Biogeochemical processes in the Northeast Atlantic continent-ocean boundary
(Northern Galician Rias, NW Iberian Peninsula)

Natalia Ospina-Alvarez

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CSIC
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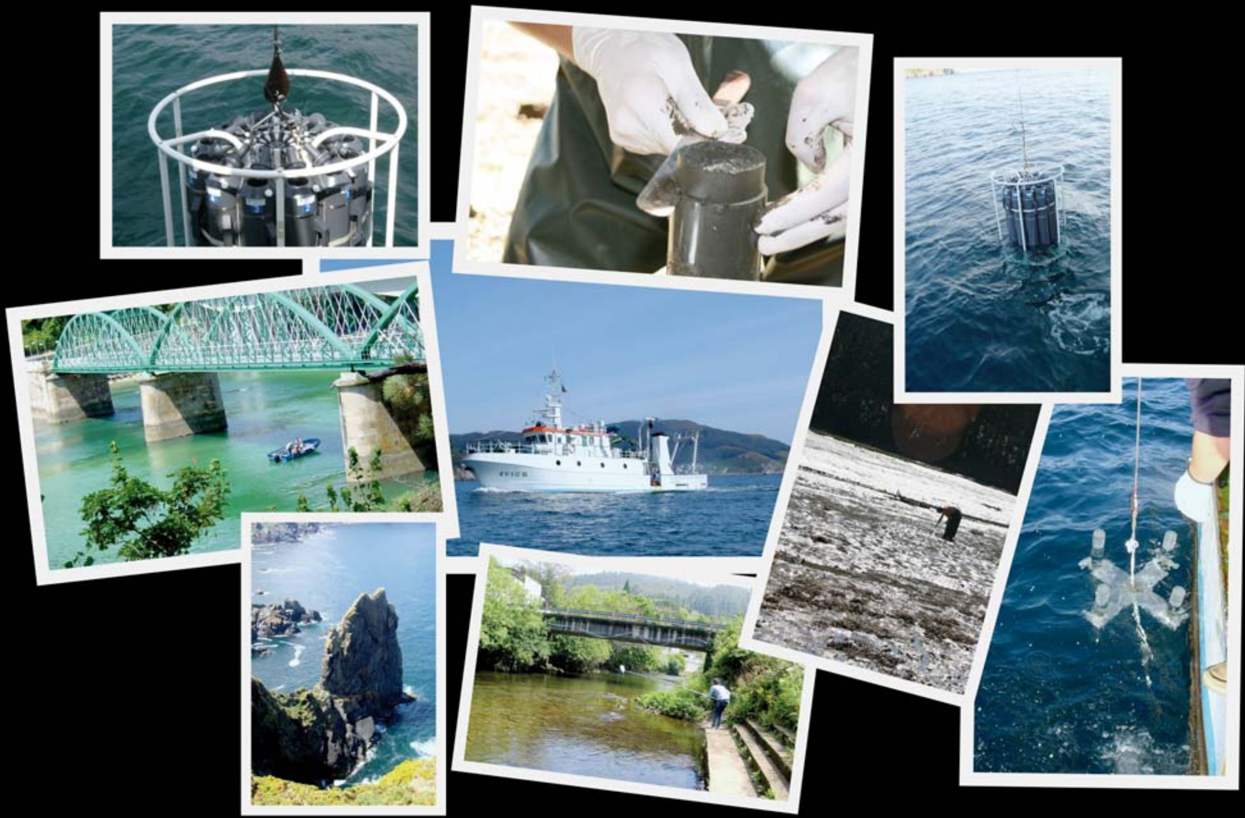
Instituto Español de Oceanografía

Universitat de Barcelona



This doctoral thesis deals with the biogeochemical processes taking place in estuarine systems known as 'rias', located at the NW of the Iberian Peninsula. Its realization has been possible thanks to financial support from the JAE-Pre program of the Spanish Council for Scientific Research (CSIC) co-funded by the European Social Fund (ESF), and the 'INTERESANTE' project, funded by the CICYT. Additionally, it is a contribution to the Spanish LOICZ program (Land-Ocean Interactions in the Coastal Zone).

‘Science knows no country,
because knowledge belongs to humanity,
and is the torch which illuminates the world.’

Louis Pasteur

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Doctoral Thesis

by Natalia Ospina-Alvarez

Biogeochemical processes in the Northeast Atlantic continent-ocean boundary (Northern Galician Rias, NW Iberian Peninsula)

Procesos biogeoquímicos en la frontera continente-océano del Atlántico Nororiental (Rías Norte de Galicia, NO Península Ibérica)

Thesis presented to obtain doctoral degree by the
University of Barcelona. Ph.D. Programme in Marine Sciences.

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Natalia Ospina-Alvarez

Barcelona, June 2012

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Paleontologia i Geociències Marines

‘Procesos biogeoquímicos en la frontera continente-océano del Atlántico Nororiental (Rías Norte de Galicia, NO Península Ibérica)’

Memoria presentada por **Natalia Ospina-Alvarez**, para optar al grado de doctora por la Universidad de Barcelona, Programa de doctorado en Ciencias del Mar (bienio 2006-2008).

Esta Tesis Doctoral ha sido realizada en el Grupo de Biogeoquímica Marina del Instituto de Investigaciones Marinas (IIM-CSIC) bajo la dirección del Dr. Ricardo Prego Reboredo y co-dirigida por el Dr. Manuel Varela Rodríguez del Centro Oceanográfico A Coruña (IEO).

Barcelona, Junio de 2012

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Preface

The present PhD thesis has been possible thanks to financial support from the JAE-Program (Ref. 07-00161JAE-Pre) of the Spanish Council for Scientific Research (CSIC) and is part of the project *Influence of meteorological forcing, land geochemistry and estuarine zone in the hydrodynamic, biogeochemical cycle of trace metal and rare earth and plankton transport in the Northern Galician Rias, NW Spain* (Acronym: INTERESANTE), funded by the CICYT (ref. CTM2007-62546-C03/MAR) and the Complementary Action Spain-Portugal (ref. 2007PT0021). Additionally, it is a contribution to the Spanish LOICZ program (Land-Ocean Interactions in the Coastal Zone).

The thesis has been organized in six chapters and written in English and Spanish. The diagram of Figure A presents an overview of the structure and the reference publications used as the main theme of each chapter (see also *Appendix I*).

Chapter 1 deals with general issues (i.e. introduction, aims and scope) that apply to the following chapters (i.e description of the study area, field and laboratory methods). The Introduction in Chapter 1 gives a context to address the reading of the thesis, even though the biogeochemical processes in marine and coastal environments are not detailed. As a theoretical framework, a list of basic literature has been included in the Appendices section (see *Appendix II*).

The successive chapters (from 2 to 5) were designed as a part of the compartments: ocean, river, sediment and estuary-ria (see Chapter 1, Figure 1.1.1). An oceanographic characterisation of the Northern Galician Rias is presented in Chapter 2. This chapter involves an extensive analysis of summer upwelling and downwelling processes, winter shelf-water upwelling, and poleward intrusion in the northern Galician shelf.

Chapter 3 deals with the fluvial contributions to the Northern Galician Rias, including the quantification of major and minor chemical elements (nutrient salts, trace elements) in the dissolved and particulate matter, chlorophyll-*a*, DIN, PON, DOC, POC and C/N ratio.

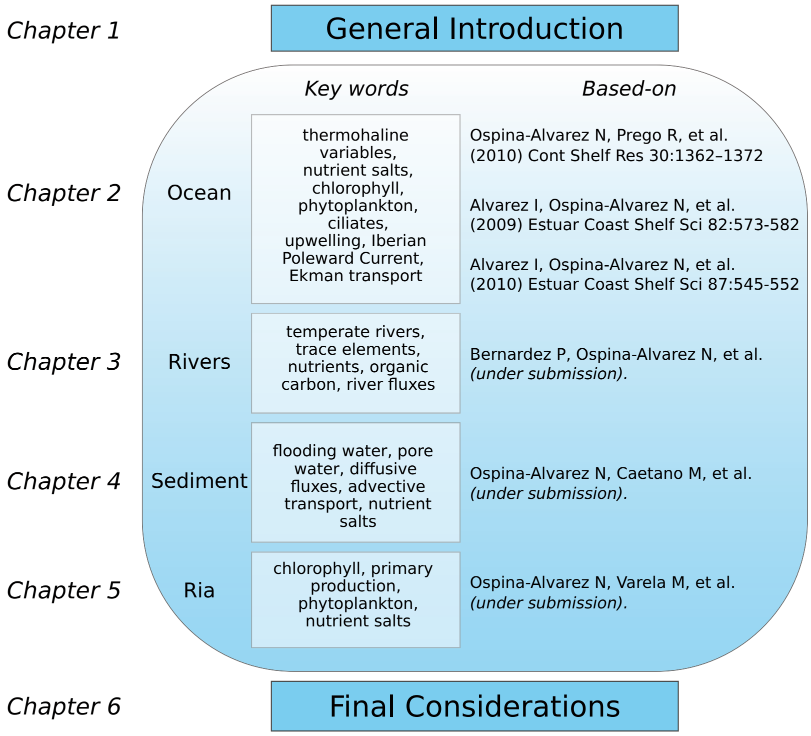

Figure A. General thesis outline

In Chapter 4 the sediment-water fluxes of nutrients in a ria coastal systems are discussed. Fluxes driven by molecular diffusion and advective transport across sediment-water interfaces during tidal flooding for the Northern Galician Rias are calculated.

Chapter 5 focuses on the hydrological, chemical and biological interactions in the Northern Galician Rias, exemplified by the case of the Ria of Barqueiro, identifying their oceanographic periods in relation to nutrient availability, primary production, phytoplankton biomass, taxonomic composition and hydrographic patterns.

The last chapter, Chapter 6, presents the general conclusions based upon the preceding chapters, and perspectives for future research. Additionally, and according to the normative for PhD thesis of the University of Barcelona, it was included copy of the original articles published and submitted for publication with their respective abstracts in English and Spanish (*Appendix III*).

Vigo, April 2012.

Acknowledgements

Agradecimientos

Una de las partes más difíciles al finalizar una tesis doctoral, es agradecer a todos aquellos que han participado en su desarrollo. No creo que sea posible dar valía a cada uno de esos aportes, tanto en el plano profesional como en el personal. Aún llenando varias páginas, es posible que omitiese contribuciones -directas e indirectas- sin las cuales no hubiera podido culminar ésta tesis. A todos y cada uno, mi más sincero y profundo agradecimiento.

Quiero destacar además de los agradecimientos incluidos al final de cada capítulo, a algunas personas que fueron determinantes en todo éste proceso:

En primer lugar, al Dr. Ricardo Prego Reboredo del Instituto de Investigaciones Marinas (IIM-CSIC), por ser el supervisor de ésta tesis doctoral. Por lo enseñado, por compartir conmigo su experiencia, pero sobre todo por la confianza depositada. Por marcarme el rumbo a seguir pero darme la libertad de gestionar mi trabajo.

A mi co-director en el Instituto Español de Oceanografía (IEO) de A Coruña, Dr. Manuel Varela, a quién siempre recuerdo sonriente y dispuesto, aún a pesar de la inclemencia del clima gallego. Por sus valiosos y certeros comentarios, mil gracias Manolo.

A todo el staff del Proyecto INTERESANTE (IIM, IEO, Universidad de Vigo) por su ayuda y compañía, tanto en los buenos como en los malos días (los de sol, los de lluvia, y los de mucha lluvia).

A mis compañeros del Grupo de Biogeoquímica Marina del IIM-CSIC en Vigo: Ana G., Ana V., Antonio, Azucena, Clara, Daniel, Juan y Susana. Por su compañía, su experiencia, su disposición, por toda su ayuda (tanto en lo científico como en lo personal). A cada uno de ellos mil gracias.

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Thanks to the staff at the Marine Environment Unit of the IPIMAR in Lisbon. To Dr. Carlos Vale and Dr. Miguel Caetano for welcoming me into your group in Lisbon and especially for their valuable criticism and their constructive suggestions, that helped me improve my work.

Thanks to all the staff of the Applied Analytical Chemistry Laboratory of the University of Warsaw in Poland, for letting me be part of their team, and particularly to Dr. Beata Krasnodębska-Ostręga for her kindness and hospitality. Bardzo dziękuję wszystkim!

I am also grateful to Dr. Antonio Bode; Dr. Miguel Caetano and Dr. Mihoko Numata, for their comments and suggestions, which greatly improved the quality of this PhD thesis.

A Andrés, por su apoyo incondicional, no sólo como hermano sino como científico.

A Martín, simplemente...'Gracias totales'.

"Cuando la gratitud es tan absoluta las palabras sobran" (A. Mutis)

Thesis Summary

Resumen

Esta tesis doctoral tuvo por objetivo general, estudiar los aspectos relacionados con los procesos biogeoquímicos que tienen lugar en las rías de la frontera continente-océano del Atlántico Nororiental, como parte de la interfase costera templada del Atlántico Este.

El punto más septentrional de la Península Ibérica a lo largo de la costa norte de Galicia, al este de Cabo Ortegal (8°W), se encuentran las rías de Ortigueira (superficie: 38 km^2), Barqueiro (10 km^2), y Viveiro (27 km^2). Estas rías forman un conjunto denominado como 'rías del norte' o 'rías altas'.

En la primera parte del Capítulo 2, se caracterizaron procesos de afloramiento (upwelling) y contra-surgencia (downwelling) en las rías del norte de Galicia mediante un evento ocurrido durante julio y agosto de 2008. Las variables termohalinas, oxígeno disuelto, nutrientes, clorofila, fitoplancton, zooplancton y abundancia de ciliados se midieron en secciones ubicadas en las rías de Viveiro, Barqueiro y Ortigueira y sus plataformas adyacentes. El transporte de Ekman se calculó a través de datos procedentes del satélite QuikSCAT, la intensidad del afloramiento fue calculada mediante el índice de afloramiento (UI) a partir del promedio diario de los vientos geostróficos; y los mapas de temperatura superficial del mar (SST) proporcionados por el satélite de la NASA GHRSST. El transporte de Ekman y el comportamiento de la SST presentaron dos patrones diferentes: (i) dirección hacia el mar y condiciones favorables de afloramiento del 13 al 22 de julio, (ii) dirección hacia la costa, y condiciones favorables de contra-surgencia del 23 de julio al 19 de agosto.

Durante el afloramiento, el diagrama TS mostró una intrusión de Agua Central del Atlántico Noreste (ENACW) que afectó la plataforma continental, pero no las rías. Las

concentraciones de sales nutrientes aumentaron con la profundidad, alcanzando sus valores máximos cerca de la boca de la ría de Ortigueira. Durante la contra-surgencia, las aguas costeras aumentaron de temperatura (18.5 a 19.8°C) y se retuvieron dentro de las rías, los nutrientes se agotaron, excepto en el interior ria, debido a los aportes fluviales. En la zona interior de la ria de Barqueiro, se observó el máximo de clorofila-*a*. Una baja abundancia de fitoplancton existió en ambas rias, aunque se detectó una marea roja de *Lingulodinium polyedrum*. Entre mayo a septiembre de 1990 a 2008, en la plataforma norte de Galicia el promedio surgencia / contra-surgencia) fue de 1.9±0.8 / 2.1±1.0 eventos por año, considerando al menos una semana con condiciones de viento favorables y promedios de UI mayores a ± 500 $m^3 \cdot s^{-1} \cdot km^{-1}$.

En la segunda parte del Capítulo 2, se describe por primera vez un evento de afloramiento invernal (febrero de 2008) en las rías del norte de Galicia (NW Península Ibérica). El 20 de febrero, después de 9 días consecutivos de condiciones favourables de afloramiento, en la parte externa de la ría de Barqueiro se observó la presencia de agua marina por debajo de 10m de profundidad, la cual remplazó el agua menos salina observada previamente en enero. Esta situación fue consistente con el análisis del transporte Ekman cerca de la costa norte de Galicia. Adicionalmente, el diagrama TS indicó una mayor influencia del afloramiento hacia el este (Viveiro-Barqueiro,Ortigueira). La concentración de nutrientes también sugirió la presencia de agua marina de origen subsuperficial con una ligera variación con respecto a la mezcla de invernal. El fitoplancton mostró condiciones de primavera relacionadas con el aumento de radiación solar asociada a los vientos favourables de afloramiento. Algunas especies (i.e. *Strombidium sp., Dictyocha speculum*, etc.) también corroboraron la intrusión del agua de plataforma en el interior de la ría.

En la última parte del Capítulo 2 se caracterizó la evolución de una masa de agua cálida relacionada con la Corriente Ibérica dirigida hacia el polo (IPC) a lo largo de la plataforma norte de Galicia durante noviembre de 2008. El efecto de la IPC también se analizó en el interior de las rías del norte de Galicia, teniendo en cuenta las características hidrográficas y biogeoquímicas medidas el 18 de noviembre. La masa de agua dirigida por la IPC se observó cerca de la boca de las rías, alrededor del Cabo Estaca de Bares, causando un descenso de sales nutrientes. Adicionalmente, dentro de las rías se encontró una ligera actividad biológica cerca de la superficie asociada a la influencia fluvial.

En el Capítulo 3 se presenta un resumen de las características del agua de los ríos Sor, Mera y Landro, ríos prístinos que desembocan en las rías del norte de Galicia (NW Península Ibérica). El análisis se basó en un seguimiento quincenal durante el año 2008, para elementos mayores y menores, en su fase disuelta y particulada (Al, As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, U, Zn), sales nutrientes (nitratos, nitritos, amonio, fosfato, silicato), materia particulada en suspensión, clorofila-*a*, y marcadores de calidad del agua (DIN, PON, DOC, POC, relación C / N). Los aportes continentales de material disuelto y particulado fluvial hacia las rías del norte de Galicia fueron evaluados, y se cuantificaron sus contribuciones anuales. Este capítulo proporciona una estimación pionera de la cantidad total de nutrientes y elementos traza en la fase disuelta y particulada descargada a sistemas de ría prístinos.

El Capítulo 4 presenta uno de los primeros estudios de éste tipo en sistemas de rías. Las concentraciones de nitrato, nitrito, amonio, fosfato y silicato se determinaron en agua fluvial, agua de inundación mareal y agua intersticial de los sedimentos intermareales, en las rías de Ortigueira y Viveiro (NW de la Península Ibérica). Los estudios de campo se realizaron por primavera vez para las rías gallegas, y comprendieron la primavera y verano de 2008. Los testigos de sedimentos y el agua de inundación mareal se muestrearon en la zona intermareal, donde los sedimentos quedan expuestos al aire, tomando varias muestras durante los primeros 20 minutos de inundación mareal. Los flujos de nutrientes de los ríos (Lourido y Landro) que desembocan en las rías, disminuyeron en el siguiente orden: $H_4SiO_4 > NO_3^- > NH_4^+$. El aporte de nutrientes de los ríos fue relativamente bajo en relación a la descarga total de la zona costera. Se observaron cambios significativos en los niveles de nutrientes en el agua de inundación mareal y agua intersticial de los sedimentos intermareales durante los cortos períodos de inundación. Los flujos de bentónicos de nutrientes debidos a la difusión molecular y al transporte inducido por la marea fueron cuantificados y comparados con el aporte de nutrientes de los ríos. Los flujos difusivos variaron desde 9.3 a 13.7 $nmol \cdot cm^{-2} \cdot d^{-1}$ para nitrato+nitrito, -1.32 a 30.1 $nmol \cdot cm^{-2} \cdot d^{-1}$ para amonio, -0.01 a 0.49 $nmol \cdot cm^{-2} \cdot d^{-1}$ para fosfato y -13.2 a 0.2 $nmol \cdot cm^{-2} \cdot d^{-1}$ para silicato. El transporte inducido por la marea siempre superó a los flujos difusivos, alcanzando una diferencia de hasta cuatro órdenes de magnitud en el caso del silicato. Estos valores indican la exportación de nutrientes desde el sedimento, la cual tiene lugar cuando el agua de inundación mareal alcanza los sedimentos intermareales. Los resultados de éste capítulo enfatizan la importancia de la marea en el intercambio sedimento-agua en sub-ecosistemas mareales.

Finalmente, en el Capítulo 5 se estudiaron diferentes parámetros físico-químicos, composición del fitoplancton, clorofila y producción primaria, durante enero de 2008 a enero de 2009 en la ría de Barqueiro. La producción primaria anual de la ría de Barqueiro fue de 280 $gC \cdot m^{-2} \cdot año^{-1}$. El valor medio de clorofila fue bajo en todos los períodos oscilando entre 0.35 $\mu g \cdot L^{-1}$ en otoño a 1.47 $\mu g \cdot L^{-1}$ en primavera. La información presentada en este capítulo, permitió definir por primera vez los periodos oceanográficos característicos para una ría del norte de Galicia, basándose en la biomasa de fitoplancton, composición taxonómica y características hidrográficas como: Primavera, Estratificación de Verano, Otoño e Invierno. El ciclo fue el habitual en zonas templadas oceánicas, con un bloom primaveral y baja biomasa el resto del año.

Thesis summary

This doctoral thesis had as overall objective, to study the main aspects concerning the biogeochemical processes taking place in the rias of the Northeast Atlantic continent-ocean boundary as part of the East Atlantic temperate coastal interface.

At the northernmost point of the Iberian Peninsula along the northern Galician coast, eastward of 8°W (Cape Ortegal), are located the Rias of Ortigueira (38 km^2 of surface), Barqueiro (10 km^2, and Viveiro (27 km^2). They form a whole named as Northern Galician Rias or Rias Altas.

