array with 8 thermistors, at 0.5, 2, 5, 8, 11, 14, 17.5 and 20 m of water depth, was deployed since July 6th till July 30th.

Bottle casts (rosette sampler with 10-L PVC Niskin bottles) were made to obtain water samples for dissolved oxygen, dissolved nutrients, chlorophyll *a* (chl *a*) and phaeopigments (phaeo), suspended particulate matter concentrations (SPM), particulate organic carbon and nitrogen concentrations (POC and PON, respectively). Dissolved oxygen was determined by Winkler potentiometric titration. The estimated analytical error was ±1 µM. Nutrient samples were determined by segmented flow analysis with Alpkem autoanalyzers following Hansen & Grasshoff (1983) with some improvements (Mouriño & Fraga 1985). The analytical errors were ±0.02 µM for nitrite, ±0.05 µM for nitrate, ammonium and silicate and ±0.01 µM for phosphate. Total dissolved inorganic nitrogen (TIN) is the sum of NO_3–N, NO_2–N and NH_4^+–N. The concentrations of chl *a* and phaeopigments were measured by fluorometry, using acetone extracts after filtration through Whatman GF/F filters. Fluorescence values from the CTD closely followed the chl *a* measurements from the Niskin bottles, obtaining a regression line: Fluorescence = 0.245 (±0.009) chl *a* + 0.26 (±0.06) (r^2 = 0.83, 135 points). This relationship was used to represent the chl *a* profiles in the Results section.

For analysis of SPM, POC and PON, between 2.5 - 5 L were filtered on pre-weighted, pre-combusted (6 h, 550 °C) Whatman GF/F filters. After being rinsed with Milli-Q water to remove the salts, filters were dried at 70°C and stored until analysis. SPM was determined gravimetrically. POC and PON were determined using a Carlo Erba Element Analyzer after Cr_2O_3 and $AgCo_3O_4$ catalysed oxidation and segregation on a Haysep-Q-column.

2.3 Sediment traps

Five Technicap PPS 4/3 sediment traps with 12 collecting cups (250 ml) were positioned at different places in the Ría during three different periods (Fig. 1). These sediment traps have a collecting area of 500 cm^2 and aspect ratio of 6.25. The first deployment started July 20th at 23:00h with a synchronized interval of 3h at station T1, T2, T3 and T4. All traps were placed at a depth of 18 m, which is below the thermocline. The second deployment started 25th July at 04:00h with an interval of 2h. Traps were deployed at T1 (18 m depth), T2 (8 and 18 m) and T5 (8 and 18 m). The third deployment started 28th July at 13:45h with an interval of 1h. Similar positions were used as for the second deployment, but at T1 no trap was placed at 8m depth. No preservation was used in any sediment trap since the deployment duration was very short.

All samples were inspected for swimmers and, when present, were hand-picked and removed (observed in only a few occasions). Samples were manually split into two for pigment and particulate matter analyses respectively. The residue for pigment analysis was filtered onto glass fiber filters (Schleicher & Schuell, No 6) and stored at -80 °C. Pigments were extracted in 90% acetone and analyzed using reversed phase HPLC according to Wiltshire et al. (1998). The residue for particulate matter analysis was filtered onto pre-weighted, pre-combusted Whatman GF/F filters, rinsed with milli-Q water to remove salts, and dried at 70 °C. The carbon and nitrogen isotopic composition of the particulate material was measured using a Carlo Erba Elemental analyzer coupled on line to a Finnigan Delta S isotope ratio mass spectrometer (IRMS). The carbon and nitrogen isotope ratios are expressed in the delta notation $\delta^{13}C$ and $\delta^{15}N$.

Additional vertical particle fluxes were estimated, using a homemade multitrap collector (MC) system. It was composed by 4 PVC trap baffled cylinders of 28 cm^2 collecting area and aspect ratio of 10.76. Sediment traps were deployed at two sites, one situated approx. 15 m from the raft, close to the position T2, and within the raft polygon, the other at the inner ría station (T6, Fig. 1). They were deployed at 18 m depth for a 24 hours period on the 19th, 22nd, 26th and 29th July.

The material collected in the cylinders was filtered under low-vacuum on pre-weighed and pre-combusted (450°C, 4h) 47 mm GF/F filters (0.7 µm pore size) for the analysis of SPM, POC and PON. Filters were dried and frozen (-20 °C) before analysis. A Perkin Elmer 2400 CHN analyser was used for the measurements of POC and PON, using an acetanilide standard daily. The precision of the method is ±0.3 µmol C L^{-1} and ±0.1 µmol N L^{-1}.

Regarding the catchment efficiency for both types of trap, data from current meters mounted at the trap mouth registered water current velocities <12 cm s^{-1} for 90% (de la Granda, pers. comm.) and 100% (Wiles, pers. comm.) of the deployment time at the IR and RF sites respectively. Baker et al. (1988) concluded that for speeds <12 cm s^{-1}, mass flux collected from moored sediment traps was indistinguishable from that collected in drifting traps, which are considered to be free of hydrodynamic biases. Therefore, although some hydrodynamic bias could have influenced the trap catchment efficiency, its influence is negligible for the results presented.

2.4 Benthic fluxes

Fluxes of nutrients (nitrate, nitrite, ammonium, phosphate and silicate), total alkalinity, oxygen and pH at the sediment-water interface were measured *in situ* by means of a benthic chamber (Ferrón et al. 2008), placed by a diver directly on the sediment surface. Four samplings were conducted during the field survey (19th, 22nd, 26th and 29th of July), just close to the experimental raft (26 m depth). Also at the IR station (Fig. 1) similar measurements were performed during the first half of July (6th, 8th, 12th, 15th). These data are used to analyse the spatial variation in benthic fluxes.

Discrete samples were withdrawn from the chamber at prefixed times with a multiple water sampler provided with 12 syringes of 50 ml (KC Denmark). Samples were split for analysis of nutrients, total alkalinity and pH. Total alkalinity was determined by potentiometric titration with HCl to a final pH of 4.4 (Pérez & Fraga 1987) and adapted for small sampling volume of 5 mL. The analytical error was ± 4 µM. The measurements of pH were analysed spectrophotometrically following Clayton & Byrne (1993). Nutrient samples were determined in the same way as described for the water column measurements.

Total CO_2 (TCO_2) was estimated from pH and total alkalinity using the carbonic system equations with the carbonic and boric acid dissociation constants of Lueker et al. (2000). Benthic fluxes were calculated by empirical linear fitting of concentration against time.

2.5 Offshore Ekman transport

As previously described in the introduction, northerly winds provoke the upwelling of subsurface ENACW (Eastern North Atlantic Central Water) in the Rías Baixas and thus regulate the oceanographic conditions in this region. Thus in order to understand the oceanographic conditions, we analyse the intensity of this upwelling based on the upwelling index. The upwelling index was estimated using the component $-Q_x$ of the Ekman transport following Bakun (1973) method:

$$-Q_x = (\rho_{air}\, C_D\, |V|\, V_Y)/(f\, \rho_{sw})$$

where ρ_{air} is the density of air (1.22 kg m^{-3} at 15°C), C_D is an empirical dimensionless drag coefficient (1.4 x 10-3 according to Hidy (1972), f is the Coriolis parameter (9.946 x 10^{-5} at 43°N), ρ_{sw} is the density of seawater (1025 kg m^{-3}) and $|V|$ and V_Y, are the average daily modulus and northerly component of the geostrophic winds centred at 43°N, 11°W, respectively. Average daily geostrophic winds were estimated from surface atmospheric pressure charts. Positive values of $-Q_x$ indicate upwelling and correspond to predominance of northerly winds.

3. Results

3.1 Hydrographic conditions and suspended particulate matter characteristics

The first two weeks of July were mainly characterized by strong northerly winds (avg $-Q_x$ = 476 ± 449 $m^3\ s^{-1}\ Km^{-1}$; Fig. 2a), that provoked the entry of cold (<13.5°C) ENACW from the shelf through the bottom ingoing layer based on the thermistor array data at the IR station (Fig. 2b). During the second half of July, winds reversed and they were mainly blowing from the southwest, with an average $-Q_x$ of 31 ± 217 $m^3\ s^{-1}\ Km^{-1}$. These conditions favoured the surface intrusion of warm water (~19°C) and the development of a strong stratification, deepening the thermocline from 10 m to 20 m depth. However, the weak upwelling event between July 25th and 27th resulted in a re-entry of subsurface ENACW, displacing the thermocline lower limit back to ~10 m depth. Finally, reversal of northerly winds on the adjacent shelf on July 28th had a clear impact on the water column structure, pushing again the thermocline downwards. This temporal evolution of the water column hydrographic conditions was also observed at the RF and CH stations according to the daily CTD profiles (Fig. 3, first row).

The nutrient distributions observed at the RF station were clearly controlled by these hydrographic conditions (Fig. 4). Nutrient levels were low above the thermocline except for nutrient injection to the photic zone during the weak upwelling events (July 19th and 26th).

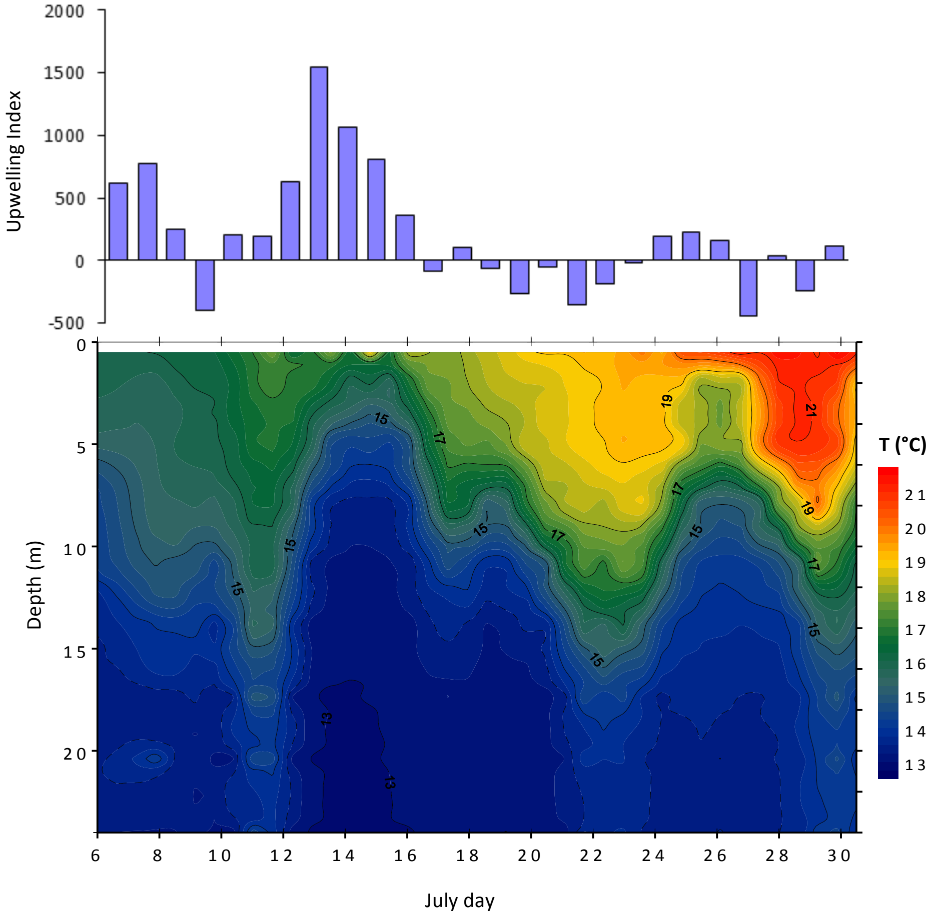


Figure 2. a) Offshore Ekman transport presented as upwelling index (-Q_x: m^3 s^{-1} km^{-1}). b) Time evolution of temperature (°C) derived from thermistor mooring at the inner Ría station.

Below the main thermocline, nutrient concentrations were high due to the presence of nutrient-rich subsurface ENACW and remineralization processes. In fact, for similar TS properties of ENACW on July 19th and 26th, we observed higher nutrient levels, except for ammonium, at the beginning of the cruise due to oxidation of organic matter as the lower oxygen levels on July 19th indicated (distribution not shown). The other two stations (IR and CH stations) responded to a similar pattern based on the nutrient relationships (Table 1). The correlation of nitrate *vs* phosphate for water samples with temperature <14 °C were not significantly different (p>0.05) for the 3 stations with slopes lower than the Redfield ratio. The N:P slope increases to the Redfield value when we consider total inorganic nitrogen (TIN) *vs* phosphate for the RF and CH station. However for the IR station, we have obtained a lower N:P ratio pointing to a faster remineralization of phosphorus *vs* nitrogen. The N:Si slope was similar at the raft and channel stations, considering only TIN and we did not observe any correlation at the IR location.

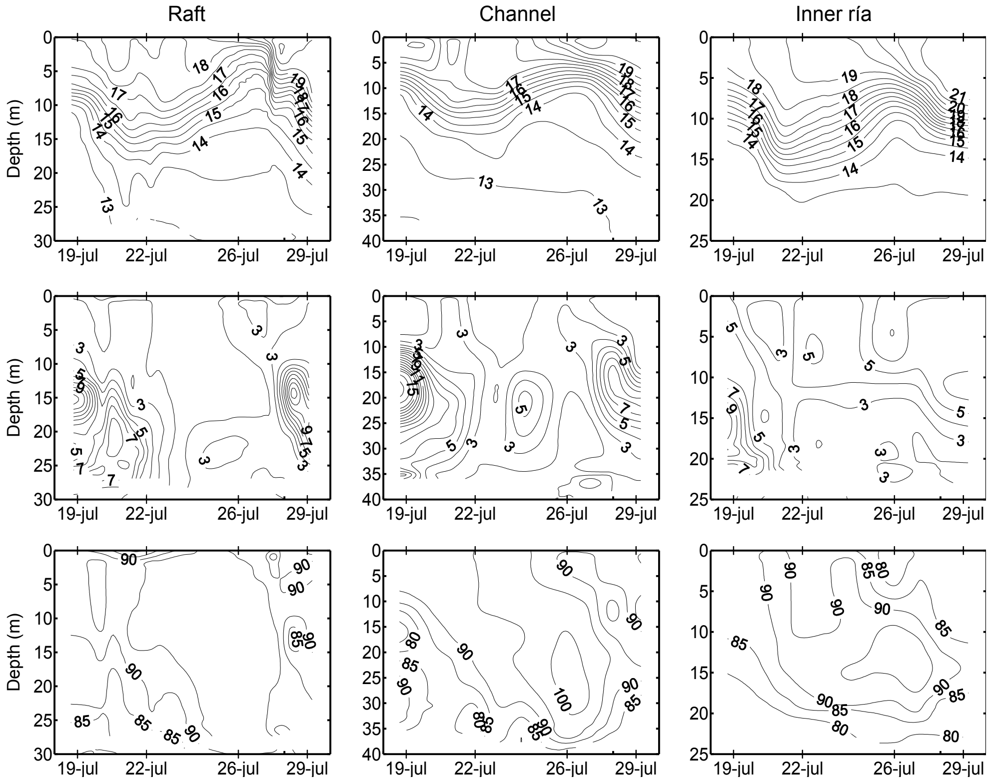


Figure 3. Time evolution of temperature (°C), chl *a* (mg m^{-3}) and transmittance (%) at the raft, channel and inner Ría stations during the MaBenE cruise. Note the different depth scale

The temporal distributions of chl *a* (Fig. 3, second row) for the RF and CH stations were very similar. The highest values were observed at the beginning and end of the survey (> 10 mg m^{-3}), during the periods of spin-down from previous upwelling events. These high values were located from the thermocline to the bottom, with maximum values just below the thermocline. For the IR station, the chl *a* distribution was similar to the other

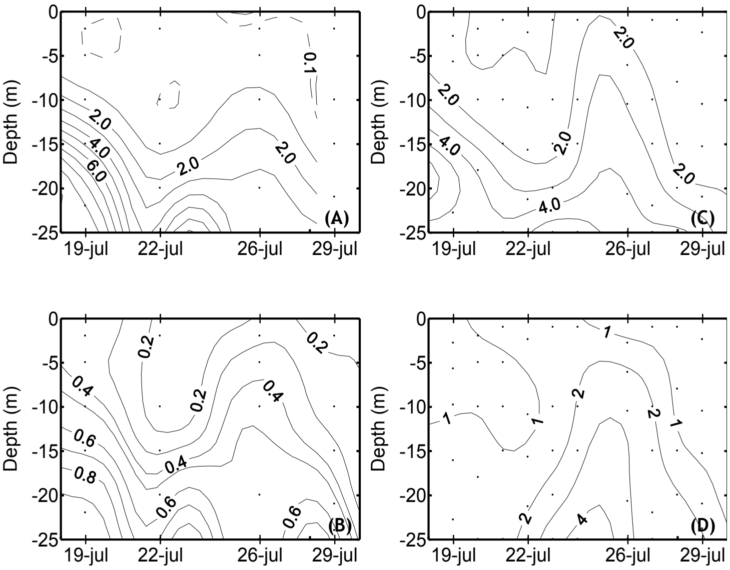


Figure 4. Time evolution of nitrate (A); phosphate (B); silicate (C) and ammonium (D) at the raft station during the MaBenE cruise. Units are µM.

Table 1. Slope, standard error, and determination coefficient of the correlations between nutrients at the 3 study locations. Units are µM.

		Raft	Channel	Inner Ría
NO_3^- *vs* HPO_4^{2-}	slope	14.7 ±2.2	13.3 ±1.9	12.1 ±1.7
	r^2 (n)	0.81 (17)	0.86 (14)	0.95 (7)
TIN *vs* HPO_4^{2-}	slope	16.2 ±2.9	16.1 ±2.4	13.5 ±3.2
	r^2(n)	0.73 (17)	0.87 (13)	0.84 (7)
NO_3^- *vs* $Si(OH)_4$	slope	1.78 ±1.5	1.53 ±1.4	n.s.
	r^2(n)	0.82 (17)	0.72 (14)	
TIN *vs* $Si(OH)_4$	Slope	1.95 ±1.7	1.94 ±1.7	n.s.
	r^2(n)	0.86 (17)	0.90 (13)	

n.s.: not significant

stations, but chl *a* maximum at the end of the survey was less pronounced. The surface chl *a* concentration was usually below 2 mg m^{-3} at the RF station; except for July 26th and 27th with chl *a* concentrations > 2 mg m^{-3}, and these surface values were lower than at the CH and IR stations.

The temporal distributions of transmittance percentage (Fig. 3, last row) mirrored the chl *a* distributions with low values associated with the chl *a* maxima and with higher percentage during the middle of the survey for the three stations.

Total suspended particulate matter concentrations (SPM) were lowest near the surface (1.03 ± 0.26 mg L^{-1}, above the main thermocline) and generally increased with depth in all stations (1.95 ± 0.52 mg L^{-1}, below the main thermocline; Table 2). POC concentrations did not exceed 0.3 mg L^{-1} most of the time and did not show strong gradients with depth. However, we did observe an increasing trend with depth of algal C in relation to non-algal C for the three stations associated with higher chl *a* concentrations below the thermocline. Algal C was calculated as the concentration of chl *a* times 25.2 ± 15.6, which was the average C:chl *a* ratio (g/g) during the campaign period. PON concentrations were significantly correlated with POC concentrations ($r^2 = 0.93$) with an average C:N ratio of 6.8 (close to the Redfield ratio). Based on these data, we did not observe significant differences in the quantity and quality of suspended particulate matter among the three study stations though the quality of the suspended matter was different above and below of the thermocline.

Table 2. Averaged values (±SD) of the quality and quantity of particulate matter above and below the main thermocline. SPM: suspended particulate matter; POC: particulate organic carbon; PON: particulate organic nitrogen; chl *a*: chlorophyll *a*.

Station	**SPM**	**POC**	**PON**	**C:N**	**Chl *a***	**δ13C**	**δ15N**	**Non Algal C/Algal C**
Unit	mg L^{-1}	mg L^{-1}	mg L^{-1}		mg m^{-3}	‰	‰	
RF_Above	1.01 ± 0.25	0.19 ± 0.05	0.03 ± 0.01	6.68	2.16 ± 2.43	-19.87 ± 0.66	6.34 ± 0.99	5.02 ± 3.18
RF_Below	1.87 ± 0.60	0.28 ± 0.15	0.05 ± 0.01	7.02	5.00 ± 3.76	-18.75 ± 0.69	5.17 ± 0.95	2.21 ± 2.80
RF_Total	1.24 ± 0.53	0.22 ± 0.10	0.04 ± 0.01	6.77	2.92 ± 3.05	-19.60 ± 0.82	6.06 ± 1.09	4.25 ± 3.29
CH_Above	1.04 ± 0.30	0.25 ± 0.07	0.04 ± 0.01	6.81	2.98 ± 2.95	-20.12 ± 0.67	6.28 ± 0.61	4.03 ± 2.47
CH_Below	1.88 ± 0.48	0.28 ± 0.15	0.05 ± 0.03	6.84	5.73 ± 5.94	-19.35 ± 1.08	5.70 ± 1.80	1.78 ± 1.30
CH_Total	1.44 ± 0.58	0.26 ± 0.11	0.04 ± 0.02	6.82	4.29 ± 4.71	-19.75 ± 0.95	6.01 ± 1.31	2.96 ± 2.26
IR_Above	1.12 ± 0.20	0.26 ± 0.07	0.04 ± 0.01	6.95	4.20 ± 1.49	-20.09 ± 0.51	7.61 ± 1.29	1.84 ± 1.62
IR_Below	2.16 ± 0.49	0.27 ± 0.06	0.05 ± 0.01	6.47	4.90 ± 2.80	-19.24 ± 0.58	5.46 ± 0.47	1.82 ± 1.33
IR_Total	1.69 ± 0.66	0.27 ± 0.05	0.05 ± 0.01	6.71	4.55 ± 2.17	-19.67 ± 0.69	6.54 ± 1.47	1.83 ± 1.41
Above_Total	1.03 ± 0.26	0.21 ± 0.06	0.04 ± 0.01	6.72	2.71 ± 2.56	-19.97 ± 0.65	6.43 ± 0.87	4.22 ± 3.00
Below_Total	1.95 ± 0.52	0.28 ± 0.13	0.05 ± 0.02	6.81	5.28 ± 4.47	-19.14 ± 0.87	5.48 ± 1.29	1.93 ± 1.86

3.2 Vertical fluxes

The rates of sedimentation of particulate matter differed substantially between stations (Table 3). The highest values were observed directly under the raft (T1), with average values ranging from 25 to 37 g DW m^{-2} d^{-1}, and the multitrap collector value (31 g DW m^{-2} d^{-1}) within this range. The high-resolution temporal variability observed underneath the raft with the Technicap sediment traps showed a large variation. This was probably partly caused by the fact that visual inspection of the filters showed, besides mussel faecal pellets, sometimes drop-off material from the raft, such as small mussel shell fragments and fragments of green macroalgae. In between and in the vicinity of the rafts, the collected DW was 5-11 g m^{-2} d^{-1}, being a factor 3 to 5 smaller than directly underneath the raft. The CH station, (see Fig. 1, T5) showed much lower values, in the order of 2 g DW m^{-2} d^{-1}. A large difference was observed between the traps deployed at 18 meters and 8 meters, with much lower values in the traps at 8 meters, especially at T5. POC concentrations were on average highly correlated with total DW (r^2: 0.91), representing about 10 % of the total DW (Table 3). Underneath the raft average POC rates varied between 2.2 and 3.9 g C m^{-2} d^{-1}. At T2 and T3 trap stations POC was trapped at a rate of 0.9 ± 0.2 g C m^{-2} d^{-1}. Much lower POC fluxes were observed in the CH station, especially at 8 meters. Similar trends were observed for PON, showing significant correlation with POC (r^2=0.99). Also chl *a* was correlated with POC (r^2=0.58). At T5, chl *a* was very low or even zero at two occasions (Table 3). The average C:N ratio for the settled material under the raft was 7.6; 7.7 for the traps located between rafts and 7.0 at T5.

The values of $\delta^{13}C$ of the settled material under the raft and in the vicinity of the rafts were similar (Table 3), whereas the $\delta^{13}C$ values at T5 were more negative during two occasions. This variation in isotopic values for $\delta^{13}C$ was related to the variation in the algal proportion of the POC in relation to non-algal POC. Higher non-algal proportions in the POC resulted in significantly more negative isotopic values for $\delta^{13}C$ (r^2=0.92 for the sediment traps at 18m).

Table 3. Integrated values of daily flux rates of settling particles for each station and each measuring period. SPM: suspended particulate matter; POC: particulate organic carbon; PON: particulate organic nitrogen; chl *a*: chlorophyll *a*. See Fig 1., for station locations.