In the first part of the Chapter 2, summer upwelling and downwelling processes were characterized in the Northern Galician Rias during July and August 2008. Thermohaline variables, dissolved oxygen, nutrient salts, chlorophyll, phytoplankton, ciliates and zooplankton abundances were measured at sections located in the Rias of Viveiro, Barqueiro and Ortigueira and their adjacent shelves. Ekman transport was calculated from data provided by QuikSCAT satellite, upwelling intensity estimated with upwelling index from the average daily geostrophic winds, and SST maps obtained from NASA GHRSST satellite. Ekman transport and SST distribution showed two different patterns: (i) seaward direction and upwelling favourable conditions on 13-22nd of July; (ii) coastward direction and downwelling favourable conditions from 23rd July to 19th August. During upwelling, TS diagram showed an intrusion of Eastern North Atlantic Central Water affecting the continental shelf but not the rias. Nutrient salt concentration increased with depth, reaching their maximum values near the mouth of Ria of Ortigueira. During downwelling, coastal water increased its temperature (18.5-19.8°C) and was retained inside rias; nutrients were nearly depleted, except for the innermost ria (estuarine zone) due to fluvial nutrient inputs. In this inner area, the maximum of chlorophyll-*a* (Ria of Barqueiro) was observed. Low phytoplankton abundances were measured in both cases, even though a short increase in the plankton biomass was observed inside rias during upwelling, while under downwelling a red tide of *Lingulodinium polyedrum* was detected.

In the Northern Galician shelf, the average of upwelling (downwelling) was 1.9 ± 0.8 (2.1 ± 1.0) events·yr^{-1} from May to September (1990-2008) considering at least one week with favourable wind conditions and UI averages out of the range of ± 500 m^3·s^{-1}·km^{-1}.

In the second part of Chapter 2, a winter shelf-water upwelling event (February 2008) was described for the first time in the Northern Galician Rias (NW Iberian Peninsula). , Inside the Ria of Barqueiro on February 20th, and after 9 consecutive days of upwelling favourable conditions the presence of seawater below 10m depth was observed. This water replaced the less saline water previously observed in January. This situation was in agreement with the analysed Ekman transport close to the northern Galician coast. In addition, TS diagram indicated a higher influence of upwelling eastward (Viveiro–Barqueiro–Ortigueira). Nutrient concentrations also suggested the presence of seawater from subsurface origin and slightly different to that of winter mixing. Plankton showed the existence of spring conditions related to solar radiation increase associated to upwelling favourable winds. The presence of some indicator species (i.e. *Strombidium sp., Dictyocha speculum,* etc.) also confirms the intrusion of shelf-water inside the ria.

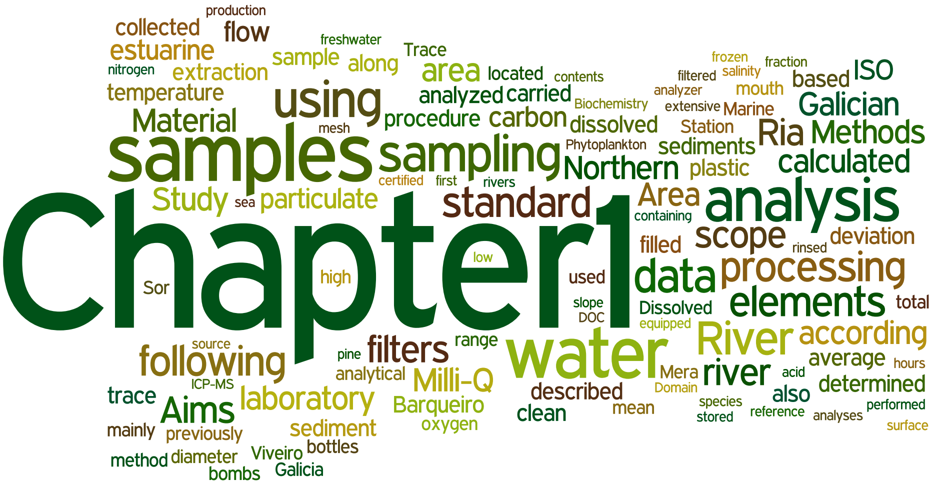
Finally in the third part of the Chapter 2, the evolution of a warm water mass related to the Iberian Poleward Current (IPC) was characterized along the northern Galician shelf in November 2008. The effect of the IPC was also analysed inside the northern Galician rias taking into account the hydrographical and biogeochemical properties measured on November 18^{th}. Water driven by the IPC was observed close to the mouth of the rias, around Cape Estaca de Bares, causing a nutrient salts decrease. Inside the rias a slight biological activity was found near surface resulting from fluvial contributions.

A summary of the water characteristics of the rivers Sor, Mera and Landro, pristine rivers that drain into the Northern Galician Rias (NW Iberian Peninsula), was presented in the Chapter 3. The analysis was based on fortnightly monitoring during 2008, for major and minor elements in the dissolved and particulate phase (Al, As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, U, Zn), nutrients (nitrate, nitrite, ammonium, phosphate, silicate), suspended particulate matter, chlorophyll-*a*, and tracers of water quality chemistry (DIN, PON, DOC, POC, C/N ratio). The studied rivers were not affected by urban, agricultural or industrial waste. Continental inputs of dissolved and particulate material via rivers flowing into the Northern Galician Rias were evaluated and annual fluxes of the chemical elements to the rias were calculated. This chapter provides a pioneering estimate of the overall amounts of nutrients and metals in the dissolved and particulate phases discharged to pristine ria systems.

Chapter 4 presents one of the first studies of its kind in ria systems. Concentrations of nitrate, nitrite, ammonium, phosphate and silicate were determined in river, tidal flooding, and pore water of intertidal sediments in the Northern Galician Rias of Ortigueira and Viveiro (NW Iberian Peninsula). The field studies were done in spring and summer 2008. Short-sediment cores and flooding waters were sampled in the intertidal area at air-exposed sediment conditions and several times during the first 20 minutes of the tidal flooding. Nutrient fluxes of rivers (Lourido and Landro) flowing into the rias decreased in the order $H_4SiO_4 > NO_3^- > NH_4^+$. Nutrients inputs from those rivers were low relatively to the total discharge to the coastal area. Striking changes of nutrient levels in flooding and pore waters of intertidal sediments were observed in the short periods of tidal flooding. Nutrient fluxes driven by molecular diffusion and tidal induced transport were quantified and compared to the nutrient river contribution. Diffusive fluxes ranged from 9.3 to 13.7 $nmol \cdot cm^{-2} \cdot d^{-1}$ for nitrate+nitrite, -1.32 to 30.1 $nmol \cdot cm^{-2} \cdot d^{-1}$ for ammonium, -0.01 to 0.49 $nmol \cdot cm^{-2} \cdot d^{-1}$ for phosphate, and -13.2 to 0.2 $nmol \cdot cm^{-2} \cdot d^{-1}$ for silicate. Tidal induced transport always exceeded diffusive fluxes, the difference reaching up to four orders of magnitude for the silicate. Those values indicate the nutrient export from sediment as tidal water floods the intertidal sediment. The overall results of this chapter emphasise the relevance of tide in promoting the sediment-water interchange in intertidal sub-ecosystems.

In the Chapter 5, physico-chemical parameters, phytoplankton assemblages, chlorophyll, and primary production were studied in the Ria of Barqueiro from January/08 to January/09. Throughout the year nutrients values, Chl-*a*, primary production and phytoplankton abundance were clearly lower when compared to those reported for the Western and Middle Galician Rias. Annual primary production for the Ria of Barqueiro was 280 $gC \cdot m^{-2} \cdot y^{-1}$. Mean chlorophyll was low in all periods ranging from around 0.35 $\mu g \cdot L^{-1}$ in winter and summer to 1.47 $\mu g \cdot L^{-1}$ in spring.

The information presented in this chapter, allowed to define for the first time the characteristic oceanographic periods for a Northern Galician Ria in relation to phytoplankton biomass, taxonomic composition and hydrographic characteristics as: Spring, Summer Stratification, Autumn and Winter. The cycle was the usual in the temperate zones, with a spring bloom and low biomass for the rest of year, with a slight increase in fall. The nutrients ratios point out that phytoplankton is limited by nitrogen.



Chapter1
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rinsed
filtered
frozen
salinity
fraction
analyzer
extensive

Chapter 1

Introducción general / General introduction

1.1. Procesos biogeoquímicos en sistemas costeros

La biogeoquímica abarca el estudio de los procesos químicos, físicos, geológicos y / o biológicos que rigen la composición del medio ambiente, lo cual incluye agua, suelo, aire, organismos vivos y la corteza terrestre.

Las zonas costeras son áreas complejas debido a su alta variabilidad en productividad, hábitats y especies (Burke et al., 2001). Están sometidas a cambios continuos, ya sea por causas naturales, como aumento del nivel del mar (Harvey and Nicholls, 2008; Oliver-Smith, 2009), sísmicas (LaJoie, 1986), mareas y corrientes oceánicas (Sleath, 1995; Pidwirny, 2006), etc., o antropogénicas, como introducción de especies exóticas (Blakeslee et al., 2011), urbanización, cambio del territorio por construcción de diques, presas, etc. (Benoit and Comeau, 2005). Muchos de estos cambios están claramente vinculados a la actividad humana (e.g. contaminación química), sin embargo, otros pueden tener una causa tanto natural como antropogénica (e.g. descargas fluviales, eutrofización). Esta heterogeneidad, tanto geográfica como temporal, es uno de los principales problemas para la gestión costera (Crossland et al., 2005).

Los sistemas costeros son muy variables e incluyen ecosistemas tan distintos como fiordos, manglares, estuarios o rías, lo cual hace de cada uno de ellos un sistema particular de estudio. Aunque existen diferentes definiciones dependiendo el enfoque usado (geográfico, político, biológico, etc.), en un contexto general, la zona costera puede definirse

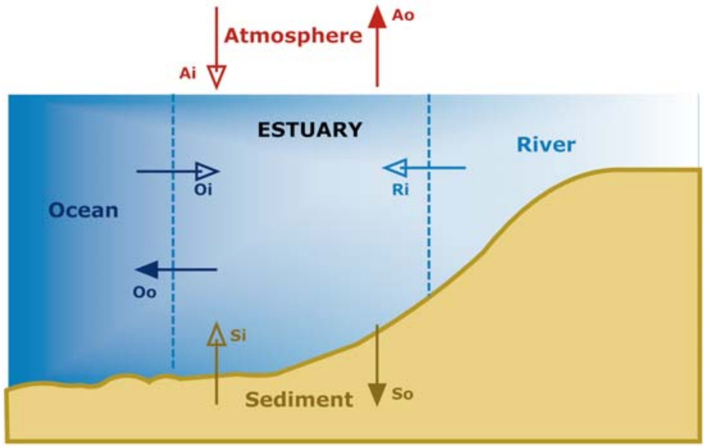

Figure 1.1.1. Schematic representation of incoming (i) and outgoing (o) fluxes of dissolved and particulate compounds in estuarine systems. *Representación esquemática de los flujos entrantes (i) y salientes (o) de compuestos disueltos y particulados en los sistemas estuarinos.*

como el espacio de transición en que se producen los principales intercambios de materia y energía entre los ecosistemas marinos y terrestres.

En la Figura 1.1.1, se presenta de manera esquemática una zona costera estuárica con sus fronteras: marina, bentónica, atmosférica y fluvial, donde tienen lugar los principales procesos de intercambio. Las zonas costeras actúan como sumidero del 75-90% de la materia particulada en suspensión proveniente de los ríos (Gattuso et al., 1998), por tanto, si conociésemos la naturaleza de los flujos a través de las zonas frontera y los procesos que los afectan (químicos, físicos, geológicos y/o biológicos) podríamos obtener el balance biogeoquímico del sistema (Dyer and Orth, 1994).

En los estuarios el acoplamiento de los procesos biogeoquímicos y físicos puede ocurrir en diferentes escalas espaciales (Geyer et al., 2000), las cuales abarcan desde kilómetros (p.e. eventos de afloramiento, ver Capítulo 2) a centímetros (p.e. flujos en la frontera sedimento-agua, ver Capítulo 4). La comprensión del rol que representan los procesos biogeoquímicos en la regulación química y biológica de los sistemas costeros es fundamental para mejorar su gestión (Hobbie, 2000; Bianchi, 2007), sin embargo, estos procesos son todavía poco conocidos (LOICZ, 2005)

Durante los últimos años, el estudio de los procesos biogeoquímicos en sistemas costeros ha sido un tema prioritario dentro

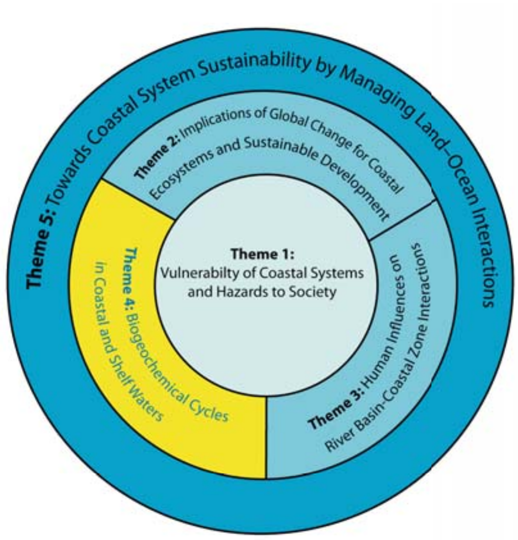

Figure 1.1.2. LOICZ research themes. *Temas de investigacion del LOICZ.*

de diversos proyectos de investigación a nivel mundial: Land Ocean Interactions in the Coastal Zone - LOICZ I; LOCZ II (LOICZ, 2005), Joint Global Ocean Flux Study - JGOFS (SCOR, 1990), Surface Ocean-Lower Atmosphere Study (SOLAS, 2004), Past Global Changes (PAGES, 2009), Integrated Marine Biogeochemistry and Ecosystem Research (IMBER, 2005).

El Programa Internacional Geosfera-Biosfera (IGBP) y el Programa Internacional sobre las Dimensiones Humanas del Cambio Ambiental Global (IHDP), a través del proyecto LOICZ, trabajan para apoyar la sostenibilidad y la adaptación al cambio global en las zonas costeras. Para alcanzar su objetivo, el LOICZ ha definido cinco temas prioritarios de investigación (Fig. 1.1.2) (LOICZ, 2005):

Tema 1. Vulnerabilidad de los sistemas costeros y riesgos para la sociedad.

Tema 2. Implicaciones del cambio global para los ecosistemas costeros y el desarrollo sostenible.

Tema 3. Influencias antropogénicas en las interacciones entre cuencas y zonas costeras.

Tema 4. Ciclos biogeoquímicos en zonas costeras y de plataforma continental.

Tema 5. Alcanzar la sostenibilidad del sistema costero mediante la gestión de las interacciones tierra-océano.

El esfuerzo científico del LOICZ está enfocado a la cuantificación de los flujos biogeoquímicos dentro de la zona costera, los cuales son altamente relevantes para el cambio global del medio ambiente (GEC) (Crossland et al., 2005). Específicamente dentro del Tema 4 del LOICZ, que sirve como marco general a ésta tesis doctoral, se han planteado los siguientes objetivos de investigación:

1. Proporcionar valoraciones cuantitativas y predicciones de la contribución de los flujos biogeoquímicos costeros (locales) a los ciclos biogeoquímicos a escalas regional y global.
2. Proporcionar acceso a las herramientas y bases de datos necesarias para permitir la valoración y la predicción de los efectos del cambio global sobre los ciclos biogeoquímicos, hábitats y ecosistemas costeros y de plataforma a una escala local.
3. Abordar aspectos científicos clave para resolver el importante papel que desempeñan el acoplamiento pelágico-bentónico, los procesos sedimentarios y los ciclos biogeoquímicos regulados por microorganismos.
4. Desarrollar y facilitar el uso de nuevas herramientas y métodos para la observación, seguimiento, análisis y predicción en la biogeoquímica de la zona costera y de plataforma.

1.2. Las rías del norte de Galicia / The Northern Galician Rias

Las rías son ensenadas costeras formadas durante la transgresión flandriense por el hundimiento de antiguos valles fluviales, y se caracterizan por lineas de costas irregulares y una plataforma de roca expuesta (Goudie, 2004). En el punto más septentrional de la Península Ibérica a lo largo de la costa norte de Galicia, al este de Cabo Ortegal (8°W), se encuentran las rías de Ortigueira (superficie: 38 km^2), Barqueiro (10 km^2), y Viveiro (27 km^2) (Fig. 1.2.1). Estas rías forman un conjunto denominado como 'rías del norte' o 'rías altas', (Fig. 1.2.2), según la clasificación tectónica propuesta por Torre Enciso (1958).

A diferencia de las rías Bajas (localizadas en la costa oeste de Galicia, i.e. al sur de Cabo Finisterre; rías Baixas en gallego) y las rías medias de Galicia (costa noroeste, i.e. entre Cabo Finisterre y Cabo Ortegal), las rías del Norte no han sido ampliamente investigadas. El conocimiento actual de esta región se basa en artículos específicos y parciales, relacionados con aspectos biológicos (Fischer-Piette y Seoane-Camba, 1962; Bode et al, 1996; Sánchez et al, 1998; daSilva et al, 2006), geológicos (Diez, 1999; Otero et al, 2000; Delgado et al, 2002; Hernández-Vega et al, 2005; Alonso y Pages, 2007; Lorenzo et al, 2007; Arenas et al, 2009) y oceanográficos (Anderson et al, 1990; Alvarez et al, 2010;

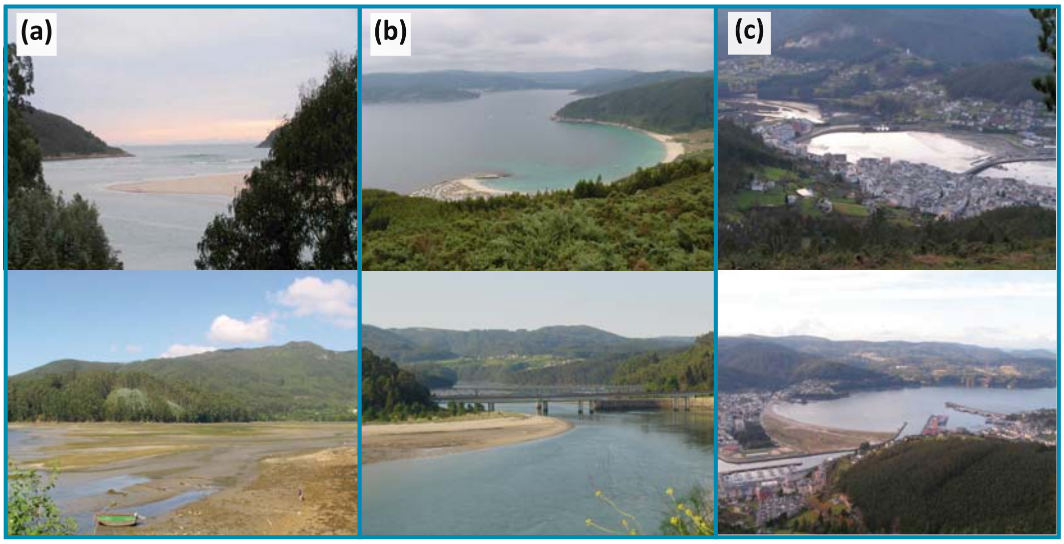

Figure 1.2.1. View of the Northern Galician Rias of Ortigueira (a), Barqueiro (b) and Viverio (c). *Pictures: N.Ospina-Alvarez, R. Prego. Vista de las rías del norte de Galicia (a), Barqueiro (b) and Viverio (c).*