Station	**Depth**	**Date**	**SPM**	**POC**	**PON**	**C:N**	**δ13C**	**δ15N**	**Chl a**
Unit	m		g m^{-2} d^{-1}	g m^{-2} d^{-1}	g m^{-2} d^{-1}		‰	‰	mg m^{-2} d^{-1}
Raft T1 (MC*)	18	14-jul-04	31.4 ± 0.3	3.76 ± 0.2	0.50 ± 0.1	8.77			29.38 ± 7.03
Raft T1	18	22-jul-04	25.5 ± 2.1	2.18 ± 0.24	0.36 ± 0.04	7.06	-19.59 ± 0.25	5.86 ± 0.23	5.22 ± 1.52
Raft T1	18	26-jul-04	25.2 ± 4.1	2.92 ± 0.46	0.41 ± 0.07	8.31	-19.36 ± 0.19	5.29 ± 0.17	12.27 ± 2.57
Raft T1	18	28-jul-04	37.2 ± 4.3	3.58 ± 0.62	0.54 ± 0.07	7.73	-19.47 ± 0.32	6.44 ± 0.16	6.81 ± 2.30
Between rafts (MC)	18	19-jul-04	16.5 ± 4.1	1.52 ± 0.58	0.22 ± 0.07	8.23			13.55 ± 4.54
Between rafts (MC)	18	22-jul-04	9.2 ± 1.3	1.11 ± 0.17	0.18 ± 0.02	7.33			2.67 ± 0.81
Between rafts (MC)	18	26-jul-04	14.5 ± 6.5	0.85 ± 0.07	0.13 ± 0.01	7.37			4.94 ± 0.54
Between rafts (MC)	18	29-jul-04	17.8 ± 0.1	1.10 ± 0.05	0.17 ± 0.02	7.65			10.28 ± 0.48
Between rafts T4	18	22-jul-04	11.0 ± 3.0	1.05 ± 0.22	0.18 ± 0.03	6.81	-19.67 ± 0.12	5.94 ± 0.21	3.78 ± 0.90
Between rafts T3	18	22-jul-04	5.3 ± 0.3	0.81 ± 0.05	0.12 ± 0.02	7.88	-19.87 ± 0.07	6.50 ± 0.39	1.98 ± 0.35
Between rafts T2	18	22-jul-04	7.4 ± 13.4	0.99 ± 0.15	0.15 ± 0.02	7.70	-19.73 ± 0.06	6.15 ± 0.15	2.17 ± 0.40
Between rafts T2	18	26-jul-04	5.8 ± 1.1	0.91 ± 0.17	0.15 ± 0.03	7.08	-19.05 ± 0.09	5.39 ± 0.08	4.34 ± 0.55
Between rafts T2	18	28-jul-04	6.2 ± 0.7	0.70 ± 0.07	0.11 ± 0.01	7.42	-19.52 ± 0.26	5.58 ± 0.20	1.76 ± 0.36
Between rafts T2	8	26-jul-04	1.7 ± 0.1	0.29 ± 0.03	0.055 ± 0.008	6.15	-19.47 ± 0.19	6.71 ± 0.24	0.15 ± 0.02
Between rafts T2	8	28-jul-04	3.1 ± 0.1	0.31 ± 0.04	0.068 ± 0.007	5.32	-20.52 ± 0.13	5.95 ± 0.16	0.48 ± 0.10
Channel T5	18	26-jul-04	1.8 ± 0.1	0.38 ± 0.05	0.064 ± 0.01	6.93	-19.03 ± 0.21	5.79 ± 0.14	0
Channel T5	18	28-jul-04	2.3 ± 0.2	0.17 ± 0.01	0.028 ± 0.004	7.08	-21.79 ± 0.36	4.83 ± 0.22	0.13 ± 0.01
Channel T5	8	26-jul-04	1.0 ± 0.07	0.05 ± 0.002	0.002 ± 0.0008	29.17	-24.55 ± 0.13	3.14 ± 0.45	0

* MC: Multitrap collector

3.3 Benthic fluxes

Figure 5 displays a comparison on the magnitude of the benthic fluxes of oxygen, total CO_2 (TCO_2) and nutrients between the RF station and the IR station. It clearly shows that

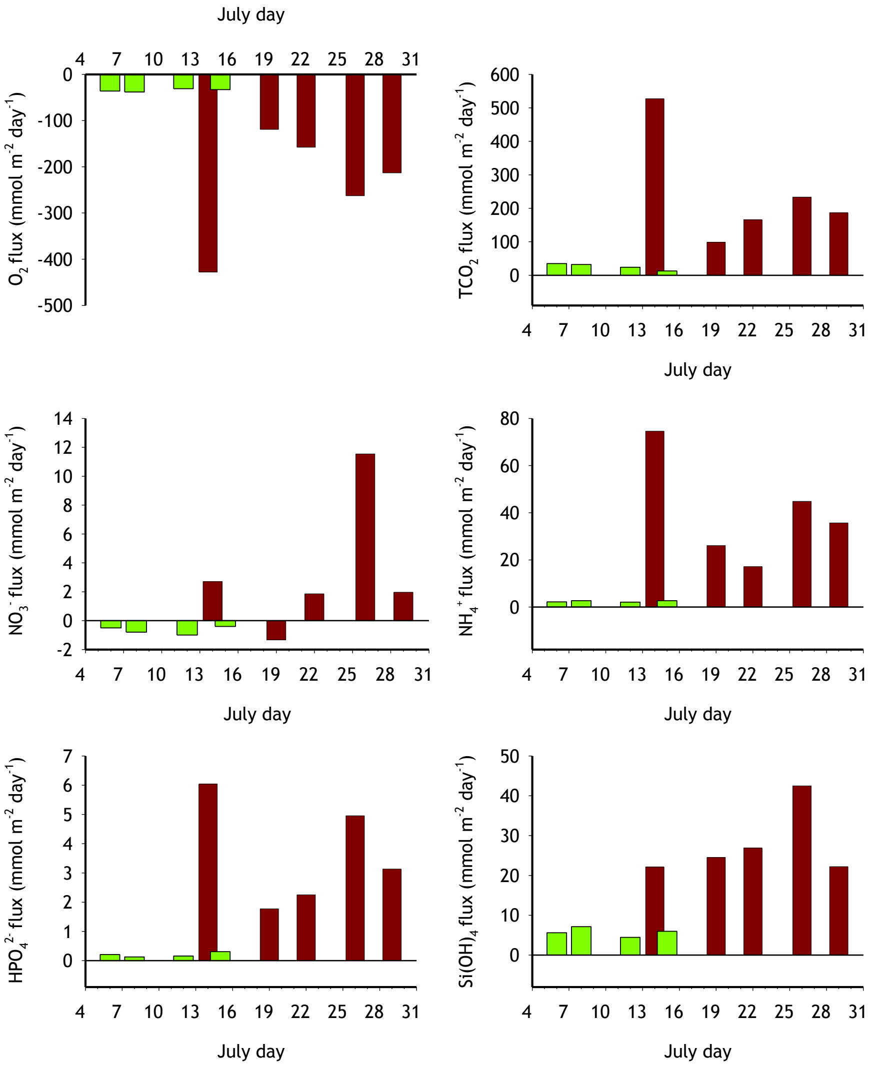


Figure 5. Bar plots showing a comparison of the oxygen, TCO_2, and nutrient benthic fluxes between the raft station (red bars) and the inner Ría station (green bars) during the sampling period.

sediment-water fluxes were significantly higher ($p<0.01$) under the raft than at the IR station. Benthic fluxes at the RF station, rates obtained for July 14th were significantly higher than for the rest of the sampling days; but even if we do not consider this day, fluxes under the RF station are still significantly higher. Besides, benthic fluxes under the raft showed much more variability than at the IR station, based on the corresponded standard deviations (Table 4).

Dissolved oxygen uptake by the sediments was on average 7 times higher under the raft, obtaining its maximum on July 14th (-428 mmol O_2 m^{-2} d^{-1}). Regarding nitrate benthic fluxes, it seems that there is a net release of nitrate from the sediment to the water column under the raft, though with a high daily variability; whereas, nitrate benthic fluxes at the IR station were consistently negative in all cases and showed much less variability, which could be the result of denitrification processes. Ammonium was the main N-containing nutrient released from the sediment. Benthic NH_4^+ fluxes were on average 39.7 ± 19.8 mmol m^{-2} d^{-1} under the raft, being 17 times higher than at the IR station. Phosphate fluxes showed a proportional difference between sites similar to the ammonium fluxes ratio (18-fold increase under the raft), obtaining average fluxes of 3.6 ± 1.6 mmol m^{-2} d^{-1} and 0.20 ± 0.1 mmol m^{-2} d^{-1} for the RF and IR station, respectively. Silicate was released to the water column in a higher amount under the raft (5 times higher), but the difference between sites was not as high as for ammonium and phosphate.

Alkalinity fluxes (Alk Corr) were corrected for the influence of ammonium and nitrate fluxes by adding the fluxes of NO_3^- and subtracting the NH_4^+ fluxes (Table 4). Assuming that calculated TCO_2 fluxes account for organic carbon remineralization and net dissolution of $CaCO_3$, we can establish an upper limit of the amount of carbon oxidized (Max Cox) as the calculated TCO_2. As Ca^{+2} fluxes were not measured, an estimate of the maximum dissolution of $CaCO_3$ was calculated as ½ Alk Corr fluxes following Berelson et al. (1998). Consequently,

Table 4. Summary of benthic fluxes at the RF and IR stations. BRQ: benthic respiration quotient. Units are in mmol m^{-2} d^{-1}. S.D.: standard deviation.

	Oxygen	**Nitrate**	**Ammonium**	**Phosphate**	**Silicate**	**Alk Corr***	**Max Ca Dis***	**Min Cox***	**TCO_2 Max Cox**	**Cox (Avge)**	**BRQ**
Raft stn											
14-Jul-04	-428 ± 7.2	2.7 ± 2.1	75 ± 6	6.0 ± 0.8	22 ± 6	650 ± 62	325 ± 31	535 ± 69	859 ± 61	697	1.6
19-Jul-04	-119 ± 0.6	-1.3 ± 0.2	26 ± 2	1.8 ± 0.1	25 ± 1	120 ± 9	60 ± 5	108 ± 9	168 ± 8	138	1.2
22-Jul-04	-158 ± 0.5	1.9 ± 0.7	17 ± 2	2.3 ± 0.3	27 ± 1	238 ± 34	119 ± 17	169 ± 35	288 ± 31	229	1.4
26-Jul-04	-263 ± 0.5	11.5 ± 1.4	45 ± 5	5.0 ± 0.8	43 ± 3	203 ± 31	101 ± 16	235 ± 39	337 ± 36	286	1.1
29-Jul-04	-213 ± 0.9	2.0 ± 0.4	36 ± 1	3.1 ± 0.3	22 ± 2	158 ± 23	79 ±12	189 ± 32	268 ± 30	229	1.1
AVERAGE	**-236**	**3.3**	**39.7**	**3.6**	**27.6**	**180**	**90**	**175**	**384**	**316**	**1.2**
S.D.	***107***	***4.3***	***19.8***	***1.6***	***7.6***	***52***	***26***	***53***	***273***	***220***	***0.2***
Inner Ría stn											
6-Jul-04	-36.2 ± 0.0	-0.5 ± 0.1	2.2 ± 0.5	0.21 ± 0.03	5.6 ± 0.4	32 ± 13	16 ± 7	27 ± 13	43 ± 12	35	1.0
8-Jul-04	-38.1 ± 0.1	-0.8 ± 0.1	2.7 ± 0.1	0.13 ± 0.02	7.1 ± 0.6	11 ± 9	6 ± 5	29 ± 9	35 ± 8	32	0.8
12-Jul-04	-30.9 ± 0.0	-1.0 ± 0.1	2.1 ± 0.2	0.16 ± 0.02	4.5 ± 0.4	-2 ± 3	-1 ± 2	25 ± 6	24 ± 5	24	0.8
15-Jul-04	-33.1 ± 0.0	-0.4 ± 0.1	2.7 ± 0.1	0.31 ± 0.02	6.0 ± 0.4	-2 ± 7	-1 ± 3	13 ± 9	13 ± 8	13	0.4
AVERAGE	**-35**	**-0.7**	**2.4**	**0.20**	**5.8**	**10**	**5**	**23**	**28**	**26**	**0.7**
S.D.	***2.8***	***0.3***	***0.3***	***0.1***	***1.1***	***16***	***8***	***7***	***13***	***10***	***0.2***

* Uncertainties are based on the propagation of random errors from measured benthic fluxes.

the lower limit of the carbon oxidation (Min Cox) was obtained subtracting maximum $CaCO_3$ dissolution rates from measured TCO_2 fluxes. Based on this assumptions, averaged carbon oxidation rates are significantly higher ($p>0.01$) under the raft than at the IR station. The benthic respiration quotient (BRQ), calculated as the ratio between the averaged Cox and the oxygen flux, was higher (1.2 ± 0.2) under the raft than at the IR station (0.7 ± 0.2).

4. Discussion and conclusions

4.1 Water column

Studies of the role of suspension filter feeders on the nutrient cycling of coastal systems have been principally focused on benthic regeneration of the biodeposits (Dahlbäck & Gunnarsson 1981, Hatcher et al. 1994, Nizzoli et al. 2005). However, direct release of nutrients in the water column from filter feeders and their epibiota can also be an important pathway of nutrient cycling (Souchu et al. 2001, Nizzoli et al. 2006, Richard et al. 2007). In fact, these last two studies have reported a contribution of mussel lines (*vs* benthic fluxes) to the total oxygen and nutrient fluxes greater than 30% in semi-enclosed lagoons.

In our case, we did not observe significant differences in dissolved inorganic nutrients and suspended particulate matter quality and quantity between the raft site and the other two study sites. We only detect a lower N:P ratio at the IR station, probably due to a faster remineralization of phosphorous over nitrogen at this location as the low N:P ratios of the benthic fluxes also suggest (Table 1). The fact that we did not detect any significant alteration of the water column biogeochemistry associated to mussel farming can result from the system dynamics. The previously reported shellfish culture areas were semi-enclosed lagoons, physically forced by tides. In contrast, the Ría de Vigo is an upwelling driven system characterized by shorter water residence time, between 14 and 7 days for the upwelling season (Álvarez-Salgado et al. 2000). Consequently, the rapid water renewal inside the Ría seems to dilute the possible effect of nutrient release from the mussel ropes.

4.2 Vertical fluxes

In this study, we have observed significant spatial variations between vertical fluxes of POC, with the highest values under the raft (average 3.2 g C m^{-2} d^{-1}). Rates of sedimented POC were 3 times higher than the vertical fluxes obtained between the rafts (0.9 g C m^{-2} d^{-1}) and 10 times higher than in the reference site (0.3 g C m^{-2} d^{-1}), supporting the hypothesis that suspended mussel farming increases sedimentation rates of SPM and organic matter (Hatcher et al. 1994, Stenton-Dozey et al. 1999, Hartstein & Rowden 2004, Callier et al. 2006). For the Rías Baixas, Cabanas et al. (1980) presented organic carbon fluxes under a mussel raft (up to 24.6 g C m^{-2} d^{-1}), much higher than our results and the values reported by Tenore et al. (1982) (up to 2.4 g C m^{-2} d^{-1}). The large difference between the vertical fluxes measured in this work and data from Cabanas et al. (1980) might be related with a different mussel growth state when the measurements were carried out. Organic carbon fluxes at the CH station are at the low range of values obtained in the Ría de Pontevedra (0.5-1.8 g C m^{-2} d^{-1}; Varela et al. 2004) and a coastal site off A Coruña (0.3-1.2 g C m^{-2} d^{-1}; Bode et al. 1998).

Sediment traps may have been influenced by resuspension processes as they were deployed 5 meters above sea-bottom at the RF and IR station which would provoke overestimation on the results obtained. However, from the transmittance profile (Fig. 3, third row) it can be observed that this variable does not decrease abruptly near the sea-bottom as expected when re-suspension occurs. On the contrary, transmittance is well correlated with chl *a* (r^2=0.5) which may indicate that lower values of transmittance are the result of higher phytoplankton biomass -just below the thermocline- and not due to the presence of material resuspended from the seabed. Furthermore, on a year sediment trap sampling at IR site, (Zúñiga et al. 2011) found that only during the winter period we observe the presence of some benthic phytoplankton species (*Paralia sulcata*). Therefore, although resuspension may occur, based on these results we believe that this process was not significantly important during the sampling period.

Regarding the quality of the sinking material, results showed no significant differences between the RF site and the CH reference site in terms of C:N ratio and isotope $\delta^{13}C$

(-19.7 ‰ and -20.4 ‰, respectively) and $\delta^{15}N$ (6.0 ‰ and 5.3 ‰, respectively). Also, Non-algalC: AlgalC ratio appeared to be significantly lower (9.83 ± 4.55) at the RF site than in the CH station (50.9) which points to a major vertical flux of material derived from phytoplankton under the raft. These data are supported by findings from Zúñiga et al. (2011), where the phaeo/chl *a* ratio in sediment traps appeared to be higher, though not statistically significant (p=0.13), under the raft (4.6 ± 3.2 S.D.) than at the IR station (1.4 ± 0.6 S.D.). The high phaeo/chl *a* ratio obtained under the raft may be the result of mussel grazing on the phytoplankton, a process on which chlorophyll is degraded to phaeopigments (Dahlbäck & Gunnarsson 1981), promoting a high sedimentation of algal decay products (Kautsky & Evans 1987). Jordan & Valiela (1982) proposed that half of the particulate nitrogen and carbon consumed by mussels is expelled as faeces; therefore it seems that mussel grazing does not alter significantly the C:N over the material processed but it may degrade chlorophyll to phaeopigments. This fact may indicate that chlorophyll collected under the raft was more degraded than at the IR station, as low values of phaeo/chl *a* reflect phytoplankton not highly degraded (Varela et al. 2004). Jordan & Valiela (1982) obtained 10 times higher deposition of phaeo than chl *a* under mussel culture. The lower C:N molar ratio at the IR station (6.9) than under the raft (8.1) also reflects a higher degraded phytoplankton sinking under the raft.

Comparison of the quality of suspended particulate matter and sediment trap material showed no difference on the C:N ratio between these two partitions for the RF and CH stations. However, the contribution of non-algal carbon was higher on the trap material than on suspended particulate matter as it could be expected taking into account that the algal carbon is more labile and thus easier to degrade.

4.3 Benthic fluxes

Even though the Rías Baixas are the most important shellfish farming area of Europe, the present manuscript shows for the first time its impact on the benthic fluxes and consequently on the sediment biogeochemistry. The high sedimentation under the suspended mussel raft provoked an intense accumulation of organic carbon and consequently intense benthic recycling processes.

Several authors observed a positive correlation between sea-bottom temperature and benthic oxygen fluxes (Klump & Martens 1989, Hatcher et al. 1994, Nicholson & Longmore 1999). In our case, we observed benthic oxygen fluxes ranged from - 119 to -428 mmol m^{-2} day^{-1} and from -30.9 to -38.1 mmol m^{-2} day^{-1} for the RF and IR stations respectively and however sea-bottom temperatures were very similar at both stations (RF and IR, 13.16 ± 0.21 °C) in July 2004. For the raft area, unexpected maximum benthic fluxes were registered during the peak of upwelling event (oxygen flux: -428 mmol m^{-2} day^{-1}), when sea-bottom temperature was at the minimum (12.91 °C). We suggest that the entrance of cold subsurface ENACW water through the Ría bottom layer probably favoured resuspension processes at the benthic boundary layer on July 14th, causing significantly higher benthic fluxes for all the variables compared to the following days. As it was expected from previous studies on the effects of mussel suspended culture on benthic oxygen fluxes (Baudinet et al. 1990, Hatcher et al. 1994, Christensen et al. 2003), oxygen uptake from the raft sediments was higher than on the reference site (IR). Benthic oxygen fluxes obtained under the raft were higher than most studies on mussel culture (Hatcher et al. 1994, Stenton-Dozey et al. 2001, Giles & Pilditch 2006) and of the same order of magnitude than those obtained by Nizzoli et al. (2005) and by Richard et al. (2007) in semi-enclosed lagoons of the Mediterranean Sea and Gulf of St Lawrence (Canada) respectively.

As expected, carbon oxidation rates were higher at the RF site (316 ± 220 mmol m^{-2} day^{-1}; Table 4) than at the IR site (26 ± 10 mmol m^{-2} day^{-1}) due to a larger availability of organic matter derived from the higher vertical carbon fluxes under the raft. Although carbon oxidation rates are not commonly reported on studies regarding mussel culture, our results are similar to those obtained by Nizzoli et al. (2006) for Goro Lagoon, where TCO_2 effluxes varied between 415 and 96 mmol m^{-2} day^{-1}. In any case, these benthic carbon oxidation rates under mussel farming are much higher than the average respiration rate (34 mmol m^{-2} day^{-1}) from 48 estuarine systems around the world compiled by Hopkinson & Smith (2005).

Based on these oxygen benthic fluxes and the estimated average carbon oxidized, we obtained the benthic respiration quotient (BRQ), which indicates to what extent the aerobic respiration and re-oxidation of reduced compounds from anaerobic respiration occur simultaneously in the sediment. Under balanced conditions, where all organic matter is either aerobically metabolized and /or all the anaerobic products reoxidized, the BRQ would be in the range of 0.7 to 1.1 (Anderson et al. 1986, Glud 2008). According to this, the higher BRQ obtained at the RF site (1.2 ±0.2) indicates that some of the reduced compounds from anaerobic respiration are not completely oxidized. By contrast, the lower BRQ (0.7 ±0.2) at the IR site may reflect that aerobic respiration is the main mineralization process at this site.

On the other hand, ammonium fluxes also support these two different benthic metabolism pathways at the RF and IR station. The NH_4^+ effluxes under the raft were 17 times higher (39.7 ± 19.8 mmol m^{-2} d^{-1}) than at the IR site (2.4 ± 0.3 mmol m^{-2} d^{-1}), pointing to a dominance of anaerobic processes under the raft. Oxidation of organic matter loading to the raft sediments generates higher benthic dissolved nitrogen fluxes, mainly in the form of NH_4^+ (Hatcher et al. 1994). The flux of ammonium under the raft was in accordance to Nizzoli et al. (2005, 2006) but much higher than most of other reported benthic fluxes (3-20 mmol m^{-2} d^{-1}) associated to mussel culture (Baudinet et al. 1990, Hatcher et al. 1994, Stenton-Dozey et al. 2001, Christensen et al. 2003, Giles et al. 2006) and also than other undisturbed coastal sediments (Nixon 1981, Devol & Christensen 1993, Berelson et al. 2003). As described by (Nizzoli et al. 2006), this situation might be the result of the predominance of sulphate reduction and subsequently oxidation of sulphide, generating more reducing conditions under the raft. In fact, Otero et al. (2006) described the formation of reducing conditions that favour the processes of sulphate reduction and methanogenesis in sediments under a mussel raft in the Rías Baixas. Following Christensen et al. (2003), under these environments characterized by high sulphide levels, nitrification is inhibited and consequently denitrification processes avoided, and the prevailing nitrogen route is dissimilative reduction of nitrate to ammonium (DNRA). Our nitrogen benthic fluxes, dominated by high NH_4^+ effluxes and very low nitrate fluxes, respond to this pattern. In contrast, nitrogen fluxes at the IR station were completely different from the RF station with much lower NH_4^+ fluxes and recurrent negative nitrate fluxes. These fluxes and the observed BRQs seem to point out the prevalence of nitrification – denitrification metabolism route in this site, though further studies are needed to explore this via.

In contrast to the observations obtained by Hatcher et al. (1994) under mussel culture, sediments in the Ría de Vigo act as a source of phosphate to the overlying water, and remineralization of organic phosphorous was much more intense under the mussel raft (3.6 ± 1.6 mmol m^{-2} d^{-1}) than at the IR site (0.20 ± 0.1 mmol m^{-2} d^{-1}). Benthic phosphate fluxes under the raft were higher than those obtained by Giles et al. (2006) and Richard et al. (2007) (max. 0.6 mmol m^{-2} d^{-1} and 1.2 mmol m^{-2} d^{-1}, respectively) and comparable to the highest fluxes (2.7 mmol m^{-2} d^{-1}) obtained in a one year study under mussel culture (Baudinet et al. 1990).

The higher release of silicate to the water column from the sediment at the RF site was probably related to a high content of diatom frustules in the mussel faeces exported from the water column to the sediment. This observation is supported by data from Zúñiga et al. (2011) that obtained much higher vertical fluxes of biogenic silica under the raft (95 mol m^{-2} d^{-1}) than at the IR site (15 mol m^{-2} d^{-1}).

4.4 1D Budget: benthic-pelagic coupling

Based on the benthic and pelagic fluxes presented here, and considering the primary production and pelagic respiration rates obtained by Arbones et al. (2008) from *in situ* 24 h incubations of oxygen collected simultaneously to our data set for the two sites, we have built up a 1D budget for the RF and the IR location (Fig. 6). In order to convert oxygen production and oxygen consumption to carbon units a photosynthetic quotient and an O_2/TCO_2 ratio for pelagic respiration of 1.4 was assumed following Fraga et al. (1998). Net community production (NCP) at the IR station during the first two weeks of July was 3.48 g C m^{-2} d^{-1}, much higher than at the raft station for the second half of July (1.28 g C m^{-2} d^{-1}). The organic carbon collected on the sediment trap at this IR station, represented 32 % of the NCP, a value which is lower than the 75% obtained by Varela et al. (2004) in the Ría de

Pontevedra, but similar to the value of 25-30% presented as the overall range for coastal areas (Berger et al. 1989). Part of this falling material is respired in the water column ~17% (0.19 ± 0.14 g C m^{-2} d^{-1}), and ~28% is oxidized at the water-sediment interface. Thus, at this location, the benthic fluxes represented 9% of the net community production in the upper photic zone. However, the situation is completely different for the RF station. At this position, both the organic carbon settled on the traps (3.16 ± 0.78 g C m^{-2} d^{-1}) and the material oxidized at the sediment-water interface (2.65 ± 0.64 g C m^{-2} d^{-1}) were much higher than the organic carbon produced at the photic zone. Carbon oxidation at the sediment-water interface represented ~84% of the settling material and ~16% is respired in the water column. Considering these 1D budgets, the importance of the benthic metabolism is enhanced at the mussel raft site, in response to the higher organic loading at this site.