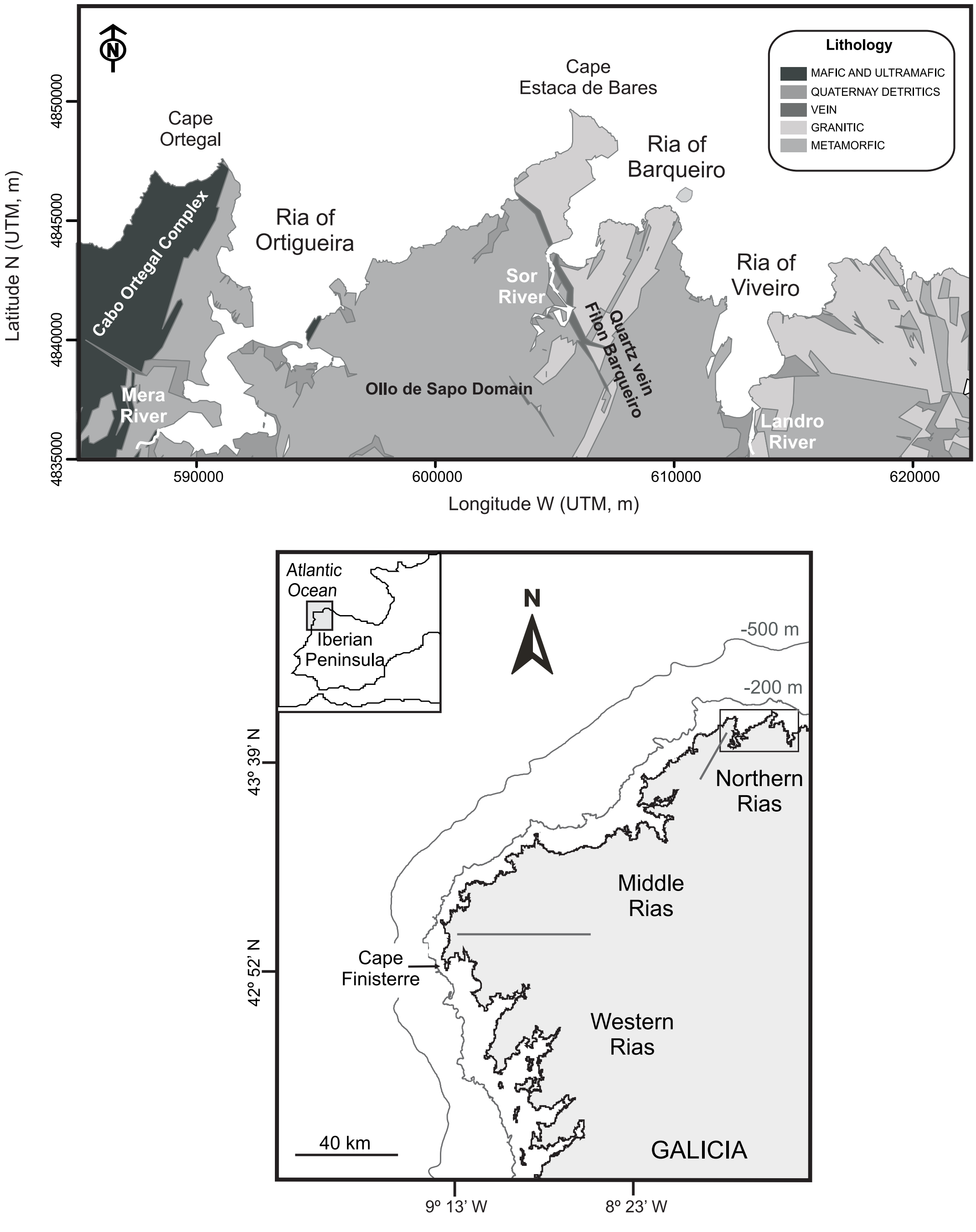

Figure 1.2.2. Geographic situation and lithological map of the study area. Lithology data available from the Spatial Data Infrastructure of Galicia http://sitga.xunta.es/sitganet/index.aspx?lang=gl. *Situación geográfica y mapa litológico del área de estudio. Datos litológicos disponibles a través de la Infraestructura de Datos de Galicia.*

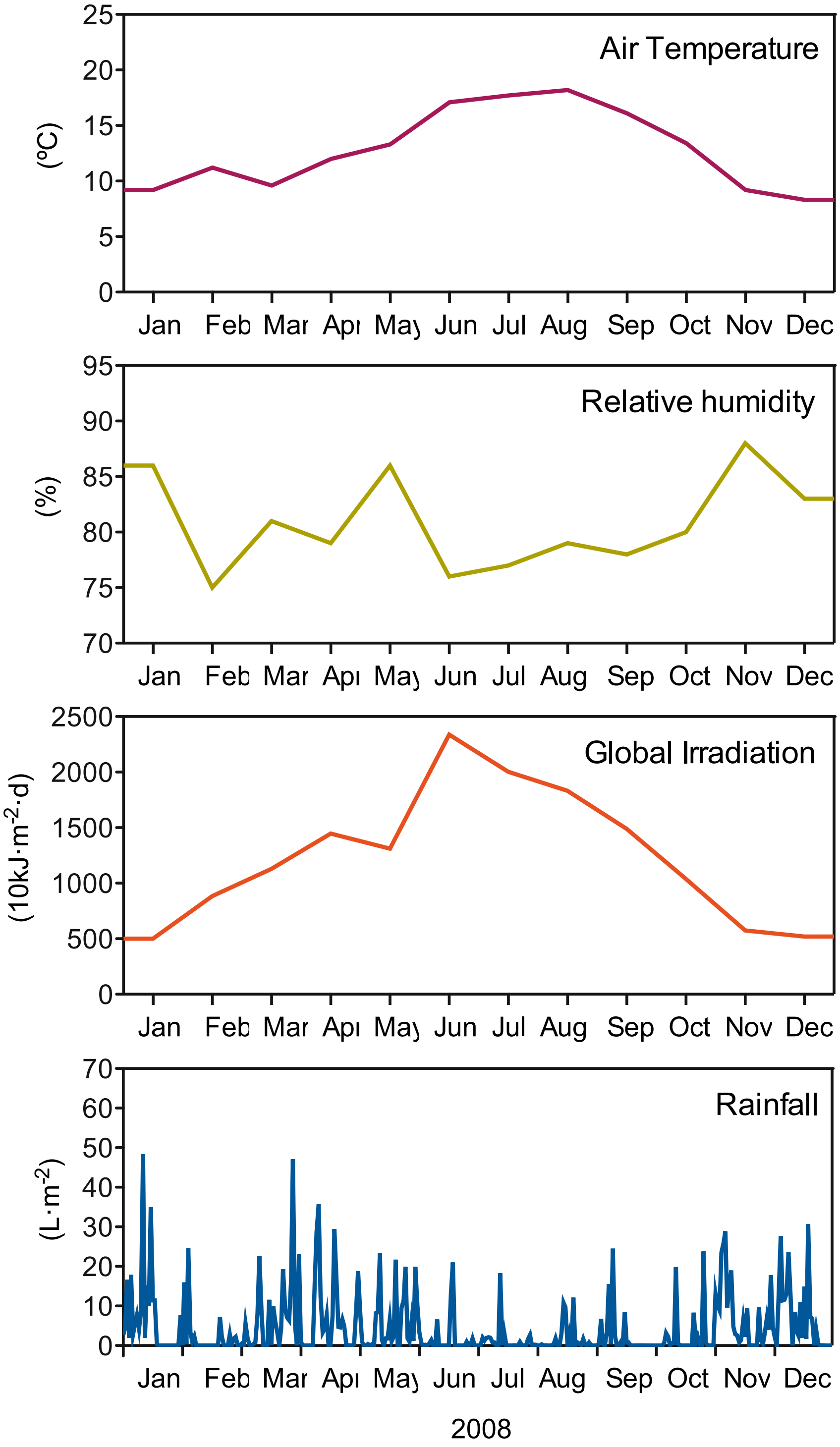

Figure 1.2.3. Fluctuation of meteorological variables at the Northern Galician Rias during 2008. (Data from 'Penedo do Galo' Station, Regional Weather Forecast Agency - METEOGALICIA). *Fluctuación de variables meteorológicas en las rías del norte de Galicia durante el año 2008 (Datos obtenidos de la estación 'Penedo do Galo', Servicio Meteorológico Regional, METEOGALICIA).*

Iglesias y Carballo, 2010).

La hidrodinámica de las rías del norte de Galicia está controlada principalmente por los procesos marinos, excepto en el interior de la zona estuárica (rango mareal de 2-4 m), que está parcialmente cerrada por barreras de playa bien desarrolladas (Lorenzo et al, 2007). Por esta razón las rías del norte de Galicia puede ser consideradas como valles profundos con forma de embudo, caracterizadas por una línea costera relativamente sumergida, abiertas al oleaje del norte, con profundidad de 30-35 m en el canal central y alrededor de 100 Hm^3 de contenido de agua.

En esta zona geográfica, el clima es húmedo templado oceánico (tipo Cfb de Köppen). Durante las campañas en el año de muestreo (2008), la temperatura media del aire fue de 10.4°C con una fluctuación térmica de 8°C y un valor promedio de humedad del 80% (datos de la estación meteorológica ‘Penedo do Galo’, Meteogalicia). La irradiación global diaria promedio fue de 1112·10 $kJ·m^{-2}$, y la precipitación media fue de 4.33 $L·m^{-2}$ con un total de 168 días de lluvia (Fig. 1.2.3). El régimen de vientos se caracteriza por los de componente oeste en otoño-invierno, mientras que en primavera y verano predominan los provenientes del Este.

Los ríos que vierten sus aguas hacia las rías del norte de Galicia son un ejemplo de un sistema natural con baja influencia antropogénica. Fluyen a lo largo de bosques de pinos y eucaliptos, con sólo una pequeña proporción de superficie cultivada en los valles de inundación. La densidad de población es baja (≈70 $h·km^{-2}$), y se concentra principalmente cerca de las desembocaduras fluviales, como en el caso de Viveiro y Celeiro.

La principal fuente de la ría de Ortigueira es el río Mera (área de la cuenca: 127 km^2), aunque pequeños afluentes como el Baleo (53 km^2), Landoi (21 km^2) y Lourido (10 km^2) también vierten sus aguas en la ría. El flujo medio anual del río Mera es de 6.0 $m^3·s^{-1}$ (Estación de aforo 443, Augas de Galicia de 2011); fluye a través de extensos bosques de pinos y eucaliptos, formando un estuario muy superficial, completamente inundado y con extensos pantanos. El río Mera tiene su origen a 752 m sobre el nivel del mar, con una pendiente media del 1.60% y una longitud de 29 km, y fluye a lo largo una litología variada de rocas metamórficas, como gneis, pizarras, cuarcitas y esquistos del dominio geológico de Ollo de Sapo (Fig. 1.2.2). También fluye a lo largo de rocas máficas, que forman parte del Complejo de Cabo Ortegal (Fig. 1.2.2), con algunas zonas de peridotitas serpentinizadas y ecoglitas situadas aguas arriba; de tal manera, que la permeabilidad de la cuenca del río es muy baja.

El río Sor desemboca en la Ria de Barqueiro, situada al oeste del Cabo Estaca de Bares (43°47'N, 7°41'W). La cuenca fluvial del río Sor cubre 202 km^2 con un caudal medio de 15.2 $m^3·s^{-1}$ (Estación de aforo 440, Augas de Galicia 2011). El río

Sor nace a 620 m sobre el nivel del mar, tiene una pendiente media del 1.28% y una longitud de 49 km. La cuenca del río Sor es muy impermeable, por lo cual, el índice de drenaje del río es alto, representando un 89% en su desembocadura, lo que indica que la mayor parte de la lluvia que cae en el área de la cuenca llega a la Ria de Barqueiro. La cuenca del río Sor, se caracteriza principalmente por matorrales y bosques de pinos y eucaliptos. En cuanto a su geología, la cuenca del Sor está formada principalmente de pizarras, gneis y cuarcitas.

La ría de Viveiro se abre hacia el norte y se separa de la Ria de Barqueiro por la Isla de Coelleira, también en el lado izquierdo del Cabo Estaca de Bares (Fig. 1.2.2). El río Landro desemboca en la cabecera de la ria, y cubre una cuenca de 271 km^2. Este río nace a 800 m sobre el nivel del mar, tiene una pendiente media del 2.64%, llegando a la ría de Viveiro después de 31 km de recorrido. Tiene un caudal medio de 9.3 $m^3 \cdot s^{-1}$ (Estación de aforo 438, Augas de Galicia 2011), y desarrolla un estuario en su parte interior, con amplios arenales y una barra. El índice de drenaje en la desembocadura del río es alto, alrededor del 60%, debido a que la permeabilidad de la cuenca es media. La cuenca del río Landro cubre un área mixta de gneises y metasedimentos del dominio de Ollo de Sapo de (Fig. 1.2.2) y de rocas graníticas-alcalinas que son parte del dominio Manto de Mondoñedo.

The Northern Galician Rias

The rias are coastal inlets formed during the Flandrian Transgression by the drowning of a former river valley, and are characterized by irregular coastlines and exposed rock platform (Goudie, 2004). The Rias of Ortigueira (38 km^2 of surface), Barqueiro (10 km^2, and Viveiro (27 km^2) (Fig. 1.2.1), are located at the northernmost point of the Iberian Peninsula along the northern Galician coast, eastward of 8°W (Cape Ortegal). They form a whole named as *Northern Galician Rias* or *Rias Altas*, (Fig. 1.2.2) according to the tectonic classification proposed by Torre Enciso (1958).

Unlike the Western Rias (i.e. south of Cape Finisterre, also know as 'Rias Baixas') and Middle Rias of Galicia (northwest coast, i.e. between Cape Finisterre and Cape Ortegal), the Northern Rias have been poorly investigated. Current knowledge of this region is based on specific and partial aspects, about biology (Fischer-Piette and Seoane-Camba, 1962; Bode et al., 1996; Sánchez et al., 1998; daSilva et al., 2006), geology (Diez, 1999; Otero et al., 2000; Delgado et al., 2002; Hernández-Vega et al., 2005; Alonso and Pagés, 2007; Lorenzo et al., 2007; Arenas et al., 2009) and oceanography (Anderson et al., 1990; Alvarez et al., 2010; Iglesias and Carballo, 2010).

Hydrodynamics of the Northern Galician Rias are mainly controlled by marine processes, except at the innermost estuarine zone (mesotidal: tidal range of 2-4 m), which is partially enclosed with well-developed beach barriers (Lorenzo et al., 2007).

For this reason the Northern Galician Rias can be considered as funnel-like incised valleys characteristic of a relatively submerged coastline (Evans and Prego, 2003), with 30-35 m depth at their open mouths to the north swell, and around 100 hm^3 of water content.

In this area, climate is wet temperate oceanic (Cfb Köppen type). The annual average air temperature (data from 'Penedo do Galo' Station, Meteogalicia) during the sampling year 2008 was 10.4 °C, with a thermal fluctuation of 8 °C and an average humidity of 79.6%. Daily global irradiation was on average 1112 $10kJ \cdot m^{-2}$. Mean rainfall in 2008 was 4.33 $L \cdot m^{-2}$ with a total of 168 days of rain (Fig. 1.2.3). Westerly winds in autumn-winter, characterized the wind regime in this zone, while in spring and summer easterly winds prevail. Nevertheless, easterly winds can be also observed in autumn-winter (Gomez-Gesteira et al., 2006).

The rivers draining the Northern Galician Rias are an example of a natural system with very reduced anthropogenic impact. They flow along pine and eucalyptus forests and scrublands with only a small proportion of cultivated areas on the floodplain. Population density is low (≈70 $inhabitants \cdot km^{-2}$), and concentrated mostly near the river mouth, as in the case of the towns of Viveiro and Celeiro.

The Mera River, situated at the head of the Ria of Ortigueira (basin area: 127 km^2) is the main fluvial source flowing into the ria, although small tributaries as the Baleo (53 km^2), Landoi (21 km^2) and Lourido (10 km^2) streams also drain into the ria. Mera annual average flow is 6.0 $m^3 s^{-1}$ (Station 443; Augas de Galicia 2011). The larger Mera River flows through extensive pine and eucalyptus forests, and forms a very shallow estuary, quite filled and containing extensive marshlands. Mera River has its source at 752 m above sea level, with a mean slope of 1.60% and a length of 29 km. It flows through a varied lithology of metamorphic rocks, e.g. gneiss, slates, quartzites and schists from the Ollo de Sapo Domain (Fig. 1.2.2). Downstream it flows across mafic rocks, which form part of the Cabo Ortegal Complex (Fig. 1.2.2), with few zones of serpentinized peridotites and ecoglites. Therefore, the permeability of the river basin is very low.

The Sor River drains into the Ria of Barqueiro, located west of Cape Estaca de Bares (43°47'N, 7°41'W). Fluvial basin of the Sor River covers 202 km^2 with an average discharge of 15.2 $m^3 s^{-1}$ (Station 440; Augas de Galicia 2011). The Sor River have its source at 620 m above sea level, with a mean slope of 1.28% and a length of 49 km. The river basin is highly impermeable, thus the drainage index of this river is high, with 89% of rain reaching its mouth. Land use in the Sor River basin is mainly scrubland and pine and eucalyptus forests. The surrounding area of the Ria of Barqueiro is mainly composed by two-mica granite and the presence of white quartz veins NWN-oriented, but catchment is mainly made up of gneisses slates and quartzites.

The Ria of Viveiro opens to the north and is separated from the Ria of Barqueiro by Coelleira Island (Fig. 1.2.2). The Landro River is located at its mouth, and covers an area of 271 km^2. This river rises to 800 m above sea level, and has a mean slope of 2.64%, reaching the Ria of Viveiro after 31 km. It has a mean discharge of 9.3 $m^3 s^{-1}$ (Station 438; Augas de Galicia 2011), with an estuary in the inner part of the inlet, with extensive marshlands and a beach barrier. The drainage index at the river mouth is high, around 60% since the permeability of the catchment is medium. The basin of the Landro River covers a mixed area of gneisses and metasediments within the Ollo de Sapo Domain (Fig. 1.2.2) and granitic alkaline rocks within the Manto de Mondoñedo Domain.

1.3. Objetivos / Aims and scope

Esta tesis doctoral responde a la siguiente pregunta:

¿Forman las rías del norte de Galicia, un grupo aparte de las otras rías gallegas de acuerdo con sus características oceanográficas y procesos biogeoquímicos?

Para responder a la pregunta anterior, el objetivo general de esta tesis es el siguiente:

Estudiar los aspectos relacionados con los procesos biogeoquímicos que tienen lugar en las rías de la frontera continente-océano del Atlántico Nororiental como parte de la interfase costera templada del Atlántico Este.

Este objetivo general se enmarca dentro de los temas prioritarios del programa internacional LOICZ, y para alcanzarlo cada capítulo de esta tesis incluyen objetivos específicos:

- Caracterizar los eventos de afloramiento/surgencia y contra-surgencia en las rías del norte de Galicia.
- Analizar la frecuencia de las condiciones meteorológicas favorables a eventos de afloramiento/surgencia y contra-surgencia en la costa norte de Galicia.
- Determinar si la Ria del Barqueiro es afectada por los eventos de afloramiento y cuál es la influencia de la entrada de nutrientes y la variabilidad estacional de los ensambles de fitoplancton.
- Caracterizar la evidencia de procesos de afloramiento invernal y sus consecuencias en los patrones biológicos y químicos en la columna de agua de las rías gallegas del Norte.
- Determinar la recurrencia durante largos periodos de tiempo de eventos de afloramiento invernal en el norte de la costa gallega.
- Comparar los patrones oceanográficos de las rías del norte de Galicia con la información existente acerca de las rías medias y bajas de Galicia.
- Caracterizar masas de agua relacionadas con la corriente ibérica que va hacía el polo (IPC) en la plataforma continental del norte de Galicia y su influencia en los patrones químicos y biológicos al interior de las rías del norte de Galicia.
- Caracterizar la materia disuelta transportada por los ríos que desembocan en las rías del norte de Galicia y la cuantificación de sus flujos anuales.
- Evaluar la descarga de sedimentos, los flujos anuales y las características del material particulado de los ríos que desembocan en las rías del norte de Galicia.
- Cuantificar la contribución de los sedimentos en el presupuesto de nutrientes en las zonas inter-mareales de las rías gallegas del Norte.

Aims and scope

The thesis aims to answer the following question:

Are the Northern Galician Rias a separate group of the other Galician Rias according to their oceanographic characteristics and biogeochemical processes?

To answer the precedent question the overall objective of this thesis is:

To study the main aspects concerning the biogeochemical processes taking place in the rias of the Northeast Atlantic continent-ocean boundary as part of the East Atlantic temperate coastal interface.

The above overall objective is outlined within the priority themes of the international program LOICZ, and to fulfill it, each chapter of this thesis include the following specific objectives:

- To characterize summer upwelling and downwelling events in the Northern Galician Rias.
- To analyse the frequency of meteorological conditions favourable to upwelling and downwelling events in the northern coast of Galicia.
- To determine whether upwelling events affect the Ria of Barqueiro and how much influence the nutrients input and the seasonal variability of phytoplankton assemblages.
- To characterize winter shelf-water upwelling evidence and its consequences on the biological and chemical patterns in the water column of the Northern Galician Rias.
- To determine the recurrence of these winter events at the northern Galician coast over long periods.
- To compare the oceanographic patterns of the Northern Galician Rias with the existing information about the Middle and Western Rias of Galicia.
- To characterize of warm water masses related to the Iberian Poleward Current (IPC) at the northern Galician shelf and its influence on the chemical and biological patterns inside the Northern Galician Rias.
- To characterize the dissolved material transported by the rivers of the Northern Galician Rias and the quantification of their annual fluxes.
- To assess the sediment discharge, annual fluxes and characteristics of the particulate material of the rivers flowing to the Northern Galician Rias.
- To quantify the sediments contribution to the budget of nutrients in intertidal areas of the Northern Galician Rias.

1.4. Materiales y Métodos / Materials and Methods

Diferentes muestras de agua (Fig. 1.4.1) y sedimentos (Fig. 1.4.2) se recogieron en las rías del norte de Galicia durante el año 2008. Su tratamiento y análisis se describe a continuación.

Oxígeno disuelto y variables termohalinas

El oxígeno disuelto se analizó en muestras de agua (margen de error de ± 0.2) siguiendo el método Winkler (Grasshoff et al., 1999) utilizando un Titrino 702-MS (Metrohm) (Fig. 1.4.3). Los porcentajes de saturación de oxígeno se calcularon a partir de la concentración de oxígeno disuelto, la salinidad y los datos de temperatura de las muestras (Aminot, 1983), con un margen de error de ± 0.2. Las muestras se fijaron y el análisis se realizó en las 24 horas posteriores a su recolección.