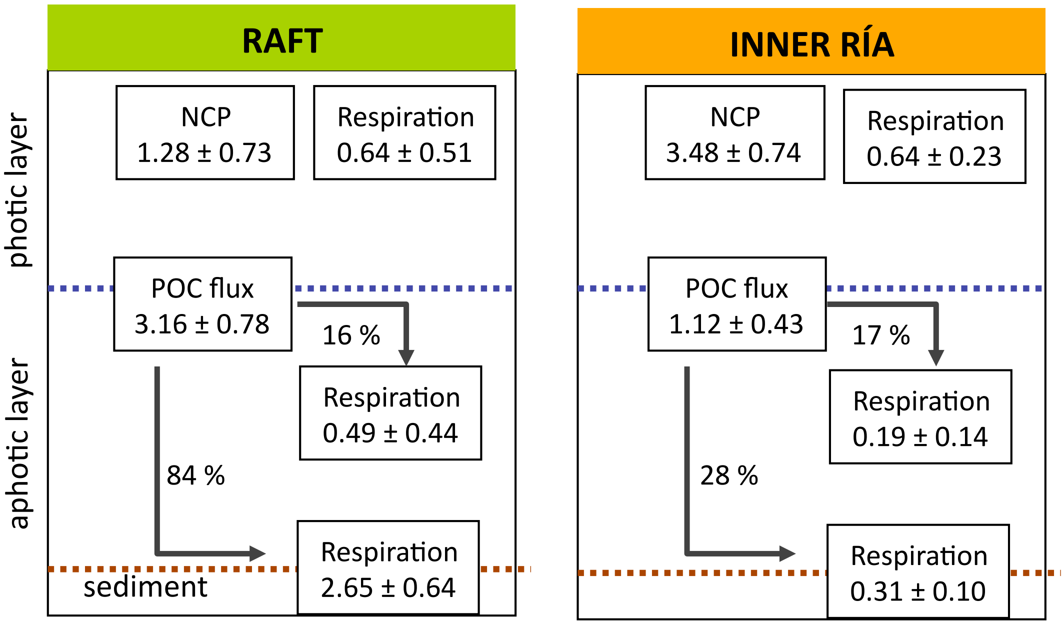


Figure 6. 1D carbon budgets for the raft (RF) and inner Ría (IR) stations. Units are g C m^{-2} d^{-1}. NCP: net community production. NCP and respiration data were obtained from Arbones et al. (2008)

However, it has to be mentioned that vertical and benthic fluxes may be affected by horizontal advection within this area and therefore limit the results shown in the 1D budget.

In summary, our study demonstrates the importance of benthic nutrient regeneration in coastal upwelling systems like the Rías Baixas and shows that mussel cultures can lead to a redistribution of organic material and nutrients. However, seasonal variability of net primary production will have an effect on the mussel harvest and consequently over the vertical and benthic fluxes. The quality and quantity of the mussels' (pseudo) faecal pellets are also dependant on the mussel growth state. Therefore, these aspects must be considered and studied before extrapolating our results to evaluate the impact of mussel farming on ecosystem nutrient dynamics.

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References

Álvarez-Salgado XA, Gago J, Míguez BM, Gilcoto M, Pérez FF (2000) Surface Waters of the NW Iberian Margin: Upwelling on the Shelf versus Outwelling of Upwelled Waters from the Rías Baixas. Estuar Coast Shelf Sci 51:821–837

Anderson LG, Hall POJ, Iverfeldt A, Der Loeff MMR Van, Sundby B, Westerlund SFG (1986) Benthic respiration measured by total carbonate production. Limnol Oceanogr 31:319–329

Arbones B, Castro CG, Alonso-Pérez F, Figueiras FG (2008) Phytoplankton size structure and water column metabolic balance in a coastal upwelling system: the Ría de Vigo, NW Iberia. Aquat Microb Ecol 50:169–179

Baker ET, Milburn HB, Tennant DA (1988) Field assessment of sediment trap efficiency under varying flow conditions. J Mar Res 46:573–592

Bakun A (1973) Coastal upwelling indices, west coast of North America, 1946-71. US Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, WA

Balzer W, Grasshoff K, Dieckmann P, Haardt H, Petersohn U (1983) Redox-turnover at the sediment water interface studied in a large bell jar system. Oceanol Acta 6:337–344

Baudinet D, Alliot E, Berland B, Grenz C, Plante-Cuny M-R, Plante R, Salen-Picard C (1990) Incidence of mussel culture on biogeochemical fluxes at the sediment-water interface. Hydrobiologia 207:187–196

Berelson WM, Heggie D, Longmore A, Kilgore T, Nicholson G, Skyring G (1998) Benthic Nutrient Recycling in Port Phillip Bay, Australia. Estuar Coast Shelf Sci 46:917–934

Berelson W, McManus J, Coale K, Johnson K, Burdige D, Kilgore T, Colodner D, Chavez F, Kudela R, Boucher J (2003) A time series of benthic flux measurements from Monterey Bay, CA. Cont Shelf Res 23:457–481

Berger WH, Smetacek V, Wefer G (1989) Ocean productivity and paleoproductivity - an overview. In: Berger WH, Smetacek V, Wefer G (eds) Productivity of the Oceans: present and past. Wiley & Sons, Berlin, p 1–34

Bode A, Varela M, Barquero S, Ossorio-Alvarez MT, Gonzalez N (1998) Preliminary Studies on the Export of Organic Matter During Phytoplankton Blooms off La Coruña (Northwestern Spain). J Mar Biol Assoc U K 78:1–15

Cabanas JM, González JJ, Mariño J, Pérez Camacho A, Boland G (1980) Estudio del mejillón y de su epifauna asociada en los cultivos flotantes de la Ría de Arosa. III. Observaciones preliminares sobre la retención de partículas y la biodeposición de una batea. Boletin Inst Esp Oceanogr 5:45–50

Callier MD, Weise AM, Mckindsey CW, Desrosiers G (2006) Sedimentation rates in a suspended mussel farm (Great-Entry Lagoon, Canada) : biodeposit production and dispersion. Mar Ecol Prog Ser 322:129–141

Christensen PB, Glud RN, Dalsgaard T, Gillespie P (2003) Impacts of longline mussel farming on oxygen and nitrogen dynamics and biological communities of coastal sediments. Aquaculture 218:567–588

Clayton TD, Byrne RH (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Res Part Oceanogr Res Pap 40:2115–2129

Dahlbäck B, Gunnarsson LÅH (1981) Sedimentation and sulfate reduction under a mussel culture. Mar Biol 63:269–275

Dame RF (1996) Ecology of Marine Bivalves: An Ecosystem Approach. CRC Press, Florida

Devol AH, Christensen JP (1993) Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific. J Mar Res 51:345–372

Ferrón S, Alonso-Pérez F, Castro CG, Ortega T, Pérez FF, Ríos AF, Gómez-Parra A, Forja JM (2008) Hydrodynamic characterization and performance of an autonomous benthic chamber for use in coastal systems. Limnol Oceanogr Methods 6:558–571

Figueiras FG, Labarta U, Reiriz MJF (2002) Coastal upwelling, primary production and mussel growth in the Rías Baixas of Galicia. Hydrobiologia 484:121–131

Fraga F (1981) Upwelling off the Galician Coast, Northwest Spain. In: Richards FA (ed) Coastal Upwelling. American Geophysical Union, Washington D.C., p 176–182

Fraga F, Ríos AF, Pérez FF, Figueiras FG (1998) Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and mineralisation of organic matter in the sea. Sci Mar 62:161–168

García-Gil S (2003) A natural laboratory for shallow gas: the Rías Baixas (NW Spain). Geo-Mar Lett 23:215–229

Gibbs M, Funnell G, Pickmere S, Norkko A, Hewitt J (2005) Benthic nutrient fluxes along an estuarine gradient: influence of the pinnid bivalve *Atrina zelandica* in summer. Mar Ecol Prog Ser 288:151–164

Giles H, Pilditch CA (2006) Effects of mussel (*Perna canaliculus*) biodeposit decomposition on benthic respiration and nutrient fluxes. Mar Biol 150:261–271

Giles H, Pilditch CA, Bell DG (2006) Sedimentation from mussel (*Perna canaliculus*) culture in the Firth of Thames, New Zealand: Impacts on sediment oxygen and nutrient fluxes. Aquaculture 261:125–140

Giordani P, Helder W, Koning E, Miserocchi S, Danovaro R, Malaguti A (2002) Gradients of benthic–pelagic coupling and carbon budgets in the Adriatic and Northern Ionian Sea. J Mar Syst 33–34:365–387

Glud RN (2008) Oxygen dynamics of marine sediments. Mar Biol Res 4:243–289

Grenz C, Cloern JE, Hager SW, Cole BE (2000) Dynamics of nutrient cycling and related benthic nutrient and oxygen fluxes during a spring phytoplankton bloom in South San Francisco Bay (USA). Mar Ecol Prog Ser 197:67–80

Grenz C, Hermin M-N, Baudinet D, Daumas R (1990) *In situ* biochemical and bacterial variation of sediments enriched with mussel biodeposits. Hydrobiologia 207:153–160

Hansen HP, Grasshoff K (1983) Automated chemical analysis. In: Grasshoff K, Enrardt M, Kermling K (eds) Methods of Seawater Analysis. Verlag Chemie, Weinheim, p 347–395

Hartstein ND, Rowden AA (2004) Effect of biodeposits from mussel culture on macroinvertebrate assemblages at sites of different hydrodynamic regime. Mar Environ Res 57:339–357

Hartstein ND, Stevens CL (2005) Deposition beneath long-line mussel farms. Aquac Eng 33:192–213

Hatcher A, Grant J, Schofield B (1994) Effects of suspended mussel culture (*Mytilus* spp.) on sedimentation, benthic respiration and sediment nutrient dynamics in a coastal bay. Mar Ecol Prog Ser 115:219–235

Herbert RA (1999) Nitrogen cycling in coastal marine ecosystems. FEMS Microbiol Rev 23:563–590

Hidy GM (1972) A View of Recent Air-Sea Interaction Research. Bull Am Meteorol Soc 53:1083–1102

Hopkinson CS, Smith EM (2005) Estuarine respiration: an overview of benthic, pelagic, and whole system respiration. In: Williams PJL (ed) Respiration in aquatic ecosystems. Oxford University Press, Oxford, New York, p 122–146

Jordan TE, Valiela I (1982) A nitrogen budget of the ribbed mussel, *Geukensia demissa*, and its significance in nitrogen flow in a New England salt marsh. Limnol Oceanogr 27:75–90

Kaspar HF, Gillespie PA, Boyer IC, MacKenzie AL (1985) Effects of mussel aquaculture on the nitrogen cycle and benthic communities in Kenepuru Sound, Marlborough Sounds, New Zealand. Mar Biol 85:127–136

Kautsky N, Evans S (1987) Role of biodeposition by *Mytilus edulis* in the circulation of matter and nutrients in a Baltic coastal ecosystem. Mar Ecol Prog Ser 38:201–212

Kemp MW, Boynton WR (1984) Spatial and Temporal Coupling of Nutrient Inputs to Estuarine Primary Production: The Role of Particulate Transport and Decomposition. Bull Mar Sci 35:522–535

Klump JV, Martens CS (1989) The seasonality of nutrient regeneration in an organic-rich coastal sediment: Kinetic modeling of changing pore-water nutrient and sulfate distributions. Limnol Oceanogr 34:559–577

Labarta U, Fernández-Reiriz MJ, Pérez-Camacho A, Pérez Corbacho E (2004) Bateeiros, mar, mejillón. Una perspectiva bioeconómica. Fundación Caixa Galicia, Santiago de Compostela

La Rosa T, Mirto S, Favaloro E, Savona B, Sarà G, Danovaro R, Mazzola A (2002) Impact on the water column biogeochemistry of a Mediterranean mussel and fish farm. Water Res 36:713–721

López-Jamar E (1978) Macrobentos infaunal de la Ría de Pontevedra. Boletin Inst Esp Oceanogr 4:113–130

Lueker TJ, Dickson AG, Keeling CD (2000) Ocean pCO_2 dissolved inorganic carbon, alkalinity and equations for K1 and K2 validation based on laboratory measurements of CO_2 in gas and seawater equilibrium. Mar Chem 70:105–119

Lund-Hansen LC, Pejrup M, Floderus S (2004) Pelagic and seabed fluxes of particulate matter and carbon, and C:N ratios resolved by sediment traps during a spring bloom, southwest Kattegat. J Sea Res 52:87–98

Maar M, Nielsen TG, Petersen JK (2008) Depletion of plankton in a raft culture of Mytilus galloprovincialis in Ría de Vigo, NW Spain. II. Zooplankton. Aquat Biol 4:127–141

Macias F, Fernandez de Landa JLA, Calvo de Anta R (1991) Composición química y mineralógica de biodepósitos bajo bateas de mejillón. Datos para la evaluación de su uso como fertilizante y/o enmendante de suelos de Galicia. Thalassas 9:23–29

Mouriño C, Fraga F (1985) Determinación de nitratos en agua de mar. Investig Pesq 49:81–96

Nicholson GJ, Longmore AR (1999) Causes of observed temporal variability of nutrient fluxes from a southern Australian marine embayment. Mar Freshw Res 50:581–588

Nixon SW (1981) Remineralization and Nutrient Cycling in Coastal Marine Ecosystems. In: Neilson BJ, Cronin LE (eds) Estuaries and Nutrients. Humana Press, Clifton, New Jersey, p 111–138

Nixon SW, Oviatt CA, Hale SS (1976) Nitrogen regeneration and the metabolism of coastal marine bottom communities. In: Anderson JM, Macfaden A (eds) The role of Terrestrial and Aquatic Organisms in Decomposition Processes. Blackwell Scientific Publications, London, p 269–283

Nizzoli D, Welsh DT, Bartoli M, Viaroli P (2005) Impacts of mussel (*Mytilus galloprovincialis*) farming on oxygen consumption and nutrient recycling in a eutrophic coastal lagoon. Hydrobiologia 550:183–198

Nizzoli D, Welsh DT, Fano EA, Viaroli P (2006) Impact of clam and mussel farming on benthic metabolism and nitrogen cycling, with emphasis on nitrate reduction pathways. Mar Ecol Prog Ser 315:151–165

Otero XL, Calvo de Anta RM, Macías F (2006) Sulphur partitioning in sediments and biodeposits below mussel rafts in the Ría de Arousa (Galicia, NW Spain). Mar Environ Res 61:305–325

Pérez FF, Fraga F (1987) A precise and rapid analytical procedure for alkalinity determination. Mar Chem 21:169–182

Petersen JK, Nielsen TG, Duren L van, Maar M (2008) Depletion of plankton in a raft culture of Mytilus galloprovincialis in Ría de Vigo, NW Spain. I. Phytoplankton. Aquat Biol 4:113–125

Piedracoba S, Álvarez-Salgado XA, Rosón G, Herrera JL (2005) Short-timescale thermohaline variability and residual circulation in the central segment of the coastal upwelling system of the Ría de Vigo (northwest Spain) during four contrasting periods. J Geophys Res Oceans 110:C03018

Prego R, Fraga F (1992) A simple model to calculate the residual flows in a Spanish ria. Hydrographic consequences in the ria of Vigo. Estuar Coast Shelf Sci 34:603–615

Richard M, Archambault P, Thouzeau G, Desrosiers G, others (2007) Summer influence of 1 and 2 yr old mussel cultures on benthic fluxes in Grande-Entrée lagoon, Îles-de-la-Madeleine (Québec, Canada). Mar Ecol Prog Ser 338:131–143

Souchu P, Vaquer A, Collos Y, Landrein S, Deslous-Paoli J-M, Bibent B (2001) Influence of shellfish farming activities on the biogeochemical composition of the water column in Thau lagoon. Mar Ecol Prog Ser 218:141–152

Stenton-Dozey JME, Jackson LF, Busby AJ (1999) Impact of Mussel Culture on Macrobenthic Community Structure in Saldanha Bay, South Africa. Mar Pollut Bull 39:357–366

Stenton-Dozey J, Probyn T, Busby A (2001) Impact of mussel (*Mytilus galloprovincialis*) raft-culture on benthic macrofauna, in situ oxygen uptake, and nutrient fluxes in Saldanha Bay, South Africa. Can J Fish Aquat Sci 58:1021–1031

Tenore KR, Boyer LF, Cal RM, Corral J, García-Fernández C, González N, González-Gurriaran E, Hanson RB, Iglesias J, Krom M (1982) Coastal upwelling in the Rias Bajas, NW Spain: contrasting the benthic regimes of the Rias de Arosa and de Muros. J Mar Res 40:701–772

Trimmer M, Gowen RJ, Stewart BM (2003) Changes in sediment processes across the western Irish Sea front. Estuar Coast Shelf Sci 56:1011–1019

Varela M, Prego R, Pazos Y (2004) Vertical biogenic particle flux in a western Galician ria (NW Iberian Peninsula). Mar Ecol Prog Ser 269:17–32

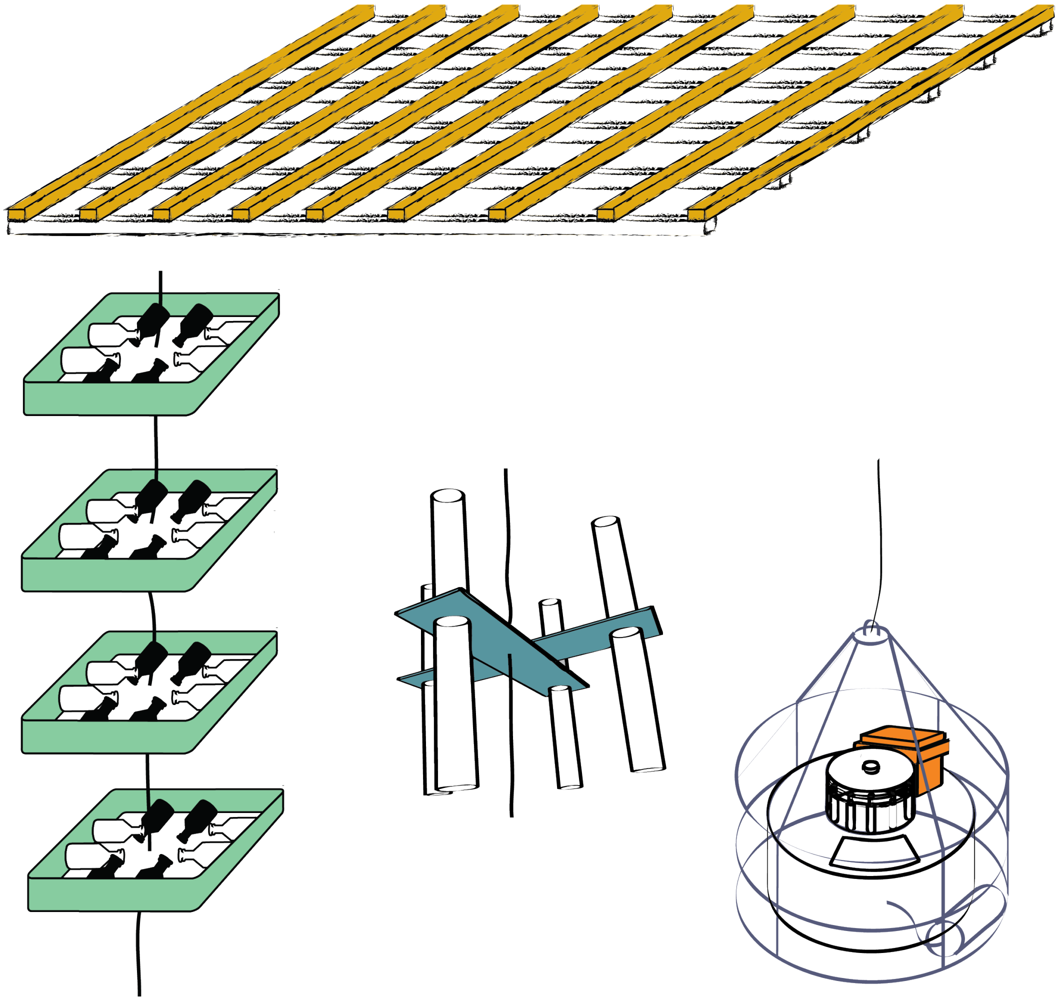
Wiltshire KH, Harsdorf S, Smidt B, Blöcker G, Reuter R, Schroeder F (1998) The determination of algal biomass (as chlorophyll) in suspended matter from the Elbe estuary and the German Bight: A comparison of high-performance liquid chromatography, delayed fluorescence and prompt fluorescence methods. J Exp Mar Biol Ecol 222:113–131

Wooster WS, Bakun A, McLain DR (1976) Seasonal upwelling cycle along eastern boundary of North-Atlantic. J Mar Res 34:131–141

Ysebaert T, Hart M, Herman PMJ (2009) Impacts of bottom and suspended cultures of mussels *Mytilus* spp. on the surrounding sedimentary environment and macrobenthic biodiversity. Helgol Mar Res 63:59–74

Zúñiga D, Alonso-Pérez F, Castro CG, Arbones B, Figueiras FG (2011) Seasonal contribution of living phytoplankton carbon to vertical fluxes in a coastal upwelling system (Ría de Vigo, NW Spain). Cont Shelf Res 31:414–424

CONCLUSIONES



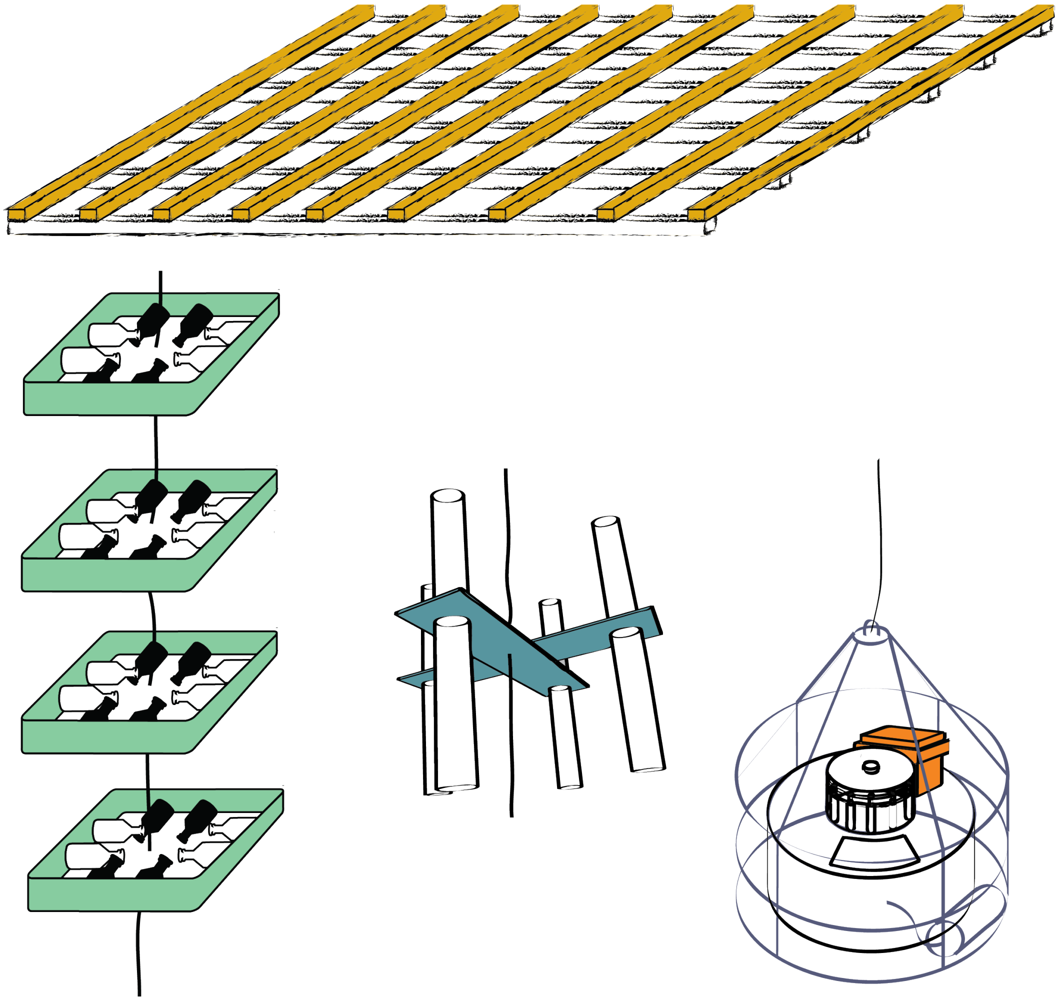
Se ha diseñado y caracterizado una cámara bentónica autónoma que permite cuantificar *in situ*, el intercambio de solutos entre el sedimento y la columna de agua, adaptada para sistemas costeros con una profundidad de hasta 100 m. La cámara bentónica cubre una superficie de sedimento de 5030 cm^2, siendo lo suficientemente grande como para incluir las heterogeneidades propias de sedimentos costeros e integrar los efectos ocasionados por la macrofauna. La cámara incuba un total de 140.8 L de agua, la cual es homogeneizada mediante tres bombas de recirculación sumergibles, alcanzando la mezcla completa del agua incubada en 4 minutos. La agitación dentro de la cámara es regulable y proporciona una velocidad tangencial promedio que varía entre 2.0 y 4.8 cm s^{-1}, en función del voltaje aplicado a las bombas. Con estas velocidades se consiguieron espesores promedio de la capa límite entre 125 y 279 µm, que son comparables a los que se obtienen en sistemas costeros.

Por primera vez en este sistema de afloramiento costero, se cuantificaron los flujos bentónicos *in situ* de oxígeno y nutrientes durante el transcurso de un año. Los flujos bentónicos de oxígeno fueron siempre hacia el sedimento con una media anual de -34 mmol O_2 m^{-2} d^{-1}, un valor que es el doble de la tasa media de respiración bentónica para las zonas costeras europeas. Los flujos bentónicos de fosfato, amonio y silicato fueron siempre hacia la columna de agua y correlacionaron negativamente con los flujos de oxígeno. A pesar de que se obtuvieron flujos negativos de nitrato durante las épocas de verano y otoño, los sedimentos de la Ría actuaron como fuente de nitrógeno inorgánico hacia la columna de agua ya que estuvieron dominados por los flujos de amonio (83%). Los flujos bentónicos de oxígeno, fosfato, amonio y silicato fueron significativamente inferiores durante invierno y no mostraron diferencias significativas durante primavera, verano y otoño. La cantidad y la calidad de la materia orgánica son factores importantes que regulan los flujos bentónicos, pero son los cambios de temperatura del agua de fondo, modulados por los pulsos de afloramiento/hundimiento los que desencadenan y controlan los flujos bentónicos a corta escala de tiempo. Se estimó que el nitrógeno y fósforo inorgánicos regenerados en el sedimento pueden representar hasta un 41 % y un 60 %, respectivamente, de la entrada de estos nutrientes en el sistema provenientes de la suma de aguas afloradas y aguas continentales.