La temperatura del agua y la salinidad del agua fluvial y estuarina se midieron in situ utilizando un equipo WTW Multiline P4 (margen de error de ±0.1), el calibrado con soluciones estándar se realizó antes de cada toma de muestras. Los perfiles verticales de temperatura y salinidad en aguas estuarinas y oceánicas se registró con un CTD Seabird-9/11plus colocado en una roseta SeaBird-32 (*RV Mytilus*) y un

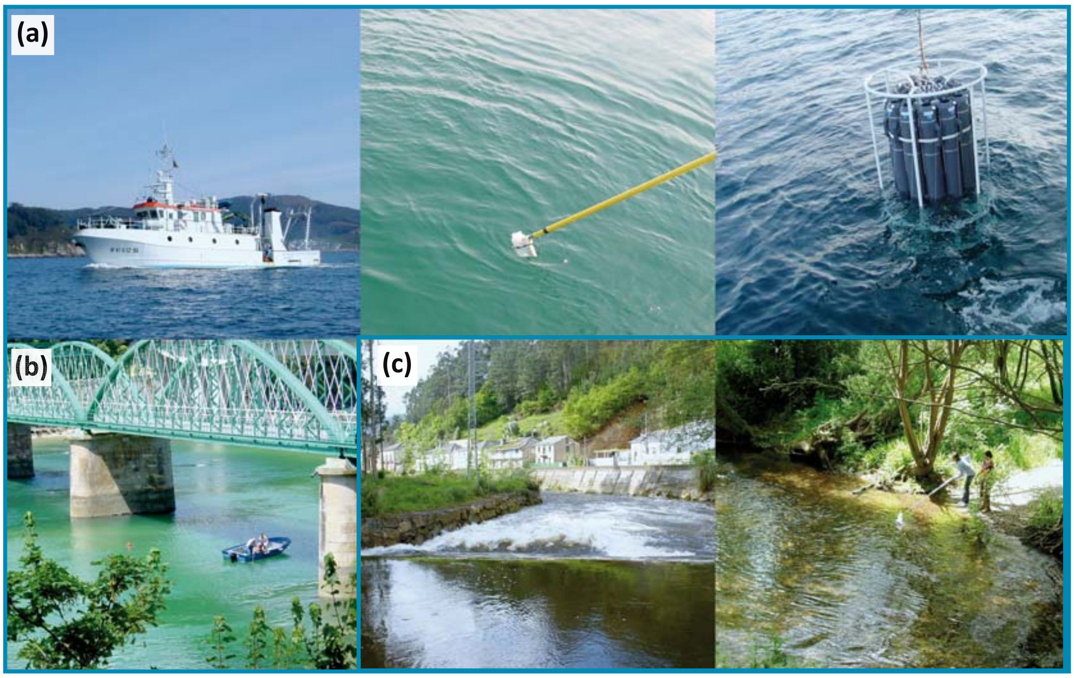

Figure 1.4.1. Water sample collection from: ocean (a), rias (b) and rivers (c). IIM-CSIC Research Project INTERESANTE. *Pictures: N.Ospina-Alvarez, R. Prego. Recolección de muestras de agua oceánica (a), de rias (b) y ríos (c). IIM-CSIC Proyecto INTERESANTE.*

Figure 1.4.2. Sediment sampling at the Northern Galician Rias. IIM-CSIC Research Project INTERESANTE. *Pictures: J. Raimundo, N.Ospina-Alvarez, R. Prego. Muestreo de sedimentos en las rías del norte de Galicia. IIM-CSIC Proyecto INTERESANTE.*

CTD SeaBird-25 con sensores PAR y de fluorescencia, colocado en una mini roseta General Oceanic (*RV Lura*).

Clorofila-*a* y producción primaria

Las muestras para análisis de clorofila-*a* se filtraron inmediatamente a través de un filtro Whatman GF/F (25 mm de diámetro, 0.7 μm) y la concentración de clorofila se determinó por espectrofluorometría (Neveux y Panouse, 1987) posteriormente a la extracción con acetona al 90%, según el método descrito por la UNESCO (1994).

La producción primaria se determinó siguiendo el método del ^{14}C utilizando incubaciones de 2h bajo condiciones simuladas in situ (Steemann-Nielsen, 1952); después de la incubación las muestras se filtraron a través de filtros GF/F y las tasas de producción primaria diaria calculadas multiplicando las tasas por hora por el

Figure 1.4.3. 702-MS Titrino (Metrohm). Marine Biogeochemistry Group, (IIM-CSIC) Vigo. *702-MS Titrino (Metrohm). Grupo de Biogeoquímica Marina, (IIM-CSIC) Vigo.*

número total de horas durante el día, excluyendo las primeras 2 horas después de la salida del sol y las últimas 2 horas antes del atardecer (Varela et al., 2005).

Carbono y nitrógeno disuelto y particulado

Para determinar el carbono orgánico particulado (POC) y nitrógeno orgánico particulado (PON) muestras de agua se filtraron a través de filtros de microfibra de vidrio (Whatman GF/F, 0.7 µm). Teniendo en cuenta que la contribución de carbonato al carbono total representa sólo hasta un 2% del carbono particulado total (Fernández et al, 1995; Palanques et al, 2002), el carbonato no fue eliminado de los filtros de POC. Los análisis se realizaron en un analizador elemental CNH EA1108 (Carlo Erba Instruments) en la Universidad de A Coruña (SAI-UDC). Para la presentación de los resultados se usaron valores en unidades molares. Las relaciones C:N (mol: mol) se calcularon en términos de POC: PON.

Las muestras para el carbono orgánico disuelto (COD) y nitrógeno orgánico disuelto (DON) se tomaron en botellas de polietileno de 50 mL previamente lavadas con HCl, y posteriormente congeladas a -20 ° C hasta su análisis. Los análisis del DOC y DON se llevaron a cabo en el laboratorio de la Unidad de Biogeoquímica Marina (INTECMAR, Vilagarcía de Arousa), utilizando un analizador Shimadzu TOC-VCSH con oxidación catalítica de alta temperatura (HTCO) y detección de infrarrojos no dispersivo (NDIR), siguiendo el procedimiento descrito por Álvarez-Salgado y Miller (1998). Los análisis de DOC fueron acreditados por la ENAC de acuerdo a la norma UNE-EN ISO/IEC 17025:2005.

Fitoplancton, zooplancton y ciliados planctónicos

Las muestras de fitoplancton se preservaron en solución de Lugol y mantenidas en la oscuridad hasta su estudio. Las muestras fueron contadas como células mL^{-1} usando un microscopio invertido Nikon Eclipse TE2000-U, siguiendo la técnica descrita por Utermöhl (1958). Entre 500 y 1.000 células fueron contadas por muestra, siguiendo la nomenclatura de especies de Tomás (1997). El carbono del fitoplancton se calculó de acuerdo a Strathmann (1967). Debido a que valvas vacías de diatomeas fueron observadas con frecuencia, se realizó una estimación de su abundancia.

Los ciliados planctónicos se muestrearon e identificaron utilizando un protocolo similar al descrito para el fitoplancton. Las muestras se sedimentaron durante 48 horas en cámaras de 100 mL. La clasificación taxonómica siguió los criterios Lynn y Small (2002). El recuento de los individuos se realizó utilizando una aumento de 200x.

Las muestras de microzooplancton (40-200 µm) se recogieron con lances verticales usando una red tipo Bongo de 20 cm de diámetro y malla de 40 µm. Las muestras se tamizaron a través de malla de nylon de 40 µm y fijadas en borato-formalina tamponada al 2% antes del examen microscópico. La clasificación taxonómica de las especies se basó en los criterios de Valdés et al. (1991). Las muestras de mesozooplancton se recogieron mediante lances oblicuos con una red tipo Juday-Bogorov con malla de 200 µm (50 cm de diámetro) y equipadas con medidores de flujo y profundidad (Bode et al., 1998). Las muestras se fijaron en formalina al 4% antes de su análisis microscópico.

Sales nutrientes

Muestras de sales nutrientes (nitrato, nitrito, amonio y fosfato) fueron recogidas en botellas plásticas de 50 mL, previamente lavadas con HCl, y congeladas inmediatamente después de su recolección a -20°C. Debido a que la polimerización de ortosilicatos puede producirse en muestras de agua dulce congelada (Kobayashi, 1966), se tomaron adicionalmente muestras de agua de los ríos utilizando tubos plásticas de 10mL. Las muestras se conservaron a 4 °C y el silicato disuelto analizado al día siguiente. Los análisis de sales nutrientes se realizaron el laboratorio del Grupo de Biogeoquímica Marina (IIM-CSIC, Vigo), utilizando un autoanalizador Integral Futura (Alianza Instrumentos) (Fig. 1.4.4) con líneas separadas de nitrato, nitrito, amonio, fosfatos y silicatos de acuerdo a los métodos estándar colorimétricos (Hansen y Koroleff, 1999). Los límites de detección, definidos como tres veces la desviación estándar de 10 mediciones repetidas de un blanco, fueron: 0.14 µM para NO_3^-, 0.002 µM para NO_2^-, 0.01 µM para NH_4^+, 0.08 µM para HPO_4^{-2} y 0.14 µM para H_4SiO_4.. Para las muestras de agua marina, la exactitud del procedimiento analítico se evaluó mediante el análisis de materiales de referencia certificados: MOOS-1 (nutrientes en agua marina, NRC, Canadá), obteniendo resultados acorde con los valores certificados. La precisión del análisis, definida como la desviación estándar relativa (RSD), fue siempre inferior al 5%.

Elementos traza

Todo el material plástico de laboratorio empleado para el muestreo, almacenamiento y tratamiento de las muestras fue previamente lavado con HNO_3 al 50% durante 48 h y lavado con agua Milli-Q. Luego fue transferido a un recipiente con HCl al 10% durante al menos una semana. Posteriormente el material fue enjuagado varias veces con agua Milli-Q y secado en una cabina de flujo laminar (ISO Clase 5) antes de su uso.

La recolección de las muestras fue realizada siguiendo la técnica 'manos limpias /manos sucias (US-EPA, 1996a), implicando dos o más personas que

Figure 1.4.4. Integral Futura autoanalyser system (Alliance Instruments). Marine Biogeochemistry Group, (IIM-CSIC) Vigo. *Autoanalizador Integral Futura (Alliance Instruments). Grupo de Biogeoquímica Marina, (IIM-CSIC) Vigo.*

colaboran con tareas específicas durante el muestreo para evitar la contaminación de las muestras (Fig. 1.4.5).

El manejo, procesamiento y análisis de muestras fue realizado en un laboratorio ultra-limpio (ISO Clase 7) (Fig. 1.4.6), utilizando guantes de polietileno libres de talco, y siguiendo técnicas limpias para elementos traza (Sander et al, 2009;. GEOTRACES , 2010).

Elementos traza en agua

Las muestras para análisis de elementos traza en agua se recogieron en botellas de LDPE de 1 litro previamente lavada con HCl y enjuagadas con agua Milli-Q. Las botellas fueron llenadas con agua Milli-Q a pH 2 y almacenadas en bolsas zip-lock hasta su uso. Todos los muestreos se realizaron siguiendo técnicas limpias para elementos traza.

En el laboratorio portátil en tierra (puerto pesquero de Celeiro, España) , y dentro de las cuatro horas siguientes a la recolección (Chapman, 1992), las muestras se separaron en su fracción disuelta y particulada dentro una cabina de flujo laminar (ISO Clase 5) (Fig. 1.4.7). La separación fue realizada por filtración usando filtros de policarbonato Pall-Gelman

Figure 1.4.5. ‘Clean hands/dirty hands’ technique. 'Dirty hands' sampler is not in direct contact with the sample. 'Clean hands' sampler is only in direct contact with the sample or cleaned items. *Pictures: T. Frick. Técnica ‘manos limpias / manos sucias’.*

Figure 1.4.6. Ultra-clean laboratory (ISO Class 7). Marine Biogeochemistry Group, (IIM-CSIC) Vigo. *Laboratorio ultra-limpio clase ISO 7. Grupo de Biogeoquímica Marina, (IIM-CSIC) Vigo.*

de 0.45 µm (Fig. 1.4.8), previamente lavados con ácido (Suprapur HCl 1%) y pesados Las muestras para análisis de elementos traza disueltos fueron acidificadas con HNO_3 Suprapur (pH <2). Posteriormente los filtros se secaron, se pesaron de nuevo y se llevó cabo el calculo de la materia particulada en suspensión (SPM, $mg \cdot L^{-1}$). Seguidamente, los filtros de PSi fueron colocados en placas petri plásticas y almacenados a -20°C hasta la digestión en el laboratorio del Grupo de Biogeoquímica Marina (IIM-CSIC, Vigo). Los filtros de policarbonato se digirieron en un horno microondas Milestone MLS 1200 Mega, con HF (6 mL al 48%) y 2 mL de HNO_3 al 65%), en recipientes de Teflon® cerrados a presión de acuerdo a la directriz EPA 3052 (US-EPA, 1996b) para matrices de tipo silíceo. El contenido de los

Figure 1.4.7. Laminar flow cabinet (ISO-Class 5) at the onshore clean laboratory of Celeiro. *Cabina de flujo laminar clase ISO 5.*

recipientes fue vertido en matraces volumétricos de 25 mL y llenados con agua Milli-Q. La manipulación y análisis de las muestras fue llevado a cabo en un laboratorio limpio (ISO clase 7-8).

Los metales particulados fueron determinados en el laboratorio del Grupo de Biogeoquímica Marina (IIM-CSIC, Vigo) por GFAAS en un espectrómetro Varian SpectrAA 220 (Figura 1.4.9) equipado con corrección de fondo Zeeman (Cd, Co, Cr, Cu, Fe, Ni, Pb, V, Zn) y por FAAS (Al) en un espectrómetro AA100 Perkin Elmer con llama de óxido nitroso-acetileno. Previamente al análisis, los filtros de SPM se digirieron por microondas (Milestone 1200 Mega) en bombas de teflón con una mezcla de HNO_3 y HF de acuerdo al método EPA 3052 (US-EPA, 1996b)

Los metales disueltos en agua fluvial y estuárica fueron determinados de acuerdo con los métodos estándar (APHA, 1995) en el laboratorio del Departamento de Medio Ambiente Acuático (IPIMAR, Lisboa) con un ICP-MS (Thermo Elemental, X-Series) equipado con una cámara de spray

Table 1.4.1. Accuracy control of the analytical procedures employed for dissolved and particulate trace elements determination

Dissolved elements		**Al (nM)**	**As (nM)**	**Cd (nM)**	**Co (nM)**	**Cr (nM)**	**Cu (nM)**	**Fe (nM)**	**Mn (nM)**	**Mo (nM)**	**Ni (nM)**	**Pb (nM)**	**U (nM)**	**V (nM)**	**Zn (nM)**
SLRS-4	Certified	2001 ± 148	9.1 ± 0.8	0.11 ± 0.02	0.56 ± 0.10	6.3 ± 0.4	28.5 ± 1.3	1844 ± 89	61.3 ± 3.3	2.2 ± 0.2	11.4 ± 1.4	0.41 ± 0.03	0.21 ± 0.01	6.3 ± 0.6	14.2 ± 1.5
	Measurec	2140 ± 40	9.5 ± 0.5	0.12 ± 0.03	0.51 ± 0.05	6.3 ± 0.5	28.2 ± 1.2	1808 ± 18	60.9 ± 3.4	2.2 ± 0.2	10.7 ± 0.8	0.41 ± 0.04	0.19 ± 0.06	6.4 ± 0.2	14.2 ± 0.5
SLEW-3	Certified		18.1 ± 1.2	-	0.71 ± 0.17	3.52 ± 0.37	-	-	29.3 ± 4.0	-	21.0 ± 1.2	-	-	-	-
	Measurec		19.3 ± 1.3	-	0.65 ± 0.16	3.27 ± 0.34	-	-	29.1 ± 4.0	-	20.3 ± 1.2	-	-	-	-
Particulate elements		**Al ($mg \cdot g^{-1}$)**	**Cd ($\mu g \cdot g^{-1}$)**	**Co ($\mu g \cdot g^{-1}$)**	**Cr ($\mu g \cdot g^{-1}$)**	**Cu ($\mu g \cdot g^{-1}$)**	**Fe ($mg \cdot g^{-1}$)**	**Ni ($\mu g \cdot g^{-1}$)**	**Pb ($\mu g \cdot g^{-1}$)**	**V ($\mu g \cdot g^{-1}$)**	**Zn ($\mu g \cdot g^{-1}$)**				
PACS-2	Certified	66.1 ± 5.3	2.11 ± 0.15	11.5 ± 0.3	90.7 ± 4.6	310 ± 12	40.9 ± 0.6	39.5 ± 2.3	183 ± 8	133 ± 5	364 ± 23				
	Measurec	65.8 ± 1.3	2.11 ± 0.07	11.4 ± 0.3	87.7 ± 1.9	306 ± 10	41.1 ± 0.7	39.5 ± 1.9	183 ± 6	135 ± 3	365 ± 17				
		As ($mg \cdot kg^{-1}$)	**Co ($mg \cdot kg^{-1}$)**	**Cr ($mg \cdot kg^{-1}$)**	**Mn ($mg \cdot kg^{-1}$)**	**Ni ($mg \cdot kg^{-1}$)**									
BCR-701	Certified	nc	nc	2.26 ± 0.16	nc	15.4 ± 0.9									
	Measurec	-	-	2.40 ± 0.01	-	17.3 ± 0.1									

Values represent measured average concentrations and standard deviations.
Certified reference materials for trace metals: SLRS-4 (river water), SLEW-3 (estuarine water) and PACS-2 (marine sediment); National Research Council (NRC), Canada.
Certified reference material BCR-701 (freshwater sediment) to check the first step of SM&T metal extraction; IRMM, Belgium.
nc: element not certified

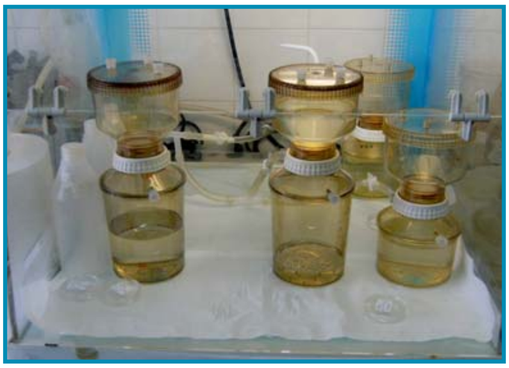

Figure 1.4.8. Filtration system for separation of water samples into dissolved and particulate fractions. *Sistema de filtración para separación de muestras de agua en fracciones disuelta y particulada.*

Figure 1.4.9. Varian SpectrAA 220 spectrometer. Marine Biogeochemistry Group, (IIM-CSIC) Vigo. *Espectofotómetro Varian SpectrAA 220. Grupo de Biogeoquímica Marina, (IIM-CSIC) Vigo.*

termostatizada por sistema Peltier y un nebulizador concéntrico Meinhard (Fig. 1.4.10). El control de calidad (QC) de las soluciones para elementos traza fue realizado cada 10 muestras y se utilizó el Indio como patrón interno para cuantificar las concentraciones de metales. Los blancos de procedimiento fueron menos del 1% de la concentración en las muestras.

Debido a que el ICP-MS es muy sensible a las interferencias en muestras con salinidad alta, las muestras estuáricas se diliyeron con agua Milli-Q (entre 1:1 y 1:10).

El límite de detección (LOD) del método de análisis se calculó usando la desviación estándar del análisis repetido de un blanco (n = 30), corregido por la t-student (97.5% de confianza; gl=n-1). La precisión del procedimiento analítico fue controlada usando materiales de referencia certificados SLRS-4 (agua de río) y PACS 2-(sedimentos marinos) (Tabla 1.4.1).

Elementos traza en sedimentos

Los elementos traza en sedimentos (fracción <2 mm) se determinaron por medio de ICP-MS (IPIMAR, Lisboa) de acuerdo con el procedimiento analítico detallado anteriormente. Previamente al análisis, las muestras de sedimentos superficiales (≈100 mg) fueron completamente digeridas con 6 mL de HF (40%) y 1 mL de Aqua Regia (HCl al 36%: HNO_3 al 60%; 3:1) en bombas cerradas de Teflón® a 100°C durante 1h (Rantala y Loring 1975). El contenido de las bombas fue vertido en matraces volumétricos de 100 mL con 5.6 g de ácido bórico y llenados con agua Milli-Q.

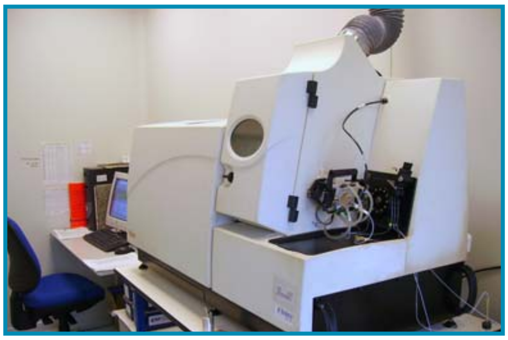

Figure 1.4.10. ICP-MS (Thermo Elemental, X-Series). Department of Aquatic Environment (IPIMAR), Lisbon. *ICP-MS (Thermo Elemental, X-Series). Departamento de Medio Ambiente Acuático (IPIMAR), Lisboa.*

La fracción lábil de los sedimentos superficiales se determinó de acuerdo al método descrito por Quevauviller et al. (1997) con el primer paso del esquema de extracción secuencial del programa SM&T de la Comisión Europea (anteriormente BCR). El pre-tratamiento y el análisis de las muestras fue llevado a cabo en laboratorio ultra-limpio clase ISO 7 (Fig. 1.4.6) dentro de una cabina de flujo laminar clase ISO 5 (Fig. 1.4.7). Muestras secas de la fracción fina del sedimento (≈0.5 g) se trataron con 20 mL de 0.11M de ácido acético y agitadas magnéticamente (MI Variel ALC), para mantener la muestra de sedimento en suspensión durante la extracción (16 horas a 22°C). Después de la extracción, los sedimentos se centrifugaron utilizando una centrifuga Beckman Avanti J-25 durante 20 min a 3000 rpm (22°C) y el sobrenadante de la fase sólida decantado y almacenado a 4°C hasta su análisis. El Cr y Ni lábil fue analizado por GFAAS en un SpectrAA Varian 220-Zeeman (IIM-CSIC, Vigo). La precisión del análisis, definida como la desviación estándar relativa (RSD) fue siempre inferior a 5%. Material certificado de referencia BCR-701 (sedimentos de agua dulce, IRMM Bélgica) fue analizado para comprobar el primer paso de la extracción de metales SM&T (Tabla 1.4.1).Los límites de detección de los elementos traza particulados, calculados como tres veces la desviación estándar de los blancos, fueron: 0.25 $\mu g \cdot kg^{-1}$ para Co, 0.05 $\mu g \cdot kg^{-1}$ para Cr y 0.12 $\mu g \cdot kg^{-1}$ para Ni.

Materials and Methods

Different samples of water (Fig. 1.4.1) and sediments (Fig. 1.4.2) were collected at the Northern Galician Rias through 2008. Their processing and analysis is described below.

Dissolved oxygen and thermohaline variables

Dissolved oxygen was analysed in the water samples (error range ±0.2) following the Winkler method (Grasshoff et al., 1999) using a 702-MS Titrino (Metrohm) (Fig. 1.4.3). Oxygen saturation percentages were calculated from the dissolved oxygen concentration, salinity and temperature data of the sample (Aminot, 1983), with an error range of ±0.2. Samples were fixed and analysed within 24 h after collection.

Water temperature and salinity in rivers and estuarine water were measured *in situ* using a WTW MultiLine P4 Set (error range ±0.1), calibrated with standard solutions before each sampling. Vertical profiles of temperature and salinity in estuarine and oceanic waters were registered with a Seabird-9/11plus CTD placed in a SeaBird-32 Rosette (*RV Mytilus*) and a CTD SeaBird-25 with PAR and Fluorescence sensors placed in a General Oceanic Mini-Rosette (*RV Lura*).

Chlorophyll-a and primary production

Samples for chlorophyll-*a* measurements were immediately filtered through a Whatman GF/F filter (25 mm diameter, 0.7 μm) and chlorophyll concentration was determinate by spectrofluorometry (Neveux and Panouse, 1987) after extraction with 90% acetone according to the method described by UNESCO (1994).

Primary production was determined by the ^{14}C method using 2 h incubations under *in situ* simulated conditions (Steemann-Nielsen, 1952); after incubation, samples were filtered through GF/F filters and daily primary production rates calculated by multiplying hourly rates by the total number of hours during the day, excluding the first 2 h after sunrise and the last 2 h before sunset (Varela et al., 2005).

Dissolved and particulate carbon and nitrogen

To determine particulate organic carbon (POC) and nitrogen (PON) water aliquots were filtered through glass microfiber filters (Whatman GF/F, 0.7 µm). Considering that the contribution of carbonate to total carbon represents only up to 2% of total particulate carbon (Fernandez et al., 1995; Palanques et al., 2002), carbonate was not removed from the filters of POC. Analyses were performed in an EA1108 elemental CNH analyser (Carlo Erba Instruments) at the University of A Coruña (SAI-UDC). Transformed data of the percentage of particulate matter to molar units were used in the presentation of results. C:N (mol:mol) ratios were calculated in terms of POC:PON.

Samples for dissolved organic carbon (DOC) and nitrogen (DON) were taken into 50 mL polyethylene bottles previously cleaned and washed with HCl, and then frozen at -20°C until analysis. DOC and DON analyses were carried out at the Laboratory of Marine Biogeochemistry Unit (INTECMAR, Vilagarcía de Arousa) using a Shimadzu TOC-VCSH analyser with high temperature catalytic oxidation (HTCO) and non-dispersive infrared detection (NDIR) following the procedure described by Alvarez-Salgado and Miller (1998). DOC analyses were accredited by ENAC according to the norm UNE-EN ISO/IEC 17025:2005.

Phytoplankton, planktonic ciliates and zooplankton

Phytoplankton samples were preserved in Lugol's solution and kept in the dark until they were studied. Samples were counted as cells mL^{-1} under a Nikon Eclipse TE 2000-U inverted microscope, following the technique described by Utermöhl (1958). Between 500 and 1.000 cells were counted per sample and the nomenclature for species was based on Tomas (1997). Phytoplankton carbon was calculated following Strathmann (1967). As empty diatoms valves were frequently observed, an estimation of their abundances was carried out. Most of these valves belonged to benthic freshwater or estuarine species and can be considered as indicators of continental influence or resuspension.

Planktonic ciliates were sampled and identified using a protocol similar to the one described for phytoplankton. Samples were sedimented during 48 hours in 100 mL chambers. Taxonomic classification was based on Lynn and Small (2002) criteria. The counting of individuals was performed at 200x magnification.

Samples of microzooplankton (40-200 µm) were collected with vertical hauls, of a 20 cm diameter bongo-type net of 40 µm mesh size, and filtering cod-ends was used. Samples were screened through 40 µm nylon mesh and fixed in 2% borate-buffered formalin before microscopic examination. Taxonomic classification of species was based on Valdés et al. (1991) criteria. Mesozooplankton samples were collected by oblique hauls a Juday-Bogorov net with 200 µm mesh size (50 cm diameter) and equipped with flow and depth meters (Bode et al., 1998). Samples were fixed in 4% formalin before microscopic analysis.

Nutrient salts

Nutrient salts samples (nitrate, nitrite, ammonium and phosphate) were collected in 50 mL acid-cleaned plastic bottles and immediately frozen at -20 °C. As orthosilicate polymerization may occur in freshwater frozen samples (Kobayashi, 1966), rivers were also sampled using

10 mL plastic bottles and preserved at 4°C and dissolved silicate was analysed next day. Nutrient salts were analysed at the laboratory of the Marine Biogeochemistry Group (IIM-CSIC, Vigo), using an Integral Futura autoanalyser system (Alliance Instruments) (Fig. 1.4.4) with separate lines to nitrate, nitrite, ammonium, phosphate and silicate according to standard colorimetric methods (Hansen and Koroleff, 1999). Detection limits as three times the standard deviation of 10 replicate measurements of reagent blank, were: 0.14 µM for NO_3^-, 0.002 µM for NO_2^-, 0.01 µM for NH_4^+, 0.08 µM for HPO_4^{-2} and 0.14 µM for H_4SiO_4. For seawater samples, the accuracy of the analytical procedure was assessed by the analysis of certified reference materials: MOOS-1 (seawater nutrients; NRC, Canada), obtaining good agreement with the certified values. The precision as relative standard deviation (RSD) was always less than 5%.

Trace elements

All plastic labware employed for sampling, storage and sample treatment was previously acid-washed for 48 h in 50% HNO_3 and rinsed with Milli-Q water, then transferred into a container filled with 10% HCl for at least a week. Labware was rinsed several times with Milli-Q water and dried in a laminar flow cabin (ISO Class 5) before use.

The sample collection was carried out following the 'clean hands/dirty hands' technique (US-EPA, 1996a) , which involves two or more people working together with specific tasks during sampling to avoid contamination of samples (Fig. 1.4.5).

Handling, processing and analysis of samples was performed in an ultra-clean laboratory (ISO Class 7) (Fig. 1.4.6), using talc-free polyethylene gloves, and following clean procedures and techniques (Sander et al., 2009; GEOTRACES, 2010).

Trace elements in water

Samples for trace elements in water were collected in 1-L LDPE bottles previously acid-washed and rinsed with Milli-Q water. Bottles were filled with Milli-Q water at pH 2 and stored in zip-lock plastic bags until use. Samplings were carried out following clean techniques for trace elements.

At the onshore clean portable-laboratory (Celeiro fishing port, Spain) and within four hours after collection (Chapman, 1992), samples were separated into dissolved and particulate fractions in a laminar flow cabinet (ISO Class 5) (Fig. 1.4.7) by filtration through Pall-Gelman polycarbonate filters (0.45 µm) (Fig. 1.4.8), previously acid washed (Suprapur HCl 1%) and weighed. Samples for dissolved trace elements analysis were acidified with Suprapur HNO_3 (pH <2). Afterward filters were dried, weighed again and suspended particulate matter (SPM, $mg \cdot L^{-1}$) calculated. SPM filters were placed into plastic petri dishes and stored at -20°C until digestion at the laboratory of the Marine Biogeochemistry Group (IIM-CSIC, Vigo). Polycarbonate filters were completely digested in a Milestone MLS 1200 Mega microwave oven with HF (6 mL 48 %) and 2mL HNO_3-65%) in closed Teflon® pressure vessels, following the EPA 3052 guideline (US-EPA, 1996b) for siliceous-type matrices. The contents of the bombs were poured into 25 mL volumetric flasks filled up with ultrapure Milli-Q water. Handling and analysis of samples were carried out in a clean laboratory (ISO class 7-8).

Particulate metals were determined at the laboratory of the Marine Biogeochemistry Group (IIM-CSIC, Vigo) by GFAAS in a Varian SpectrAA 220 spectrometer (Fig. 1.4.9) equipped with Zeeman background correction (Cd, Co, Cr, Cu, Fe, Ni, Pb ,V, Zn) and FAAS (Al) on a Perkin Elmer AA100 with a nitrous oxide-acetylene flame. Prior to analysis, filters containing SPM were microwave-digested (Milestone 1200 Mega) in Teflon bombs using a mixture of HNO_3 and HF according to US-EPA method 3052.

Dissolved metals in river and estuarine waters were determined following standard methods (APHA, 1995) at the laboratory of the Department of Aquatic Environment (IPIMAR, Lisbon) using a quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer (Fig. 1.4.10). Quality Control (QC) solutions for trace elements were run every 10 samples and Indium as internal standard was used to quantify metal concentrations. Procedural blanks were less than 1% of element concentrations in the samples.

As ICP-MS is highly sensitive to interferences by high salt contents, estuarine samples were diluted (between 1:1 and 1:10) with Milli-Q water.

Limit of detection (LOD) of the analytical procedure was calculated as standard deviation of replicate analyses of a blank (n=30) corrected by student's t- statistic (at 97.5% confidence; df= n-1). The accuracy of the analytical procedure was controlled by the analysis of certified reference materials SLRS-4 (river water) and PACS-2 (marine sediment) (Table 1.4.1).

Trace elements in sediments

Trace elements in sediments (based on <2 mm size fraction) were determined by ICP-MS (IPIMAR, Lisbon) according to the analytical procedure detailed above. Before analysis surface sediment samples (≈100 mg) were completely digested with 6 mL of HF (40%) and 1 mL of Aqua Regia (HCl-36%: HNO_3-60%; 3:1) in closed Teflon® bombs at 100°C for 1 h (Rantala and Loring 1975). The contents of the bombs were poured into 100 mL volumetric flasks containing 5.6 g boric acid and filled up with ultrapure Milli-Q water.

The labile fraction in surface sediments was determined according to Quevauviller et al. (1997) by the first step sequential extraction scheme of the Standards, Measurement and Testing programme (SM&T, formerly BCR) of the EU Commission. Pre-treatment and analysis of samples were carried out in an ultra-clean laboratory ISO Class 7 (Fig. 1.4.6) and in a laminar flow cabin ISO Class 5 (Fig. 1.4.7). Aliquots of dry sediment fine fraction (≈0.5 g) were treated with 20 mL of 0.11M acetic-acid and a magnetic shaker (MI Variel ALC) was used to keep the sediment sample in suspension during extraction (16 h at 22°C). After extraction, sediments were centrifuged using a Beckman Avanti J-25 centrifuge for 20 min at 3000 rpm (22°C) and the supernatant from the solid phase was decanted and stored at 4°C until analysis. Labile Cr and Ni were analysed by GFAAS in a Varian SpectrAA 220-Zeeman (IIM-CSIC, Vigo). The precision as relative standard deviation (RSD) was always less than 5%. Certified reference material BCR-701 (freshwater sediment, IRMM Belgium) was analysed to check the first step of SM&T metal extraction (Table 1.4.1). LOD of particulate trace elements, calculated as three times the standard deviation of the blanks, were: 0.25 $\mu g \cdot kg^{-1}$ for Co, 0.05 $\mu g \cdot kg^{-1}$ for Cr and 0.12 $\mu g \cdot kg^{-1}$ for Ni.


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Chapter 2

Oceanographic characteristics of the Northern Galician Rias

2.1. Oceanographical patterns during summer upwelling-downwelling events

Introduction

Coastal upwelling is one of the main processes controlling the circulation in the upper layers of the ocean waters (Fraga, 1981). During upwelling events, colder and saltier waters from deeper layers, inject nutrients into the illuminated surface layers, favouring phytoplankton growth (Wooster and Reid, 1963). Due to the high productivity of these world regions they are profusely researched (Cushing, 1969). This is the case of the Current System of California (Bograd et al, 2009; Hickey and Royer, 2008), Peru-Humboldt (Silva et al. 2009; Karstensen and Ulloa, 2008), Canaries (Barton, 2008; Pastor et al. 2008) and Benguela (Burls and Reason, 2008; Shannon, 2009). In the North Atlantic Ocean, the Eastern North Atlantic Upwelling System extends from the south of Dakar at 10°N to the tip of the Iberian Peninsula at 44°N (Wooster et al., 1976). Its upper boundary is in the Galician coast where upwelling of Eastern North Atlantic Central Water (ENACW), located between 70-500 m depth, usually occurs during spring and summer (Fraga, 1981; Rios et al., 1992). ENACW upwelling intensifies between the Cape Finisterre and Punta Rocundo (42°52’-43°17’N) and high concentrations of nitrate can be detected along the upwelling core in the Western Rias coast (Fraga, 1981; Prego et al., 1999a). Galicia is situated in the north-western corner of the Iberian Peninsula, has three different littoral orientations. This makes the effect of northerly prevailing wind conditions (Torres et al., 2003; Alvarez et al., 2005a; Gómez-Gesteira et al., 2006) on upwelling development to be different both

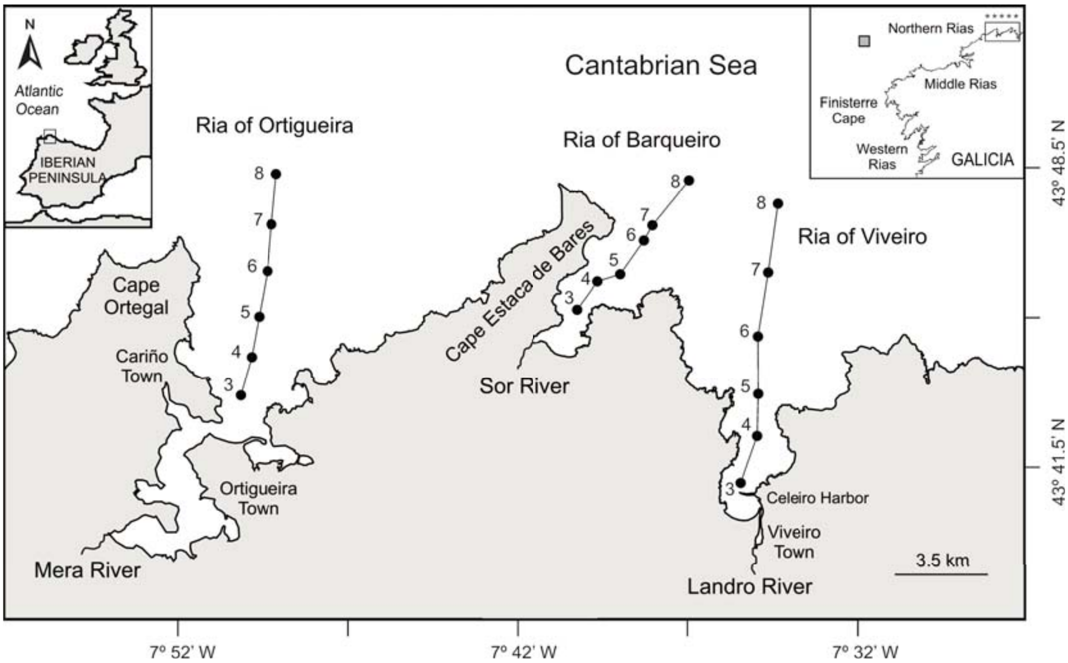


Figure 2.1.1. Map of the Northern Galician Rias showing the sampling stations (black circles) of cruises carried out in July and August 2008. Asterisks in the upper-right map represent the five control points considered to analyse wind data provided by the QuikSCAT satellite. Gray square on the map (right corner) correspond to the control point (43.5°N, 10.5°W) for Ekman transport data considered from 1990 to 2008.

in probability and intensity at north of Cape Ortegal (Northern Rias), between Capes Ortegal and Finisterre (Middle Rias), and south of Cape Finisterre (Western Rias) (Fig. 2.1.1).

Upwelling events in the Western Rias have been intensively studied from hydrographical (Fraga, 1981; Alvarez-Salgado et al., 1993; Prego et al., 2001; Herrera et al., 2008) and biogeochemical (Tenore et al., 1982; Blanton et al., 1984; Prego et al., 1995; Alvarez-Salgado et al., 1996; Bernárdez et al., 2006) points of view. The relationship between upwelling and thermohaline variables has been studied extensively in the western Galician coast (Nogueira et al., 1997; Pardo, 2001; Torres, 2003; Dale et al., 2004; Alvarez et al., 2005b) because the emergence of low temperature and high salinity in the surface and subsurface waters (Hu et al., 2001) is a good indicator of upwelling. In contrast with upwelling events south of Finisterre which are more intense and closer to the coast, upwelling in the Northern Rias is discontinuous and remains mainly near the edge of the continental shelf (Prego and Bao, 1997). Upwelling in the Middle Rias of Artabro Gulf, is characterized by the no intrusion of ENACW into the rias, while the opposite occurs in the Western Rias where ENACW upwells inside them (Prego and Varela, 1998).

In contrast with the Western Galician Rias, Northern Galician Rias has been scarcely investigated, with some researches focussing on biological (Sánchez et al., 1998) and sedimentary aspects (Otero et al., 2000; Lorenzo, 2007). Upwelling studies have not been extensively undertaken in this northern Galician zone, except for some recent researches. Gonzalez-Pola et al. (2005) studied an early spring pulse in the western Cantabrian shelf-slope; Alvarez et al. (2009) analysed the evidence of a winter upwelling event in the northern Rias. The upwelled seawater inside the estuaries has a shelf bottom origin and it is not associated with Eastern North Atlantic Central Water or the Iberian Poleward Current as observed in the Western Rias (deCastro et al., 2006; Prego et al., 2007; deCastro et al., 2008); Alvarez et al. (2010) analysed summer upwelling frequency along the Cantabrian Coast from 1967 to 2007 and monitored sea temperature related to wind forcing in the Ria of Barqueiro.

The hydrographical, biogeochemical, plankton pattern and frequency of summer upwelling events for the Northern Rias remains nearly unknown. Moreover, downwelling episodes have not been described, such as in the Western Rias (deCastro et al., 2004; Torres and Barton, 2007). These episodes could be associated with red tides episodes (Fraga et al., 1988; Prego, 1992; Tilstone et al., 1994) that were not reported for the Northern Rias yet.

According to the wind patterns and coastal orientation, it may be hypothesise that the upwelling events in the Northern Rias and neighbouring shelf must be different to that of the rest of Galician rias. In this way, physical, chemical and biological, data were obtained in favourable and unfavourable upwelling conditions in July-August 2008. In summary, the aims of this section are: (i) to characterize a summer both, upwelling and downwelling events in the Northern Galician Rias; (ii) to analyse the frequency of meteorological conditions favourable to upwelling and downwelling events in the northern coast of Galicia; (iii) to compare the oceanographic patterns of the Northern Rias with the existing information about the Middle and Western Rias.

Materials and Methods

Hydrographical and biochemical seawater sampling

Two cruises were conducted on board the *RV Mytilus* and *RV Lura* to investigate the oceanographic characteristics in the water column of the Northern Galician Rias during an upwelling and downwelling processes (Fig.2.1.1). The first cruise was carried out on July 16-17t^{h} after one week of upwelling favouring prevailing winds, and the second on August 19-20th during the upwelling relaxation phase, which started on 23rd July and was dominated by western winds. Eighteen seawater stations were visited in the rias of Ortigueira, Barqueiro and Viveiro (Fig. 2.2.1). Six stations, between 10 and 100 m, were studied in every ria during July and seven stations during August. Vertical profiles of temperature and salinity were measured with a Seabird-9/11plus CTD placed in a SeaBird-32 Rosette (*RV Mytilus*) and a CTD SeaBird-25 with PAR and Fluorescence sensors placed in a General Oceanic Mini-Rosette (*RV Lura*). Water samples at each station were collected at standard depths (0, 5, 10, 20, 40, 60, 80 and 90 m) using General Oceanic Niskin bottles of 5-L (*RV Lura*) or 12-L (*RV Mytilus*), for chemical and biological sub-sampling. Samples of dissolved oxygen, nutrient salts and chlorophyll-*a* were processed and analysed according to Chapter 1, *Section Materials and Methods.*

Biological seawater sampling

Particulate organic carbon and nitrogen (POC and PON, respectively) and plankton abundances of different groups were measured at station 5 (20 m depth) located in the middle of the channel of the Ria of Barqueiro.