Mediante la integración de datos *in situ* de producción primaria, respiración tanto pelágica como bentónica y flujos verticales de carbono se estimó el metabolismo neto del sistema costero de la ría de Vigo a escala estacional. Se elaboró un balance anual de carbono en el que además de los procesos anteriores se incluyeron las pérdidas de carbono del sistema a través de la extracción de cultivo de mejillón, actividades pesqueras y de marisqueo. La respiración bentónica representa en media anual, un 34 % de la respiración total del sistema. El metabolismo neto del ecosistema en la ría de Vigo es proporcional a producción primaria bruta *in situ*. La ría de Vigo es netamente autótrofa a escala anual (317 ± 113 g C m^{-2} d^{-1}) aunque el metabolismo bentónico reduce la producción neta de la comunidad en un 23 %. El aporte de carbono orgánico procedente de aportes continentales representa un 2.3 % del metabolismo neto. El carbono orgánico extraído del sistema por cultivo de mejillón y actividades pesqueras supone un 3 % de metabolismo neto del ecosistema, y está dominado en su mayor parte por el cultivo de mejillón (89 %). Sin embargo, basándonos en la eficiencia de transferencia de energía entre niveles tróficos del 10 %, se calculó que el conjunto de actividades pesqueras, marisqueras y de cultivo de mejillón requieren hasta un 38 % de la producción neta de la comunidad. Finalmente, se estimó que el carbono producido *in situ* en la ría de Vigo y disponible para ser exportado a la plataforma adyacente o ser enterrado en el sedimento, representa una cuarta parte de la producción primaria bruta.

En base al análisis de las propiedades de la columna de agua, flujos verticales y flujos bentónicos en dos estaciones en la ría de Vigo, una de ellas afectada por el cultivo de mejillón, se estudió la influencia del cultivo de mejillón en batea sobre el acoplamiento pelágico-bentónico en la Ría de Vigo. Las tasas de sedimentación de carbono orgánico particulado fueron hasta 3 veces más elevadas bajo la batea de mejillón (3.2 g m^{-2} d^{-1}) con respecto a la estación de referencia y además la materia orgánica sedimentada bajo la batea tenía mayor contribución de carbono fitoplanctónico. Los flujos bentónicos de oxígeno y nutrientes fueron significativamente superiores bajo la batea, llegando a ser 17 veces más altos en el caso del amonio. Los procesos de respiración anaeróbica parecen tener mayor importancia bajo la influencia del cultivo de mejillón lo que se ve reflejado en cocientes de respiración bentónica más altos (1.2 ± 0.2) comparados con los obtenidos en la estación de referencia (0.7 ± 0.2). Mediante un balance de carbono 1D para ambas estaciones, se observó que la respiración en la columna de agua es similar en ambos casos, sin embargo, los sedimentos bajo la influencia de la batea respiran aproximadamente un 84 % del material orgánico que les llega mientras que este valor es de un 28 % en la estación de referencia. Las altas tasas de sedimentación de material orgánico bajo la batea propician un metabolismo bentónico de carbono muy superior (2.7 ± 0.6 g C m^{-2} d^{-1}) al carbono inorgánico generado en una zona no afectada por el cultivo de mejillón (0.3 ± 0.1 g C m^{-2} d^{-1}) Por lo tanto, estos resultados apuntan a que existe un acoplamiento pelágico-bentónico mayor y más rápido en las áreas afectadas por el cultivo de mejillón.

RESUMEN



Bajo este epígrafe se sintetizan los resultados obtenidos en el desarrollo de esta Tesis doctoral que se ha dividido en cuatro capítulos. El primer capítulo se centró en el diseño, elaboración y caracterización hidrodinámica de una cámara bentónica autónoma para su uso en zonas costeras. En el segundo capítulo se cuantificaron los flujos bentónicos atendiendo a su variación estacional así como a los factores que regulan estos flujos. En el tercer capítulo se llevó a cabo un estudio en el que se integraron datos, tomados *in situ* y de forma simultánea, de producción primaria, respiración pelágica y bentónica además de flujos verticales, para estimar el metabolismo neto del ecosistema y se elaboró un balance de carbono anual para la ría de Vigo, en el que se incluyeron las pérdidas de carbono en forma de extracción de mejillón de cultivo en batea, pesca y marisqueo. En el último capítulo, se estudió la influencia del cultivo de mejillón en suspensión sobre el acoplamiento pelágico-bentónico en la ría de Vigo, comparando dos estaciones, una en el medio de un polígono de bateas de mejillón y otra en una estación de referencia.

1. Caracterización de una nueva cámara bentónica

La medición del intercambio de solutos a través de la interfase agua-sedimento ha ganado importancia durante los últimos años ya que influye sobre la concentración y especiación de varios elementos de la columna de agua (Aller 1980). Hasta la fecha, han sido diversos los métodos que se han utilizado para estimar los flujos bentónicos. De entre las técnicas desarrolladas, las cámaras bentónicas ofrecen varias ventajas. Al realizar medidas *in situ*, evitan la manipulación del sedimento. Además de ello, la superficie de sedimento cubierta por la cámara puede ser relativamente grande, incluyendo de esta manera la variabilidad a pequeña escala y la contribución de la fauna bentónica. Glud & Blackburn (2002) establecen que para evaluar correctamente la actividad del bentos al cuantificar los flujos bentónicos, las medidas deben de hacerse preferentemente mediante cámaras bentónicas y de tamaños relativamente grandes. En aguas costeras de la península ibérica ya se han empleado cámaras bentónicas para la medición de los flujos (ej. Forja et al. 2004, Ortega et al. 2005). Sin embargo estas cámaras bentónicas, además de necesitar la actividad de un buceador autónomo, tenían que estar físicamente conectadas al barco para la recolección de las muestras. En este contexto, este trabajo muestra el desarrollo y la verificación de una nueva cámara bentónica diseñada para su uso en sistemas costeros.

Esta nueva cámara bentónica está compuesta por una estructura de acero inoxidable sobre la que se montaron todos los componentes del sistema. En el centro de la estructura se coloca la propia cámara bentónica, una cámara de PVC opaca y de forma cilíndrica con una altura de 28 cm, que cubre una superficie de sedimento de 5030 cm^2. El volumen de la cámara es de 140.8 ± 3.5 L. En la parte superior de la cámara, tres puertas de PVC, son operadas mediante un motor de 12 V DC. Durante el fondeo de la cámara bentónica estas puertas permanecen abiertas para evitar en la medida de lo posible las perturbaciones en el sedimento. Una vez que la cámara bentónica está asentada en el fondo, estas puertas se cierran para garantizar el sellado del agua incubada. El sistema posee además un muestreador (KC Denmark) para tomar hasta un total de 12 muestras de agua de 50 mL. Dentro de la cámara bentónica existen sensores de temperatura (SBE-39), pH (SBE-18), oxígeno (SBE-43) y turbidez (Seapoint Turbidity Meter) mediante los cuales se obtienen medidas continuas de estas variables durante el tiempo de incubación.

El equipo dispone de control en tiempo real de los datos de muestreo y de los sensores implantados. Una boya de comunicación en superficie conecta la cámara bentónica mediante un cable electromecánico. Todo el sistema está controlado mediante un Data Logger CR10X Campbell Scientific. Se comprobaron satisfactoriamente dos sistemas de comunicación con la cámara bentónica para el envío y recepción de datos. (1) un sistema de comunicación de doble vía mediante comunicación GSM (Global System for Mobile communications) y (2) un sistema de comunicación mediante radio frecuencia de 869 MHz, que permite comunicarse con la boya a superficie de la cámara bentónica a una distancia de 4 km. Uno de los factores más importantes en el uso de estas cámaras bentónicas es el sistema utilizado para la homogeneización del agua incubada dentro de la cámara (Boynton et al. 1981). En este caso, el agua incubada en la cámara es homogeneizada mediante tres bombas sumergibles (Totton DC 30/5), conectadas a los sistemas de energía, los cuales pueden regular el voltaje de entrada y por lo tanto, la velocidad de corriente dentro de la cámara. La mezcla completa del agua incubada se consigue en 4 minutos. Se estudió el campo de velocidades en 3D así como la distribución de la capa límite de difusión (DBL) dentro de la cámara bentónica en experiencias de laboratorio empleando como fondo una capa de sedimento o un falso fondo de neopreno incluyendo placas de disolución de alabastro. Se compararon dos sistemas distintos de expulsión del agua a través de las bombas. Las velocidades tangenciales a 5 cm sobre el fondo, para el sistema finalmente escogido, estuvieron dentro de un rango entre 2.0 cm s^{-1} y 4.8 cm s^{-1}, dependiendo del voltaje aplicado a las bombas, lo que generó espesores promedio de la DBL desde 125 µm a 279 µm. La velocidad tangencial y los espesores promedio de la DBL correlacionaron siguiendo la siguiente fórmula: $V_T = 615x[DBL]^{-1.02}$ (R^2= 0.97). Finalmente, se realizaron satisfactoriamente medidas de flujos bentónicos en dos sistemas costeros someros: la ría de Vigo (NO de España) y la bahía de Cádiz (SO de España).

2. Flujos bentónicos: variación estacional y factores que los regulan

El acoplamiento biogeoquímico entre los ambientes pelágico y bentónico se incrementa en los sistemas costeros afectados por el afloramiento, ya que las altas tasas de producción primaria, características de estos sistemas, favorecen un mayor aporte vertical de materia orgánica hacia el sedimento (Varela et al. 2004) y, por tanto, mayor disponibilidad de esta materia orgánica para su remineralización en el sedimento (Jahnke 1996). Los flujos bentónicos se ven afectados por diversos factores entre los que se encuentran la temperatura y la concentración de oxígeno disuelto del fondo marino, el aporte de materia orgánica al sedimento y los procesos de bioturbación y excavación por parte de la macrofauna bentónica. Hasta la actualidad, los únicos estudios sobre flujos bentónicos en el afloramiento costero del NO de la península Ibérica incluyen un trabajo en la plataforma continental (Epping et al. 2002) y otro en la ría de Pontevedra (Dale & Prego 2002). Ambos estudios estiman los flujos bentónicos difusivos mediante incubación en laboratorio de testigos de sedimento. Dentro de este contexto, en el capítulo III de la Tesis se cuantificaron, por primera vez en este sistema de afloramiento, los flujos bentónicos *in situ* de oxígeno y nutrientes a lo largo de un año, a fin de abordar la variabilidad estacional, los factores que los controlan y evaluar la importancia de los mismos en la productividad potencial del sistema. Este trabajo se engloba dentro del proyecto 'Acoplamiento entre los flujos verticales y bentónicos en la ría de Vigo' (FLUVBE, CICYT: REN2003-04458/MAR) Se realizaron un total de 16 campañas oceanográficas entre los meses de abril de 2004 y enero de 2005, en una estación situada en el canal central de la ría de Vigo. Se midieron las propiedades biogeoquímicas de la columna de agua, los flujos verticales de materia orgánica particulada por medio de trampas de sedimento y los flujos bentónicos *in situ* de oxígeno y nutrientes mediante el uso de la cámara bentónica desarrollada en el capítulo II (Ferrón et al. 2008).

Como consecuencia de la degradación de materia orgánica, los flujos bentónicos de oxígeno fueron siempre negativos y tuvieron un rango entre -18 y 50 mmol O_2 m^{-2} d^{-1}, con una media anual de -34 mmol O_2 m^{-2} d^{-1}. Este valor es el doble de la tasa media de respiración bentónica para las zonas costeras europeas (Gazeau et al. 2004) y coincide con la media global de respiración de los sistemas estuáricos (Hopkinson & Smith 2005). Los flujos bentónicos de los nutrientes amonio, fosfato y silicato fueron siempre positivos, hacia la columna de agua. A pesar de que los flujos de nitrato fueron hacia el sedimento durante las estaciones de verano y otoño, los sedimentos de la ría actuaron como fuente de nitrógeno inorgánico hacia la columna de agua durante todo el año, ya que los flujos bentónicos de nitrógeno estuvieron dominados por los flujos de amonio (83 %). Los flujos de oxígeno, amonio, fosfato y silicato fueron significativamente inferiores en invierno pero no mostraron diferencias significativas durante las otras épocas estacionales. Las fuertes correlaciones entre estos flujos señalan que la respiración aeróbica juega un papel importante en la remineralización de la materia orgánica. Tanto la cantidad como la calidad de la materia orgánica son factores importantes que controlan los flujos bentónicos, pero son los cambios de temperatura del agua de fondo, modulados por los pulsos de afloramiento/hundimiento, los que desencadenan y controlan los flujos bentónicos a cortas escalas de tiempo. Los flujos de nitrato variaron de una manera totalmente diferente al resto de flujos bentónicos, no correlacionando con ninguno de ellos. Estos flujos se ven afectados por la concentración de oxígeno disuelto y nitrito en las aguas de fondo, siendo hacia el sedimento cuando la concentración de oxígeno es menor y la concentración de nitrito mayor. Los resultados apuntan a que la entrada de aguas afloradas, ricas en nitrito favorecen los procesos de desnitrificación directa respecto al acoplamiento nitrificación-desnitrificación, aunque ambos procesos pueden ocurrir al mismo tiempo ocasionando los flujos negativos de nitrato en las épocas de verano y otoño. El estudio evalúa además, la importancia de los flujos bentónicos sobre la producción primaria potencial en el sistema, obteniendo que, el nitrógeno y el fósforo inorgánicos remineralizado en el sedimento puede representar hasta un 41 % y un 60 %, respectivamente, de la entrada de nutrientes al sistema provenientes de la suma de aguas afloradas y aguas continentales.