Planktonic ciliates were sampled and identified using a protocol similar to the one described for phytoplankton. Samples of microzooplankton (40-200 μm) were collected with vertical hauls, of a 20 cm diameter bongo-type net of 40 µm mesh size, and filtering cod-ends was used. A detailed explanation about processing and analysis of the samples is provided in Chapter 1, *Section Materials and Methods.*

Hydrological and biogeochemical sampling of rivers

Daily river flow data of the main rivers running into the three Northern Rias during July and August were supplied by the *Aguas de Galicia* company dependent on the 'Consellería de Medio Ambiente' of the *Xunta de Galicia.* The flows were area corrected considering the whole river basin area: 270, 202 and 127 km^2 of Landro, Sor and Mera Rivers, respectively. These three rivers were sampled four times near their mouth: 2nd, 15th and 30th July and 18th August. Salinity was measured using a WTW MultiLine F/Set-3 (error range: ±0.1). Dissolved oxygen concentrations were measured at the next sampling day by Winkler titration of samples to calculate saturation percentages (Aminot, 1983), with an error range of ±0.2. Nutrient salts samples (nitrate, nitrite, ammonium and phosphate) were collected in 50 mL plastic bottles and immediately frozen at -20°C; then they follow the previously cited procedure used for the seawater nutrient samples. As orthosilicate polymerization may occur in freshwater frozen samples (Kobayashi, 1966), rivers were also sampled using 10 mL plastic bottles and preserved at 4°C and dissolved silicate was analysed next day. The accuracy of the analytical procedure was assessed by the analysis of certified reference materials: MOOS-1 (seawater nutrients; NRC, Canada), obtaining good agreement with the certified values. The precision as relative standard deviation (RSD) was always less than 5%. Samples for chlorophyll-*a* analysis were also taken and processed as the seawater samples.

Satellite and meteorological data

Maps of Sea Surface Temperature (SST) have been elaborated using the NASA GHRSST satellite database that combines measurements of several thermal infrared (AVHRR, MODIS, AATSR and SEVIRI) and microwave (AMSR-E and TMI) satellite sensors. The data set has a precision of 0.1K, a spatial resolution of 5 km and a daily temporal resolution. Details of the processing at NASA-JPL can be found at ftp://podaac.jpl.nasa.gov/GHRSST/doc/GHRSST_guide_doc.pdf.

Surface wind fields from July to August 2008 were provided by the QuikSCAT satellite, and retrieved from the Jet Propulsion Laboratory web site (http://podaac.jpl.nasa.gov/quikscat/qscat_data.html). The data set consists of global grid values of meridional and zonal components of wind measured twice daily on an approximately 0.25°×0.25° grid with global coverage. QuikSCAT data are given in an ascending and descending pass. Data corresponding to one pass present numerous shadow areas, therefore, an average between both passes was considered to increase the coverage. It is necessary to take into account that wind data close to coast (≈ 25 km) are not available due to the existence of a small coast mask, nevertheless, a statistical comparison between QuikSCAT wind measurements and high resolution numerical models was carried out along the Galician coast (Penabad et al., 2008), revealing similar results between models and satellite data. Ekman transport was calculated using the wind speed from the QuikSCAT satellite at 5 control points located along the northern Galician coast at latitude 44.25°N and from 8.25°W to 7.25°W (Fig. 2.1.1).

Ekman transport data provided by the Pacific Fisheries Environmental Laboratory (PFEL) (http://www.pfeg.noaa.gov) were considered from 1990 to 2008. The PFEL distributes environmental index products

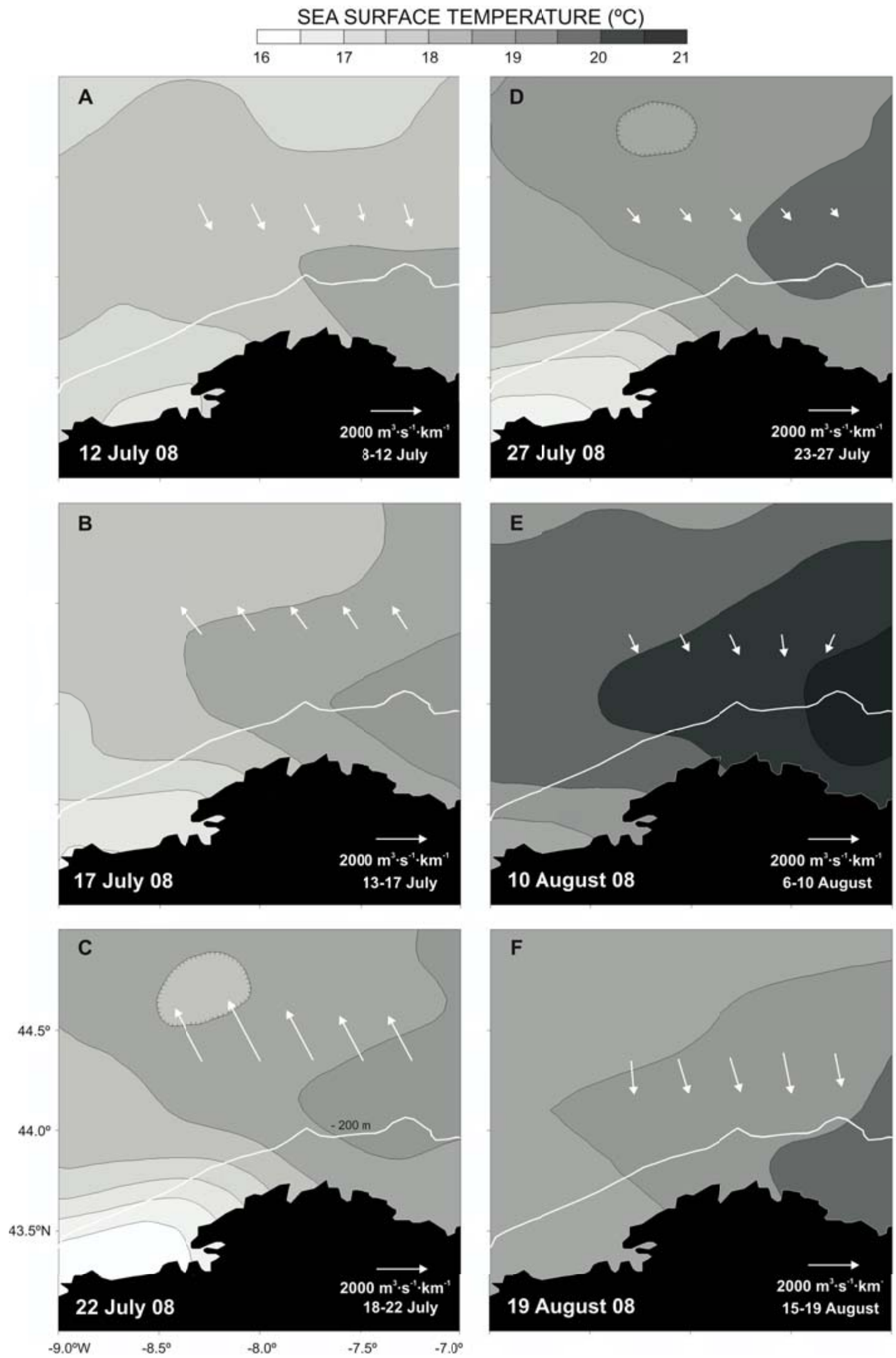


Figure 2.1.2. Maps of temporal evolution of the Sea Surface Temperature (SST) and Ekman transport pattern (white arrows) along the northern Galician coast during the upwelling-downelling event. SST images correspond to the date shown on the lower-left corner of each frame. Ekman transport was calculated averaging the surface wind fields from QuikSCAT satellite data to the SST date and three previous days (lower-right corner of each frame).

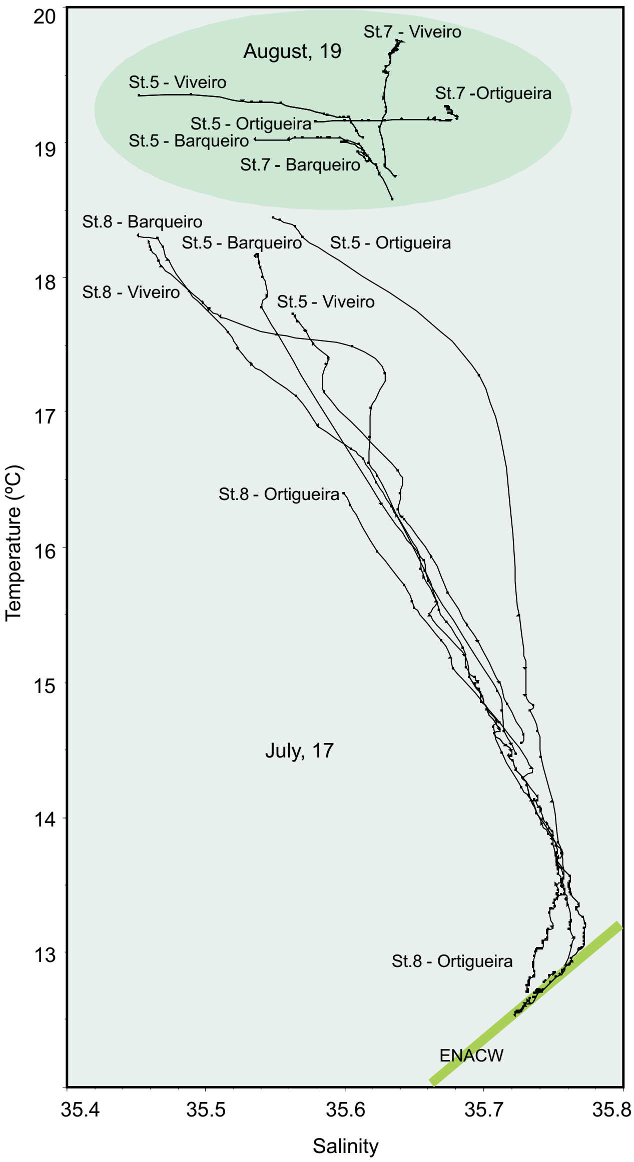


Figure 2.1.3. TS diagram corresponding to the stations located at the mouth (St. 5) and at the continental shelf (July: St.8 and August: St.7) of the rias of Ortigueira, Barqueiro and Viveiro (see Fig. 2.1.1). Grey band in the lower-right corner corresponds to the Eastern North Atlantic Central Water mass (ENACW).

and time series databases to cooperating researchers, taking advantage of its long association with the U.S. Navy's Fleet Numerical Meteorology and Oceanography Centre (FNMOC). For our purposes six-hourly Ekman transport data model derived from Sea Level Pressure were considered at a control point located at 43.5° N, 10.5° W (Fig. 2.1.1, gray square). Data were averaged to obtain daily series. Considering that UI can be defined as the Ekman transport component in the direction perpendicular to the shore-line (Nykjaer and Van Camp, 1994; Gomez-Gesteira et al. 2006), then the Qy component of the Ekman transport can be considered as the UI for the Northern Galician Rias (UIN=+Qy). Positive values of UI ($km \cdot m^{-3} \cdot s^{-1}$) indicate upwelling-favourable conditions. Conversely, negative values indicate downwelling-favourable onshore Ekman transport. Along the western coast of the Iberian Peninsula (Western Rias), the northerly component of shelf wind-stress causes upwelling favourable conditions (UIW=-Qx) with offshore Ekman transport (Wooster et al., 1976; Bakun and Nelson, 1991) and southerly winds result in the opposite effect.

Results

Meteorological conditions and seawater transport

Images of SST along the Northern Galician Rias each five days between July 12 and August 19 of 2008 are presented in Fig. 2.1.2. This Figure also shows the Ekman transport. At the beginning of July (days 8-12; Fig. 2.1.2.a) transport was mainly directed southeastward, i.e. upwelling unfavourable according to the coastline direction. Then, for the days previous to the cruise carried out in July (days 13-17, Fig.

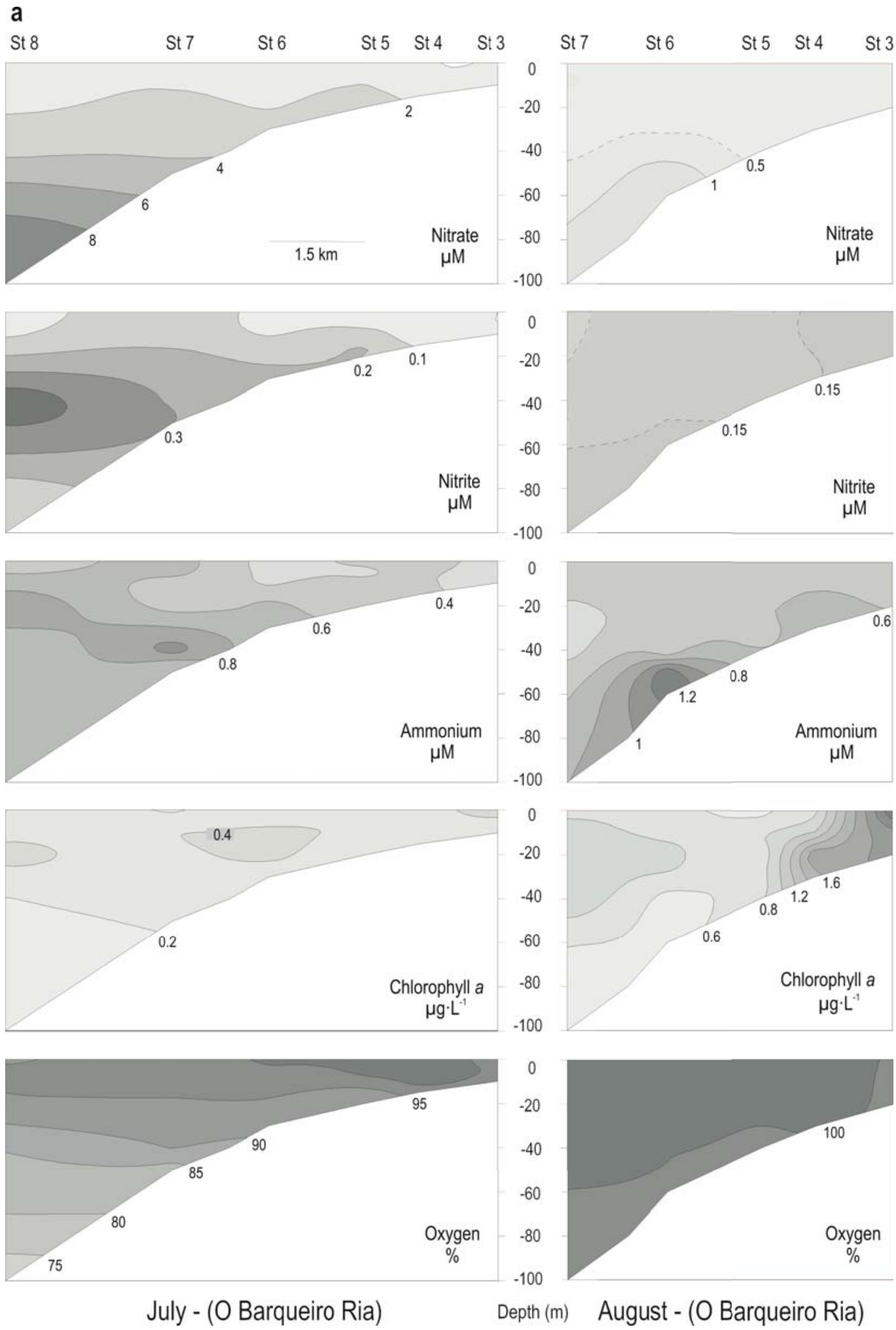
Table 2.1.1. Master variables of the three main rivers flowing into the headwaters of the Northern Galician Rias. The measurements were made fortnightly during the months of the sea cruises

		Date				
River	Parameter	2 July	15 July	30 July	18 August	Unit
	Upwelling Index	-962	1421	-813	-713	$m^3·s^{-1}·km^{-1}$
Mera	Flow	1.49	1.19	0.40	0.71	$m^3·s^{-1}$
	Temperature	16.1	17.3	17.0	17.4	ºC
	Dissolved oxygen saturation	-	97.5	-	95.5	%
	Nitrate	49.8	46.9	49.4	57.8	µM
	Nitrite	0.15	0.24	0.17	0.33	µM
	Ammonium	0.52	1.01	0.21	0.45	µM
	Phosphate	0.19	0.16	0.15	0.02	µM
	Silicate	198	204	215	197	µM
	Chlorophyll-*a*	-	0.62	-	0.55	$µg·L^{-1}$
Sor	Flow	7.27	7.52	6.56	6.79	$m^3·s^{-1}$
	Temperature	18.3	19.1	19.7	20.3	ºC
	Dissolved oxygen saturation	-	98.0	-	98.0	%
	Nitrate	38.1	32.2	39.3	35.3	µM
	Nitrite	0.12	0.23	0.14	0.22	µM
	Ammonium	0.33	0.58	0.22	1.18	µM
	Phosphate	0.16	0.13	0.14	0.02	µM
	Silicate	101	99	107	94	µM
	Chlorophyll-*a*	-	0.41	-	0.45	$µg·L^{-1}$
Landro	Flow	4.82	3.65	2.80	2.59	$m^3·s^{-1}$
	Temperature	16.2	17.3	16.1	18.8	ºC
	Dissolved oxygen saturation	-	96.6	-	94.9	%
	Nitrate	43.1	41.0	41.3	49.2	µM
	Nitrite	0.14	0.23	0.16	0.27	µM
	Ammonium	0.28	4.00	0.57	1.42	µM
	Phosphate	0.16	2.91	0.17	0.11	µM
	Silicate	150	-	160	150	µM
	Chlorophyll-*a*	-	0.92	-	0.64	$µg·L^{-1}$

2.1.2.b), the transport pattern varied; it was completely different pointing northwestward (upwelling favourable) along the coast and showing approximately the same direction and amplitude at each point. This situation remained during the very next days, (from July 18th to 22nd, Fig. 2.1.2.c), but the transport pattern changed again at the end of the month (days 23-27, Fig. 2.1.2.d) toward southeastward direction although with low intensity. This upwelling unfavourable behaviour persisted (Fig. 2.1.2.e) and increased in August; transport was mainly directed southward (days 1-19, Fig. 2.1.2.f) showing the same direction and amplitude at each point resulting in downwelling favourable conditions.

July Upwelling event

The TS diagram of thermohaline data (Fig. 2.1.3) measured inshore (st.5, Fig. 2.1.1) and offshore (st.8) of the three Rias


a
St 8
St 7
St 6
St 5
St 4
St 3
St 7
St 6
St 5
St 4
St 3
Nitrate
µM
1.5 km
Nitrite
µM
Ammonium
µM
Chlorophyll a
µg·L-1
Oxygen
%
Depth (m)
July - (O Barqueiro Ria)
August - (O Barqueiro Ria)

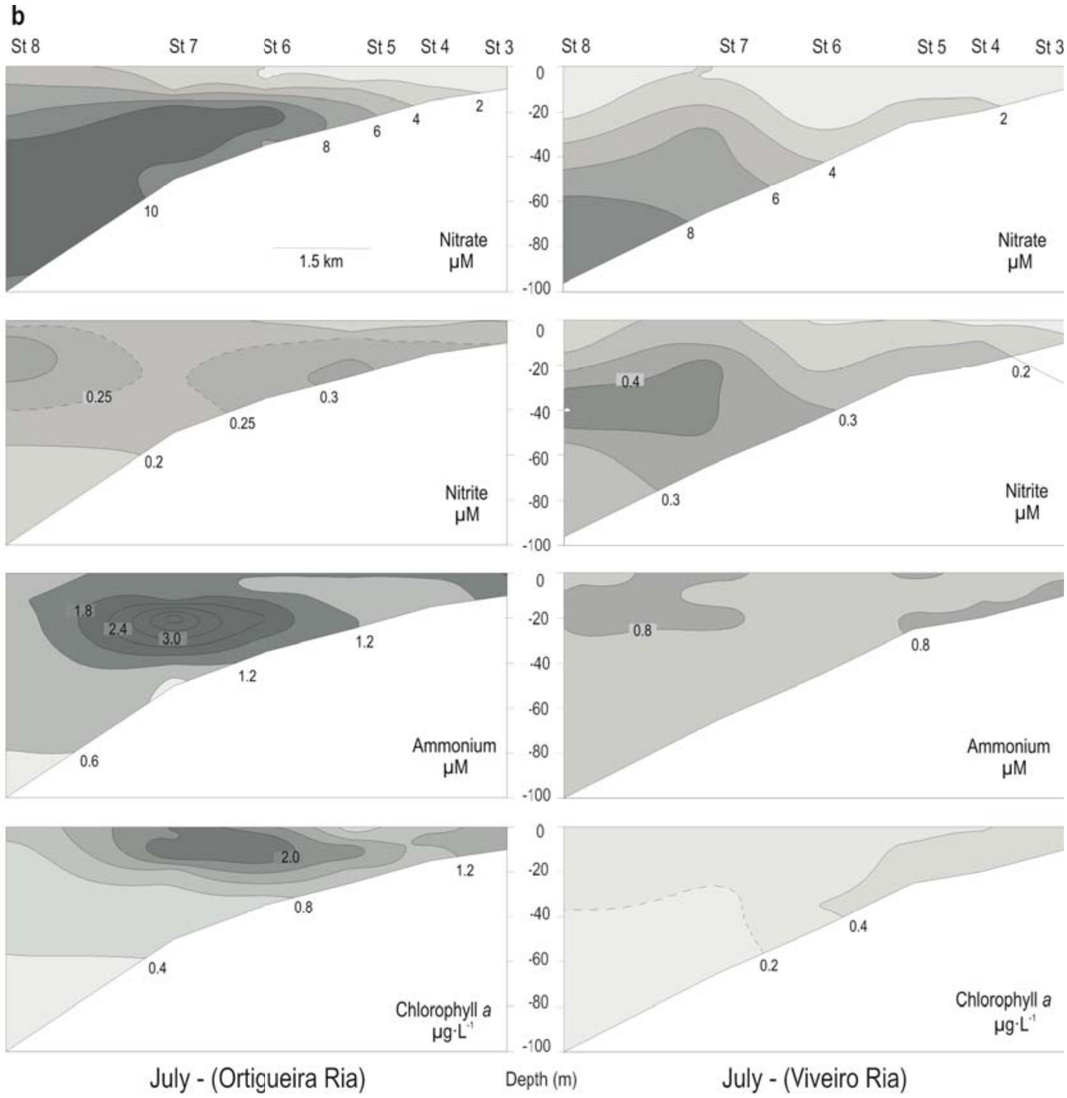


Figure 2.1.4. Contour maps of nitrate, nitrite, ammonium and chlorophyll-*a* concentrations and dissolved oxygen saturation percentages along the main channel (sections in Fig.2.1.1) on July 17 for the three Northern Rias (a, right panel and b) and on August 19 for the Ria of Barqueiro (a, left panel).

under upwelling (July 17th, 2008) and downwelling (August 19th, 2008) conditions (Fig.2.1.2) shows the presence of a saltier and colder water mass associated with the ENACW during the favourable upwelling event of July. During July the main variables measured in the rivers are shown in Table 2.1.1. The flow of rivers ranged from 0.4 to 7.5 $m^3 \cdot s^{-1}$ and temperature and dissolved oxygen saturation from 16.1 to 19.7°C and from 96 to 98%, respectively. Concentration levels of nutrient salts were in the range of 32-50 μM for nitrate, 0.1-0.2 μM for nitrite, 0.2-4.0 μM for ammonium, 0.1-2.9 μM for phosphate and 99-215 μM for silicate while the values for Chlorophyll-*a* ranged between 0.4-0.9 $\mu g \cdot L^{-1}$. The Sor River is quasi-pristine.

In the rias and their neighbouring shelf, nutrient salts concentrations (Fig.2.1.4.a and Fig.2.1.4.b) increased with depth, reaching their maximum concentrations near bed. Nitrate was practically depleted in the inner surface waters of the rias of

Barqueiro and Viveiro and the highest values were measured at the bottom near the shelf break (in both rias: 9.2-9.5 µM nitrate). The Ria of Ortigueira presented a similar distribution pattern but without nutrient depletion, with values from 1 to 13 µM nitrate as result of upwelling inputs and remineralisation processes in the shelf seawater column reflected by the high ammonium concentrations at mid seawater layers (up to 4.6 µM, Fig.2.1.4.b). Phosphate (0.0-0.6 µM) and silicate (0.7-5.1 µM) showed similar trends to those of nitrate in the three rias, however the highest concentrations were at the top of the innermost ria stations (1.9 µM of phosphate in the Ria of Ortigueira and 7.9 µM of silicate in the Ria of Barqueiro). Dissolved oxygen was only measured in the Ria of Barqueiro and showed a clear horizontal stratification (Fig.2.1.4.b), with well-oxygenated surface waters at surface (102%) and decreased oxygen saturation at the bottom (72%).

Chlorophyll-*a* was low (0.1 to 0.7 µg·L^{-1}) in the rias of Barqueiro and Viveiro, however an important increase up to 2.7 µg·L^{-1} was observed in the Ria of Ortigueira at st.6 and 7 with the highest concentration in the first 20 m (Fig.2.1.4.a and Fig. 2.1.4.b). Plankton abundances were quantified at st.5 in the Ria of Barquiero (Fig.2.1.1). The mean abundances of phytoplankton (mean of four depths sampled; Table 2.1.2, July) were dominated by naked flagellates with mean abundances of 500 cells·mL^{-1}. Larger phytoplankton showed a predominance of diatoms, with 42 cells·mL^{-1}. Auxospores of *Chaetoceros, Pseudo-nitzschia delicatissima, Guinardia delicatula, Leptocylindrus minimus* and *L. mediterraneus* were the dominant species. Dinoflagellates were less abundant than diatoms (abundances of 11 cells·mL^{-1}). *Amphidinium flagellans, Prorocentrum minimum, Heterocapsa niei* and small species of Gymnodinium were the dominant taxa in July. Other groups displayed negligible abundances. Planktonic ciliates showed very low abundances, around 0.15 cells·mL^{-1}. *Lohmaniella oviformis* and *Strombidium acutum* were the dominant taxa (Table 2.1.2, July). Microzooplankton abundance in July was high, around 12000 indiv·m^{-3}, and dominated by larvae of copepods (nauplii), bivalves and gastropods. Mesozooplankton abundance was also high with values above 5000 indiv·m^{-3}, with copepods (mainly copepodits), and apendicularia as the dominant groups (Table 2.1.3, July).

August Downwelling event

Temperature and salinity on 19th August 2008 at St.5 and St.7 situated inside rias and in their neighbouring shelf respectively, displayed a little variability; they varied from 35.4 and 19.6°C near surface to 35.7 and 18.6°C near bed. The TS diagram showed a clear difference with respect to the upwelling situation of July (Fig.2.1.3). Under these environmental conditions a depletion of nutrient salts was observed along the water column of the Ria of Barqueiro (Fig. 2.1.4.a) and offshore seawaters. Maximum concentrations of nutrients were low close to the bottom: 1.4 µM of nitrate, 0.16 µM of nitrite, 1.4 µM of ammonium, 0.15 µM of phosphate (at surface in the innermost ria station) and 3.5 µM of silicate. The main nutrient source to this old-poor seawater was the fluvial outputs. The Sor River on 18th August 2008 (Table 2.1.1) contributed to the Ria of Barqueiro with 0.25 molN·s^{-1} (96% as nitrate), 0.14 mmolP· s^{-1}, 0.64 molSi· s^{-1}, which was used by phytoplankton in the innermost ria zone where the highest concentration of chlorophyll-*a* was measured (2.40 µg·L^{-1}). There was a slight increase of POC and PON concentrations inside the Ria of Barqueiro from July to August (St.5, from 920 mgC·m^{-2} and 175 mgN·m^{-2} to 1370 mgC·m^{-2} and 210 mgN·m^{-2}), similarly to

C:N (mol:mol) ratio increasing from 6.2 to 7.4.

Mean abundances of phytoplankton measured in August throughout the water column (Table 2.1.2) revealed that small flagellates were, as in July, the most abundant component of phytoplankton, with abundances higher than 1000 cells·mL^{-1}. Phytoplankton species composition of larger phytoplankton showed a dominance of diatoms. *Chaetoceros* auxospores, *Rhizosolenia* and *Thalassiosira* species, displayed similar abundances as those of July, while *P. delicatissima, G. delicatula, L. minimus* and *L. mediterraneus* clearly decrease in August. A significant increase was observed for small *Navicula* species, *Navicula transitans, Nitzschia longissima* or *Paralia sulcata*. Dinoflagellates remained with similar abundances, reaching around 10 cells·mL^{-1}. Dominant species in July, dropped their abundances in August, and the more salient peculiarity is the high increase of the red tide forming species *Lingulodinium polyedrum* (from 10% of total dinoflagellates in July to 76% in August, Table 2.1.2). In any case, low phytoplankton abundances were observed both, in July and August, in dinoflagellates and diatoms as well. Planktonic ciliates were slightly higher than in July, with abundances around 1 cells·mL^{-1}. The taxa present in July, increased their abundances and some other species appeared as dominant in this date. This is the case of *Myrionecta rubra* and *Tontonia gracillima* (Table 2.1.2), Microzooplankton abundance clearly decreased as compared to those of July, reaching around 6000 indiv·m^{-3}, with copepods nauplii larva as dominants, followed by bivalve larvae and some species of tintinnids (Table 2.1.3, August). Mesozooplankton also decreased with mean abundances about 3000 indiv·m^{-3}. Dominance shared among different groups, with copepods displaying

Table 2.1.2. Mean abundance of phytoplankton and ciliates at station 5 in the Ria of Barqueiro in July and August 2008

Plankton group	July	August
Phytoplankton (cels·mL^{-1})		
(a) Dinoflagellate		
Amphidinium flagellans	1.88	0.37
Cochlodinium helix	0.19	0.19
Gymnodinium spp. small	1.50	0.00
Gyrodinium fusiforme	0.21	0.00
Heterocapsa niei	1.51	0.19
Karlodinium cf. *micrum*	1.31	0.00
Lingulodinium polyedrum	0.11	7.68
Prorocentrum minimum	3.35	0.74
Protoperidinium steinii	0.05	0.24
Total dinoflagellate	11.12	10.14
(b) Diatoms		
Auxoesporas de *Chaetoceros* spp.	7.70	7.83
Amphora spp.	0.76	0.00
Cerataulina pelagica	0.19	0.37
Chaetoceros cf. *convolutus*	0.21	1.69
Chaetoceros danicus	0.19	0.37
Chaetoceros decipiens	0.37	0.00
Chaetoceros gracilis	0.37	0.76
Cocconeis spp.	0.37	0.94
Grammatophora marina	0.01	0.19
Guinardia delicatula	3.34	0.01
Guinardia striata	0.19	0.01
Gyrosigma spp.	0.56	0.56
Leptocylindrus mediterraneus	2.78	0.00
Leptocylindrus minimus	4.28	1.48
Navicula distans	0.20	0.05
Navicula spp. small	0.37	5.57
Navicula transitans	0.74	2.60
Nitzschia longissima	1.52	4.82
Paralia sulcata	0.10	3.34
Pseudo-nitzschia cf. *delicatissima*	8.30	0.74
Pseudo-nitzschia spp.	1.11	2.41
Proboscia alata	0.19	0.20
Rhizosolenia imbricata	2.04	2.78
Rhizosolenia setigera	0.63	0.19
Thalassiosira nana	2.27	2.64
Thalassiosira spp.	2.41	2.23
Total diatoms	42.32	42.01
(c) Flagellates		
Flagellates 3-10 µm	532.14	1120.46
(d) Planktonic ciliates (cels·mL^{-1})		
Lohmaniella oviformis	0.05	0.27
Myrionecta rubra	0.00	0.31
Tontonia gracillima	0.00	0.19
Strombidium acutum	0.02	0.05
Leegardiella sol	0.01	0.05
Srombidium epidemum	0.00	0.04
Strombidium sp.	0.01	0.02
Total ciliates	0.14	1.07

Table 2.1.3. Mean abundance of zooplankton at station 5 in the Ria of Barqueiro in July and August 2008

Plankton group	July	August
Zooplankton (individuals·m^{-3})		
(e) Microzooplankton (40-200 µm)		
Copepods		
Nauplii larvae	7295	3415
Calanoids	68	49
Ciclopoids	545	212
Harpacticoids	34	0
Larvae		
Bivalves	2523	1536
Gasteropods	1023	392
Tintinnids		
Eutintinnus sp.	102	16
Rhabdonella elegans	102	654
Favella spp.	0	114
Other groups		
Apendicularia	136	49
Total microzooplankton	11898	6438
(f) Mesozooplankton (>200 µm)		
Apendicularia	749	501
Cladocerans		
Evadne nordmanni	7	8
Evadne spinifera	0	354
Podon intermedius	72	23
Copepods		
Acartia clausi	736	19
Acartia juveniles	768	60
Calanus juveniles	33	8
Centropages chierchiae	65	49
Centropages juveniles	788	45
Clausocalanus spp.	0	30
Copepodits	1902	320
Ditrichocorycaeus anglicus	0	11
Euterpina acutifrons	0	15
Isias clavipes	163	8
Nauplii larvae	39	11
Oithona nana	13	0
Oithona similis	169	222
Oncaea media	13	72
Paracalanus parvus	931	494
Parapontella brevicornis	26	0
Gastropods larvae	319	260
Crustacean larvae		
Braquiura zoea	20	4
Cirripods cypris	46	8
Cirripods nauplii	189	313
Decapods	26	4
Euphausacians	0	11
Bivalves larvae	46	369
Echinoderms larvae	0	23
Fish larvae	7	11
Sifonofora	0	19
Total copepods	5646	1364
Total mesozooplankton	7131	3289

higher densities, followed by apendicularia, cladocerans and bivalves larvae (Table 2.1.3, August).

Wind-induced conditions in the Northern and Western coast of Galicia

The upwelling phenomenon occurring in the areas close to northern and western coasts of Galicia can be compared from results shown in the Fig.2.1.5. In this Figure, values of daily upwelling index during the upwelling seasons from 1990 to 2008 calculated at the 43.5°N-10.5°W point were represented on an UIW versus UIN axes system. The northerly component of shelf wind-stress causes upwelling favourable conditions in the Western Galician coast (UIW=-Qx) while the same occurs with the easterly component to the Northern coast. The figure corresponds to UI favourable in both coasts (positive UIW and UIN). UI points situated inside the figure fit to the linear regression UIN/UIW=0.94 indicating that the upwelling conditions were 6% higher in the western shelf.

Discussion

The Ekman transport sequence in the western Cantabrian Sea (Fig.2.1.2), resulting from the wind pattern triggered the high pressures crossing on Galicia (Wooster et al., 1976; Fiuza et al., 1982; Torres and Barton, 2007; Alvarez et al., 2008), suggests that the observed upwelling and downwelling events may be as usual in the northern Galician coast as in the Western Rias area during the upwelling season (Prego, 1992; Tilstone et al., 1994; Diz et al., 2006).

During the upwelling event, ENACW was detected on the shelf off the Northern Rias (from 65 m depth to the bottom, Fig. 2.1.3). Upwelling did not reach the surface water, where high temperatures were observed, especially at the inshore stations. Both facts seem to be usual resulting in a significant difference with respect to the rias located close (Varela et al., 2005) and south (Rosón et al., 1997; Prego et al., 2001) Cape Finisterre because upwelling penetrates inside them, raising up to surface layers (Alvarez-Salgado et al 1993; Alvarez et al., 2005a). Another difference is the origin of the upwelled water mass. Western of Cantabrian Sea is characterized by the presence of ENACW from sub-polar origin (ENACWP) (Fraga, 1981; Llope et al., 2006) while in the event of July 2008 (Fig. 2.1.3), the subtropical branch (ENACWT), formed along a front near the Azores (Fiuza et al., 1983; Rios et al., 1992), upwelled in the northern Galician coast, as it occurs in the Finisterre upwelling in the western coast (Blanton et al., 1984).

After the spring bloom of phytoplankton in the Western Rias the ENACWT transport nutrient salts to the photic layer (Fraga 1981, Prego et al., 1999b) during the upwelling events turning these rias into eutrophic zones (Varela et al., 2008). This was not observed in the Northern Rias where low nitrate and chlorophyll concentrations were measured in the water column (Fig.2.1.4.a). This highlights that upwelling did not affect these rias and they could be considered as mesotrophic systems. The innermost or estuarine ria zone may be an exception, even though this matter deserves more attention. However, the whole northern shelf was not evenly affected by the wind-induced upwelling. The Ortigueira zone was the most influenced with a significant vertical mixing in the lower layer of the water column, as shown by the TS diagram (Fig.2.1.3). The consequence is a higher input of nutrient salts to the photic layer, a subsequent phytoplankton growth and a remineralisation area marked both, by chlorophyll and ammonium maxima (Fig. 2.1.4.b).

Nevertheless, this process occurs out the Ria of Ortigueira but near its mouth. The Ortigueira case as compared to Barqueiro and Viveiro shelves could be only a consequence of the Cape Estaca de Bares effect because upwelling processes are more intense and persistent at southern areas of the capes (Crepon et al. 1984), as it was observed in the neighbouring Cape Peñas (Molina, 1972; Botas et al., 1990; Llope et al., 2006) and Cape Ajo (Lavín et al., 1998) in the central Cantabrian coast. On the other hand, in the Western Rias the remineralisation supplies recycled nutrients at the inner ria (Alvarez-Salgado et al., 1996; Prego, 2002), while in the Northern Rias this process is negligible.

During the downwelling event temperatures higher than those of upwelling were observed in the Northern Rias (Fig.2.1.3). Western winds moved the surface seawater coastward as indicated by the Ekman transport (Fig.2.1.2), a process similar to those observed in other Galician Rias (Cabanas and Alvarez, 2005). Waters were retained inside the rias, and nutrients were almost exhausted (Fig. 2.1.4.a). In these circumstances, river outflow might be the main nutrient source and consequently phytoplankton is constrained to the innermost ria zone as shown by the chlorophyll-*a* distribution. (Fig.2.1.4.a). This can also explain the slight increase of POC and PON concentration inside the Ria of Barqueiro from July to August associated with a higher C:N ratio as a consequence of an enhanced remineralisation related to downwelling. However, remineralisation in the Northern Rias was not as important as in Western Rias where high concentrations of recycled nutrients maintain a high biological activity (Alvarez-Salgado et al., 1996; Varela et al., 2004). In any case, low phytoplankton abundances were observed both, in July and August, although the enrichment of the water due to the upwelling may be reflected in an increase in the biomass of some species of phytoplankton and zooplankton (Tables 2.1.2 and 2.1.3), e.g *Pseudo-nitzschia* cf. *delicatissima* which abundance is associated with nitrate and nitrite concentrations (Kaczmarska et al. 2007, Loureiro, 2009). Other species of diatoms can be dominant in any season when silicate concentrations in water are greater than 2 µM (Egge and Aksnes 1992); this would explain why there are no great differences between the mean abundance of diatoms during July and August.

In the case under study at the northern shelf, there were nine days of upwelling favourable conditions previous to sampling, with average UI of 1095 $m^3 \cdot s^{-1} \cdot km^{-1}$. It occurred only ten times during the interval of 1990-2008. The poor intensity of upwelling events for the western Cantabrian coast was reported by Alvarez et al. (2010) who estimated a probability of around 17% for upwelling favourable conditions of at least five days from June to September. The downwelling occurred in the northern region after seven days with an average UI of -660 $m^3 \cdot s^{-1} \cdot km^{-1}$. The events in the Northern coast can be characterized by defining conditions to favourable upwelling (+UIN) and downwelling (-UIN) periods: at least one week with averages out of the range of ±500 $m^3 \cdot s^{-1} \cdot km^{-1}$. Under these conditions, the average of upwelling events per year was 1.9 ± 0.8 from May to September during the studied period of nineteen years with an average of 12 ± 4 days of easterly winds and UI of 870 ± 270 $m^3 \cdot s^{-1} \cdot km^{-1}$ Nevertheless, in 1997 no events were observed. The wind-forcing pattern in the Northern coast of Galicia is less favourable to upwelling (75% of events) and downwelling (95% of events) than in the Western zone (Fig.2.1.5). The difference between the two Galician regions increases when the lasting and intensity of the upwelling process are considered. UI values (up to 1390 ± 180 $m^3 \cdot s^{-1} \cdot km^{-1}$; Alvarez et al., 2005a) and event time scale (10-15 days; Nogueira et al., 1997) are higher in the western shelf.

The frequency of downwelling was 2.1 ± 1.0 $event \cdot yr^{-1}$ (13 ± 7 days of westerly winds and 760 ± 200 $m^3 \cdot s^{-1} \cdot km^{-1}$) with no cases in 1990, four in 1999 and three events higher than -1000 $m^3 \cdot s^{-1} \cdot km^{-1}$ in the whole period. From May to September, downwelling was like upwelling events in frequency. Downwelling was lower in intensity but they can last longer than upwelling. There were only six chained upwelling-downwelling transitions, including the one studied, during the period 1990-2008. This scarcity in upwelling-relaxations processes could explain why, red tides events were not yet reported for the Northern Rias while they are a typical event during downwelling in the Western Rias (Figueiras et al., 1994). In any case, the August downwelling was associated to a small red tide of *Lingulodinium polyedrum* which dominated the dinoflagellates community (Table 2.1.2).

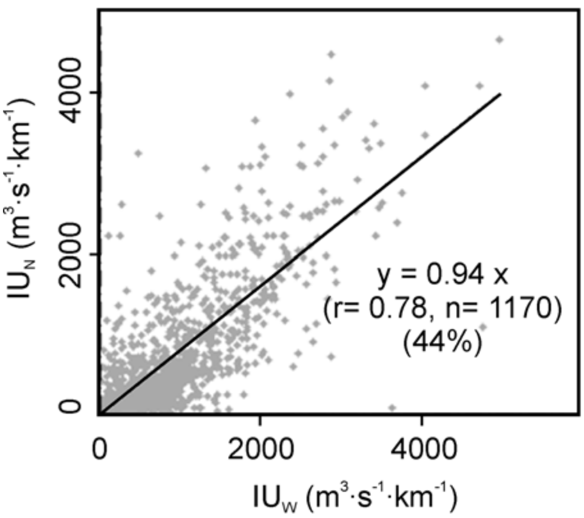


Figure 2.1.5. Daily upwelling index (UI) for the Northern Galician coast (UI_N) vs. the Western Galician coast (UI_W) calculated at the control point 43.5°N, 10.5°W. Data belong to the upwelling season (May-September) over the period of 1990-2008. Positive values of UI_W and UI_N correspond with UI favourable conditions in both coasts. Straight line shows the linear fit (as y=ax, p-value <0.001). The percentage of total data considered is also indicated.