3. Metabolismo neto del ecosistema y extracción de recursos vivos marinos

El metabolismo neto del ecosistema (NEM) representa el balance entre la producción primaria y la respiración total en un ecosistema (Kemp et al. 1997). Estudios sobre el NEM indican el estado trófico del sistema al tiempo que proporcionan una idea de cómo el sistema procesa los nutrientes inorgánicos y la materia orgánica (Smith & Hollibaugh 1997). De entre los diferentes métodos existentes para medir el NEM, las medidas directas permiten la división entre los procesos de respiración y producción, estimando la contribución relativa de cada compartimento tanto pelágico como bentónico en el metabolismo total del ecosistema (Staehr et al. 2012). El principal objetivo de este trabajo fue explorar la importancia de la respiración bentónica en la ría de Vigo y evaluar hasta que punto determina el estado trófico del ecosistema. Para ello, se analizó la respiración bentónica en relación a medidas simultáneas hechas *in situ* de producción primaria, tasas de respiración pelágica y exportación vertical de partículas durante las cuatro campañas estacionales realizadas en el marco del proyecto FLUVBE. En base a todas estas medidas, el objetivo principal del trabajo fue determinar el metabolismo neto del ecosistema en la ría de Vigo a escala estacional y anual. A partir de aquí, se elaboró un balance 2D de carbono anual, en el que además se incluyeron las pérdidas de carbono del sistema a través de la extracción de cultivo de mejillón, de actividades pesqueras y de marisqueo.

El sistema pelágico de la ría de Vigo fue netamente autotrófico durante los períodos de primavera y verano, y autotrófico o prácticamente en balance durante otoño e invierno. Los resultados muestran que la respiración bentónica es un proceso metabólico de alta importancia en este sistema costero, representando, de media un 34% de la respiración total del sistema, lo que incluye a esta zona costera en el rango superior para estuarios (Hopkinson & Smith 2005). Los procesos de remineralización bentónica ganan importancia durante los períodos de otoño e invierno, en los cuales la respiración bentónica alcanza un 40% y 44% respectivamente, de la respiración total del sistema. El metabolismo neto del ecosistema en la ría de Vigo es proporcional a la producción primaria bruta (GPP) *in situ*, de manera contraria a lo que ocurre en muchos ecosistemas estuáricos en los que se ha encontrado una relación inversa entre el NEM y la GPP (Smith & Hollibaugh 1993). La ría de Vigo es netamente autotrófica en una escala anual (317 ± 113 g C m^{-2} yr^{-1}) incluso a pesar de que el metabolismo bentónico reduce la producción primaria neta de la comunidad (NCP) en un 23%. El aporte de carbono orgánico proveniente de aguas continentales (Evans et al. 2011) representa solamente un 2.3 % del total del metabolismo neto. El carbono orgánico anual extraído de pesca y cultivo de mejillón, estimado a partir de diferentes referencias bibliográficas, ascendió a 10 g C m^{-2} yr^{-1}, lo cual supuso un 3% del metabolismo neto del ecosistema, dónde la extracción de mejillón de cultivo representó el 89% del total extraído. Sin embargo, si nos basamos en la eficiencia en la transferencia de energía entre niveles tróficos del 10%, se estima que el conjunto de cultivo de mejillón y las actividades pesqueras, requieren hasta un 38% de la NCP. Este valor es superior al encontrado por Pauly & Christensen (1995) para las áreas de afloramiento (25.1 %) y para arrecifes y zonas costeras (8.3%). El carbono orgánico producido *in situ* en la ría de Vigo y disponible para ser exportado a la plataforma adyacente o ser enterrado en el sedimento, representa una cuarta parte de la producción primaria bruta y es favorecido durante el afloramiento estival.

4. Efectos del cultivo de mejillón en el acoplamiento pelágico-bentónico

El acoplamiento entre los ambientes pelágico y bentónico juega un papel clave en los ecosistemas costeros, en gran medida debido a la elevada regeneración de nutrientes que tiene lugar en los mismos (Balzer et al. 1983). En muchos ecosistemas costeros, la presencia de densas poblaciones de bivalvos procedentes de la acuicultura, como el cultivo de

mejillón de bateas, puede ejercer un fuerte control ‘top – down’ dada su gran capacidad de filtración de la materia particulada en suspensión en la columna de agua. Fruto de esta actividad alimentaria resulta la formación de biodepósitos de heces y pseudo-heces de materia orgánica e inorgánica que sedimentan rápidamente, lo que conlleva el incremento de la remineralización de la materia orgánica y una intensa regeneración de nutrientes en la interfase sedimento-agua. Este trabajo estudió la influencia del cultivo de mejillón en batea sobre el acoplamiento pelágico-bentónico en la ría de Vigo durante el mes de Julio de 2004. Se realizaron medidas de las propiedades de la columna de agua en tres estaciones en la ría de Vigo: bajo una batea de mejillón (1), y en dos estaciones de referencia localizadas en el canal principal (2) y en la parte más interna de ría (3). Se midieron los flujos bentónicos de nutrientes disueltos, oxígeno disuelto y carbono inorgánico por medio de una cámara bentónica en las estaciones (1) y (3). Además se emplearon trampas de sedimento para la estimación de flujos verticales de material orgánico particulado en 6 posiciones en la ría, que incluyeron estaciones bajo la influencia de bateas de mejillón y otras localizadas en zonas de referencia. La estructura de la columna de agua en las estaciones (1-3) fue muy similar, caracterizada por condiciones de afloramiento en la primera semana de muestreo y una posterior estratificación en la segunda mitad del mes de Julio, en la que se observó una fuerte termoclina, cuya profundidad fluctuó principalmente modulada por el régimen de viento. Los flujos verticales de carbono orgánico particulado bajo la batea de mejillón (3.2 g C m^{-2} d^{-1}) fueron 3 veces mayores que los flujos obtenidos entre bateas y 10 veces superiores a los obtenidos en la estación de referencia del canal central, confirmando la hipótesis de que el cultivo intenso de mejillón en batea aumenta las tasas de sedimentación de materia orgánica. El análisis de isotopos de carbono ($\delta^{13}C$) y nitrógeno ($\delta^{15}N$) mostraron además que, la calidad del material sedimentado no fue significativamente distinta bajo la batea y en las estaciones de referencia. Sin embargo, la ratio entre el carbono ‘no algal’ y el carbono ‘algal’ fue significativamente menor bajo la batea, lo que indica que la materia orgánica sedimentada bajo la batea presenta una mayor contribución de carbono fitoplanctónico.

Los flujos bentónicos de oxígeno disuelto, amonio, fosfato y silicato obtenidos bajo la batea fueron significativamente superiores a los observados en la estación de referencia del interior de la ría. Además, se obtuvo además que el cociente de respiración bentónica (BRQ) fue más alto (1.2 ± 0.2) en los sedimentos de batea que en la estación de referencia (0.7 ± 0.2), lo que implica una prevalencia de procesos de respiración aeróbica en la estación de referencia frente a la mayor importancia de procesos anaeróbicos en los sedimentos de batea. Los flujos bentónicos de amonio llegan a ser 17 veces más altos en la estación de batea, probablemente causados por las condiciones reductoras del sedimento que inhiben los procesos de nitrificación (Christensen et al. 2003).

Se realizó un balance 1D de carbono en el que se compararon la estación de referencia y la estación de batea utilizando los valores de producción primaria y respiración pelágica de Arbones et al. (2008) y un cociente fotosintético de 1.4 (Fraga et al. 1998). En la estación de referencia, aproximadamente un 17 % del carbono orgánico que sedimenta es respirado en la columna de agua y un 28 % es respirado en el sedimento. Por su contra, en la estación de batea, a pesar de que el flujo vertical de carbono orgánico fue 3 veces superior a la estación de referencia, se respiró un 84 % del carbono orgánico depositado mientras que un 16 % fue remineralizado en la columna de agua. Ello pone de manifiesto la importancia del metabolismo bentónico bajo la batea (2.7 ± 0.6 g C m^{-2} d^{-1}), siendo muy superior al carbono inorgánico producido en la estación de referencia de la zona interna de la ría (0.3 ± 0.1 g C m^{-2} d^{-1}). Los resultados obtenidos muestran, por primera vez, el importante papel que tiene el cultivo de mejillón en el acoplamiento pelágico-bentónico en este sistema de afloramiento costero.

5. References

Aller RC (1980) Diagenetic processes near sediment-water interface of Long Island Sound. I. Decomposition and nutrient element geochemistry (S, N, P). Adv Geophys 22:237–350

Arbones B, Castro CG, Alonso-Pérez F, Figueiras FG (2008) Phytoplankton size structure and water column metabolic balance in a coastal upwelling system: the Ría de Vigo, NW Iberia. Aquat Microb Ecol 50:169–179

Balzer W, Grasshoff K, Dieckmann P, Haardt H, Petersohn U (1983) Redox-turnover at the sediment water interface studied in a large bell jar system. Oceanol Acta 6:337–344

Boynton WR, Kemp WM, Osborne CG, Kaumeyer KR, Jenkins MC (1981) Influence of water circulation rate on in situ measurements of benthic community respiration. Mar Biol 65:185–190

Christensen PB, Glud RN, Dalsgaard T, Gillespie P (2003) Impacts of longline mussel farming on oxygen and nitrogen dynamics and biological communities of coastal sediments. Aquaculture 218:567–588

Dale AW, Prego R (2002) Physico-biogeochemical controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system. Mar Ecol Prog Ser 235:15–28

Epping E, Zee C van der, Soetaert K, Helder W (2002) On the oxidation and burial of organic carbon in sediments of the Iberian margin and Nazaré Canyon (NE Atlantic). Prog Oceanogr 52:399–431

Evans G, Prego R, Marshall JE (2011) Organic matter in ria sediments: Relevance of terrestial sources and temporal variations in rates of accumulation. Estuar Coast Shelf Sci 94:246–254

Ferrón S, Alonso-Pérez F, Castro CG, Ortega T, Pérez FF, Ríos AF, Gómez-Parra A, Forja JM (2008) Hydrodynamic characterization and performance of an autonomous benthic chamber for use in coastal systems. Limnol Oceanogr Methods 6:558–571

Forja JM, Ortega T, DelValls TA, Gómez-Parra A (2004) Benthic fluxes of inorganic carbon in shallow coastal ecosystems of the Iberian Peninsula. Mar Chem 85:141–156

Fraga F, Ríos AF, Pérez FF, Figueiras FG (1998) Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and mineralisation of organic matter in the sea. Sci Mar 62:161–168

Gazeau F, Smith SV, Gentili B, Frankignoulle M, Gattuso J-P (2004) The European coastal zone: characterization and first assessment of ecosystem metabolism. Estuar Coast Shelf Sci 60:673–694

Glud RN, Blackburn N (2002) The effects of chamber size on benthic oxygen uptake measurements: A simulation study. Ophelia 56:23–31

Hopkinson CS, Smith EM (2005) Estuarine respiration: an overview of benthic, pelagic, and whole system respiration. In: Williams PJL (ed) Respiration in aquatic ecosystems. Oxford University Press, Oxford, New York, p 122–146

Jahnke RA (1996) The global ocean flux of particulate organic carbon: Areal distribution and magnitude. Glob Biogeochem Cycles 10:71–88

Kemp WM, Smith EM, Marvin-DiPasquale M, Boynton WR (1997) Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Mar Ecol Prog Ser 150:229–248

Ortega T, Ponce R, Forja JM, Gómez-Parra A (2005) Fluxes of dissolved inorganic carbon in three estuarine systems of the Cantabrian Sea (north of Spain). J Mar Syst 53:125–142

Pauly D, Christensen V (1995) Primary production required to sustain global fisheries. Nature 374:255–257

Smith SV, Hollibaugh JT (1993) Coastal metabolism and the oceanic organic carbon balance. Rev Geophys 31:75–89

Smith SV, Hollibaugh JT (1997) Annual cycle and interannual variability of ecosystem metabolism in a temperate climate embayment. Ecol Monogr 67:509–533

Staehr PA, Testa JM, Kemp WM, Cole JJ, Sand-Jensen K, Smith SV (2012) The metabolism of aquatic ecosystems: history, applications, and future challenges. Aquat Sci 74:15–29

Varela M, Prego R, Pazos Y (2004) Vertical biogenic particle flux in a western Galician Ria (NW Iberian Peninsula). Mar Ecol Prog Ser 269:17–32