2.2 A winter upwelling event in the Northern Galician Rias: Frequency and oceanographic implications

Introduction

The western Galician coast, south of Cape Finisterre, is the northernmost limit of the Eastern North Atlantic Upwelling System (ENAUS), which extends from 10°N to about 44°N (Wooster et al., 1976). Upwelling has important biological implications due to the high input of nutrients that trigger the great primary productivity of this coast, supporting an intense mussel raft culture (Blanton et al., 1987). Coastal upwelling is commonly observed along the western Galician coast during spring–summer and has been extensively studied during the last decades (Fraga, 1981; Prego et al., 2001; Alvarez et al., 2005a; Alvarez- Salgado et al., 2006; Gomez-Gesteira et al., 2006; Alvarez et al., 2008). Upwelling injects a colder nutrient-rich deeper water (Prego et al., 1999a), known as Eastern North Atlantic Central Water mass (ENACW; Fiuza, 1984; Rios et al., 1992) into the Western Galician Rias (locally named Rias Baixas). Although this coastal upwelling is basically a spring–summer process linked to NE winds, it has also been observed in autumn–winter under some special conditions. Alvarez et al. (2003) characterized a winter upwelling event in January 1998, pumping seawater driven by the Iberian Poleward Current into the Pontevedra Ria. The mechanism driving this winter upwelling was similar to the one observed in summer, but the poleward intrusion varied the ria thermohaline properties and residence time, making it much more salty and rendering it poor in nutrient salts; nonetheless the taxonomic composition of the phytoplankton community did not change noticeably, changing only in relative proportions (Prego et al., 2007). deCastro et al. (2006) studied an autumnal upwelling event in November 2001 inside the Ria of Vigo.

Thermohaline variables revealed that the upwelled water mass was ENACW. These studies are not isolated events because deCastro et al. (2008) found six upwelling events in the Western Rias during the wet season (November to February) from 2000 to 2005 with features similar to the ones observed in summer.

North of Cape Finisterre is the northern Galician coast. Eastward of 8°W (Cape Ortegal), approximately along the 43.6°N parallel are located the Northern Galician Rias (locally named Rias Altas). This coastal zone can be considered as the westernmost limit of the Cantabrian littoral where easterly winds parallel to the coast generate occasional spring–summer coastal upwelling at the eastern and middle Cantabrian coast (Botas et al., 1990; Fontan et al., 2008), cooling and fertilising surface waters resulting in a primary production increase (Fernandez and Bode, 1991; Llope et al., 2006). Nevertheless, these phytoplankton productive events are less important than those observed in the Western Rias, south of Cape Finisterre (Varela et al., 2005). At the northern Galician coast, upwelling is also present although is not a common event. Previous studies showed that in north of Cape Finisterre, upwelling is discontinuous and remains near the edge of the continental shelf (Prego and Bao, 1997). It is already known that upwelling events with similar features can occur at both sides of Cape Finisterre but with different probability and intensity. Torres et al. (2003) described the Galician upwelling region from July 1999 to May 2001 using 2 years of wind data from the QuikSCAT satellite. They found that the wind patterns may alternate producing brief

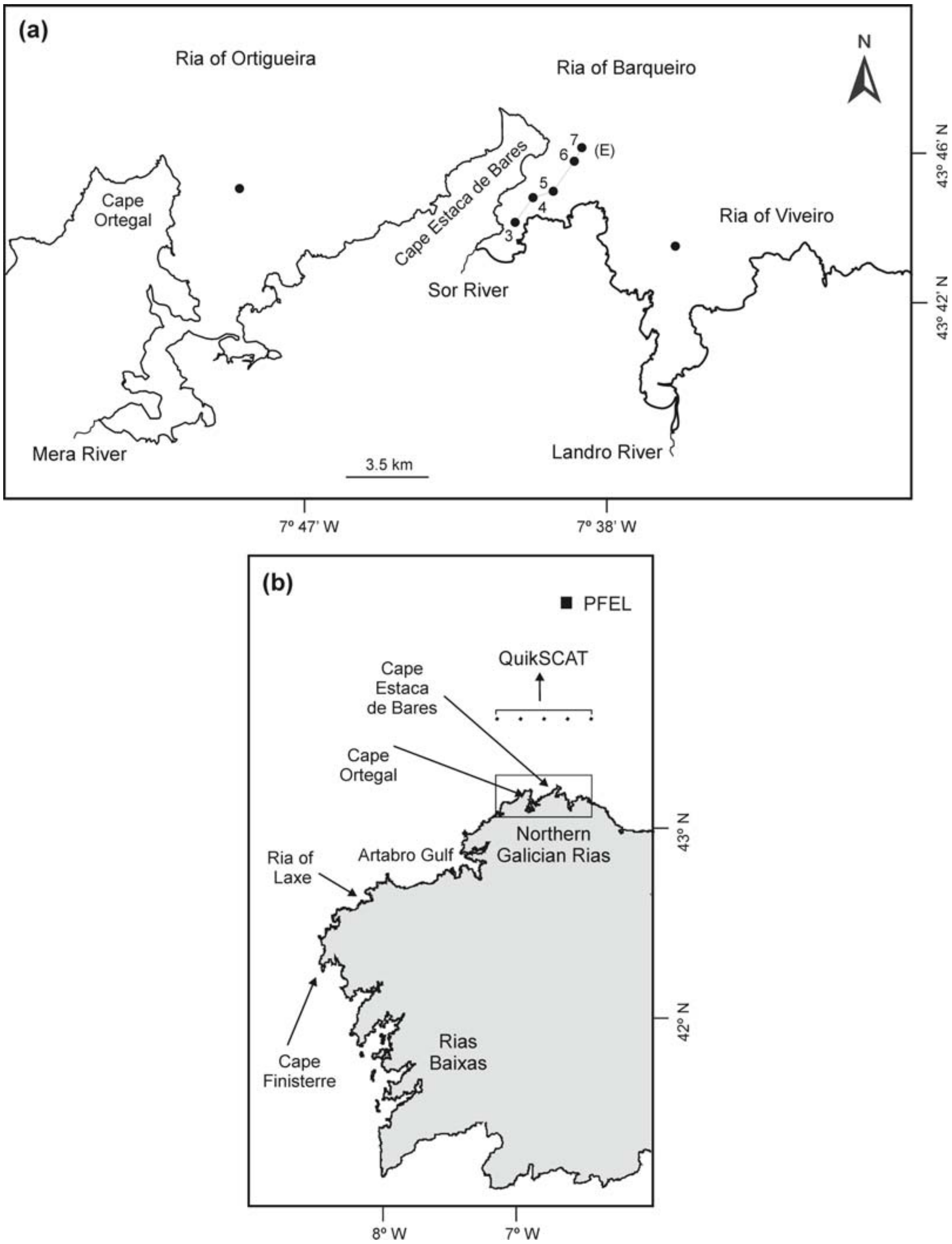


Figure 2.2.1. Map of the Northern Galician Rias showing the sampling hydrographic stations (a, black circles). Black square represent the point where data from the PFEL database were obtained and black points represent the 5 control points considered to analyse wind data provided by the QuikSCAT satellite (b).

episodes of upwelling at the northern or western coast, or a combined pattern may occur producing weak upwelling on both coasts. In addition, Gomez-Gesteira et al. (2006) analysed Ekman transport close to the Galician coast using forecasted winds from November 2001 to October 2004. They found that upwelling reaches a maximum probability of 60% at western coast during summer and a minimum probability of around 15% in December–January. On the other hand, the probability of upwelling favourable conditions never surpasses 30% at the northern coast, with two maxima in March and September and a minimum in December– January. These results were corroborated by Alvarez et al. (2008) using QuikSCAT satellite data from November 1999 to October 2005. There are no studies involving upwelling events inside the Northern Galician Rias. Nevertheless, other types of studies have been developed focussing on biological characteristics, as the mortality in populations of flat oyster (Montes et al., 1991, 1992) and the salt marsh and sedimentary characteristics (Otero et al., 2000; Delgado et al., 2002; Lorenzo et al., 2007). Clearly, there is a lack of knowledge about the upwelling development in this area and its influence on biological processes. Thus, the aim of this section is (1) to characterize a winter shelf-water upwelling evidence (February, 2008) and its consequences on the biological and chemical patterns in the water column of the Northern Galician Rias, and (2) to find out the recurrence of these winter events at the northern Galician coast over a long period (1967–2007).

Data used for analysis

Atmospheric variables

Surface wind fields from January to February 2008 were provided by the QuikSCAT satellite, and retrieved from the Jet Propulsion Laboratory web site (http://podaac.jpl.nasa.gov/ quikscat/qscat_data.html). The data set consists of global grid values of meridional and zonal components of wind measured twice daily on an approximately 0.25°×0.25° grid with global coverage. QuikSCAT data are given in an ascending and descending pass. Data corresponding to one pass present numerous shadow areas, therefore, an average between both passes was considered to increase the coverage. Wind speed measurements range from 3 to 20 $m^3 \cdot s^{-1}$, with an accuracy of 2 $m^3 \cdot s^{-1}$ and 20° in direction. The reference height of wind data is 10 m. In addition, it is necessary to take into account that wind data close to coast (≈ 25 km) are not available due to the existence of a small coast mask. Five control points were considered along the northern Galician coast at the latitude 44.25°N. The obtained discrete series covers from 8.25°W to 7.25°W (Fig. 2.2.1.a, black points). Previous studies have shown that QuikSCAT data are comparable to modelled data in this area (Gomez-Gesteira et al., 2006; Alvarez et al., 2008). Actually, a statistical comparison between satellite wind measurements and high resolution numerical models was carried out (Penabad et al., 2008), revealing similar results between models and satellite data.

Ekman transport was calculated using wind data from QuikSCAT satellite, W, the sea water density, ρ_w= 1025 kg m^{-3}, a dimensionless drag coefficient, C_d=1.4×10^{-3}, and the air density, ρ_a= 1.22 kg m^{-3}, by means of:

$$Q_x = \frac{\rho_a C_d}{\rho_w f}\left(W_x^2 + W_y^2\right)^{1/2} W_y \quad and$$
$$Q_y = -\frac{\rho_a C_d}{\rho_w f}\left(W_x^2 + W_y^2\right)^{1/2} W_x$$

f is the Coriolis parameter defined as twice the vertical component of the Earth's angular velocity, Ω, about the local vertical given by $f = 2\Omega \sin(\theta)$ at latitude θ. Finally, x subscript corresponds to the zonal component and the y subscript to the meridional one.

Ekman transport data from January 1967 to December 2007 were provided by the Pacific Fisheries Environmental Laboratory (PFEL) (www.pfel.noaa.gov). The PFEL distributes environmental index products and time series databases to cooperating researchers, taking advantage of its long association with the U.S. Navy's Fleet Numerical Meteorology and Oceanography Centre (FNMOC). FNMOC produces operational forecasts of the atmosphere and the ocean state several times daily and maintains archives of several physical variables. For our purposes six-hourly Ekman transport data were considered at the control point 45.5°N, 7.5°W located in front of the northern Galician coast (Fig. 2.2.1.b, black square) on an approximately 1°×1° grid. These data lie on a coarser spatial grid than the QuikSCAT ones although with a longer temporal extent which allows analyzing the temporal variability of upwelling. Data were averaged to a daily timescale.

The daily Ekman transport calculated from both databases can be compared taking into account the common period between both databases (1999-2007) at the control point located in front of the northern Galician coast (45.5°N, 7.5°W). This comparison was made in terms of the correlation coefficient ($r_{a,b}$, a: QuikSCAT data, b: PFEL data), which was calculated by:

$$r_{a,b} = Cov(a,b)/\sigma_a \times \sigma_b$$

In addition, the amplitude difference was analysed in terms of the dimensionless parameter:

$$\alpha = \sqrt{\sum_{i=1}^{N} a_i^2 \Big/ \sum_{i=1}^{N} b_i^2}$$

The obtained correlation coefficient for both components is around 0.8-0.9 (significance level >99%) showing a good correlation between both databases. The amplitude parameter for the zonal component (1.01) shows that the PFEL data amplitude is slightly smaller than the QuikSCAT one, while for the meridional component this parameter (0.93) shows that the PFEL data amplitude is slightly higher than the QuikSCAT one.

Upwelling Index (UI) can be defined as the Ekman transport component in the direction perpendicular to the shoreline (Nykjaer and Van Camp, 1994; Gomez-Gesteira et al. 2006). Although the shoreline angle along the northern Galician coast changes slightly from the eastern to the western limit, macroscopically it can be considered approximately parallel to the equator. Thus, the Q_y component can be directly considered as the UI. Positive (negative) UI values mean upwelling favourable (unfavourable) conditions.

Sea variables

Two cruises were carried out in the Northern Galician Rias onboard the *RV Lura* in January 22-23 and February 20-21, 2008. Thermohaline variables were measured at five stations located along the main channel of the Ria of Barqueiro with depths increasing from 7 m inshore to 50 m offshore (Fig. 2.2.1.a). In addition, a control point was also considered near the mouth of Ria de Ortigueira and Ria de Viveiro (Fig. 2.2.1.a, station 6). Temperature and salinity profiles were measured by means of a General Oceanic Rosette, including a CTD 25 SeaBird with PAR and Fluorescence sensors. The water column at each station was also sampled using General Oceanic Niskin bottles of 5 L. Aliquots were collected along the main channel of the Ria of Barqueiro at standard depths (0, 5, 10, 20, 30 and 40 m) from surface to near bed to analyse dissolved oxygen concentration, nutrient salts, and chlorophyll-*a*.

At station 5, located at the central part of the main channel of the Ria of Barqueiro (Fig. 2.2.1.a), were also measured at the same standard depths: particulate organic carbon (POC) and nitrogen (PON); primary

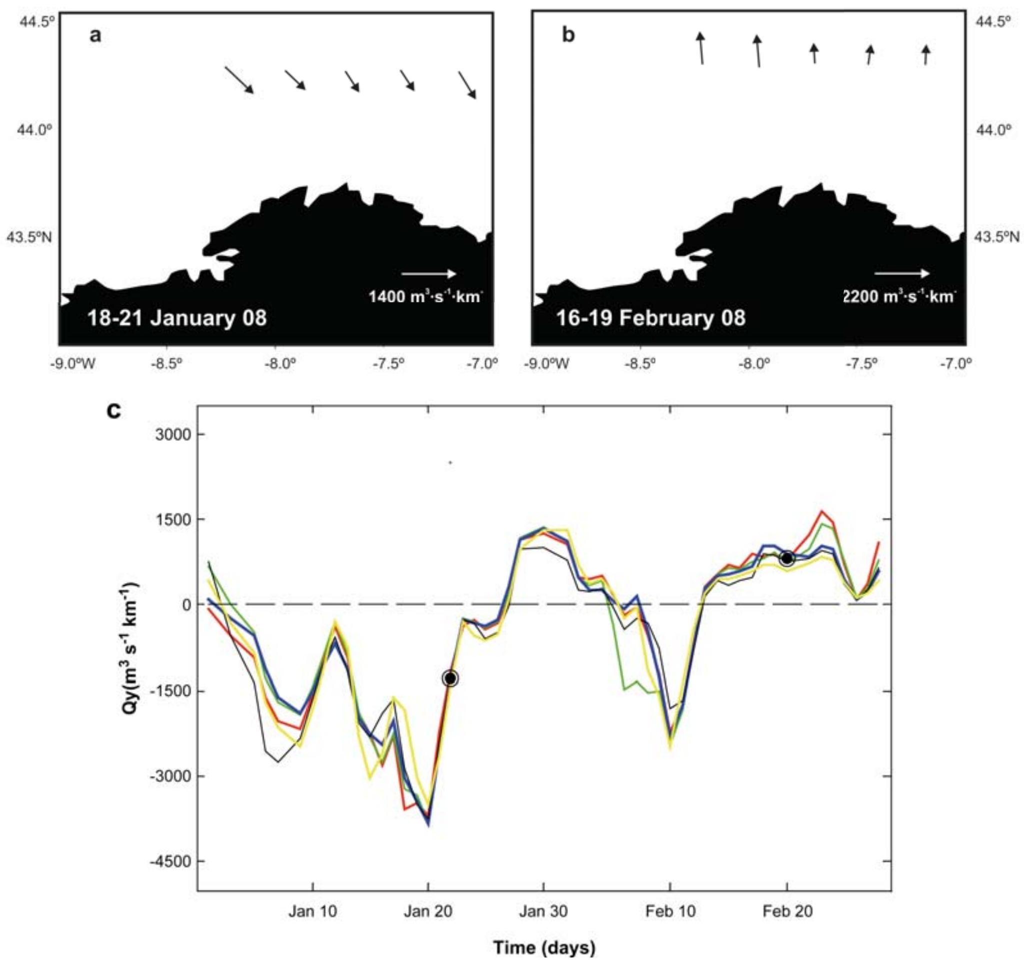


Figure 2.2.2. Ekman transport calculated at 5 control points (see Fig. 2.2.1b) in the area of the northern Galician rias corresponding to the cruises carried out in January (a) and February (b) 2008. Data were averaged for 4 days before each cruise. (c) Temporal evolution of the meridional component of Ekman transport (Qy) at the 5 control points from January to February 2008. Black points represent the date of each cruise.

production and phytoplankton abundances. A detailed explanation about processing and analysis of the samples is provided in Chapter 1, *Section Materials and Methods*.

Suspended particulate matter fluxes to sediment were also measured at station 5 using a multitrap collector system deployed 5 m over the sea-bed and anchored for a 24 h period. The trap system was described in Knauer et al. (1984) following the JGOFS protocols (UNESCO, 1994) (for a complete description of the system see Varela et al 2004).

In addition to the measured variables during these cruises, salinity and temperature CTD data (Sea-Bird 9/11) measured on 15 February 2008 (R/V Cornide de Saavedra) at six stations from 69 to 2742 m depth along the 8° W meridian (Cape Ortegal) were kindly supplied by the 'Instituto Español de Oceanografia-IEO' (project 'Radiales Profundos 02-08').

Results and Discussion

Atmospheric conditions

Figure 2.2.2 shows the Ekman transport behaviour in the area of the

Northern Galician Rias corresponding to the cruises carried out in January (a) and February (b) 2008. Ekman transport was calculated at 5 control points by means of wind data provided by the QuikSCAT satellite and was averaged for 4 days before each cruise. In January (Fig. 2.2.2.a), transport was mainly directed southward (upwelling unfavourable) showing approximately the same direction and amplitude at each point. In February (Fig. 2.2.2.b), the transport pattern was completely different pointing northward (upwelling favourable) along the coast and with the maximum intensity at the western area.

To analyse the temporal evolution of the Ekman transport, the Qy component was represented at the 5 control points from January to February 2008 (Fig. 2.2.2.c). The five control points showed a similar behaviour in direction and amplitude. During January and February, two periods of positive Qy values were observed with maximum values on the order of 1500 $m^3 \cdot s^{-1} \cdot km^{-1}$. The first one covers from January 26 to February 5 and the second one from February 12–28. Thus, the cruise corresponding to February 20–21 was carried out after 9 consecutive days of upwelling favourable conditions. For the rest of the period under study, the meridional component showed negative values with two important minima around.

Oceanographic conditions

To characterize the hydrographical, biogeochemical and phytoplankton patterns observed in the Northern Galician Rias during the two cruises under scope, the distribution of thermohaline variables, nutrient salts and planktonic material was studied along the main channel of the Ria of Barqueiro (see Fig. 2.2.1.a).

In January, the salinity distribution along the main channel of the Ria of Barqueiro (Fig. 2.2.3, left panel) showed values between 35.0 near surface and 35.7 near bed with a higher stratification near surface. Temperature range throughout the water column (not shown) was small (13.2–13.7°C) with a thermal inversion typical of winter weather conditions and density (not shown) was mainly the result of the salinity gradient showing isolines similar to the ones observed for salinity, with a small variation decreasing from 26.3 $kg \cdot m^{-3}$ near surface to 26.8 $kg \cdot m^{-3}$ near bed. Salinity values corresponding to February (Fig. 2.2.3, right panel) ranged from 34.1 near surface to 35.8 near bed. This high salinity value was observed from around 10 m to near bed suggesting the presence of seawater. The lowest salinity values were measured near surface at the inner part of the ria due to the freshwater input (average flow of sampling date and the five previous days: 10.2 ± 0.3 $m \cdot s^{-1}$). In addition, the water column was more stratified near surface (≈5 m) than near bed. Temperature distribution (not shown) displayed low vertical variations with a thermal inversion (13.5° C near surface, 13.6° C near bed) and density (not shown) was similar to the salinity distribution ranging from 25.7 $kg \cdot m^{-3}$near surface to 26.9 $kg \cdot m^{-3}$near bed. Thus, thermohaline properties under 10 m depth were practically homogeneous.

The TS diagram corresponding to data measured on 15 February 2008 along the 8°W meridian (Fig. 2.2.4) showed how the water column was vertically homogeneous west of Cape Ortegal (station A, B and C; Fig. 2.2.4) due to winter cold conditions and to the lack of continental water supply. Note that the winter prevailing current is poleward in this area. East of Cape Ortegal, salinity and temperature values measured at the mouth of the northern rias showed that in February TS salinity profiles were not lineal. Surface seawater layer becomes heterogeneous due to the freshwater discharges from the rivers flowing into the rias and to a shelf-water intrusion, which reached the subsurface layer. As well, TS diagram indicates a higher influence of

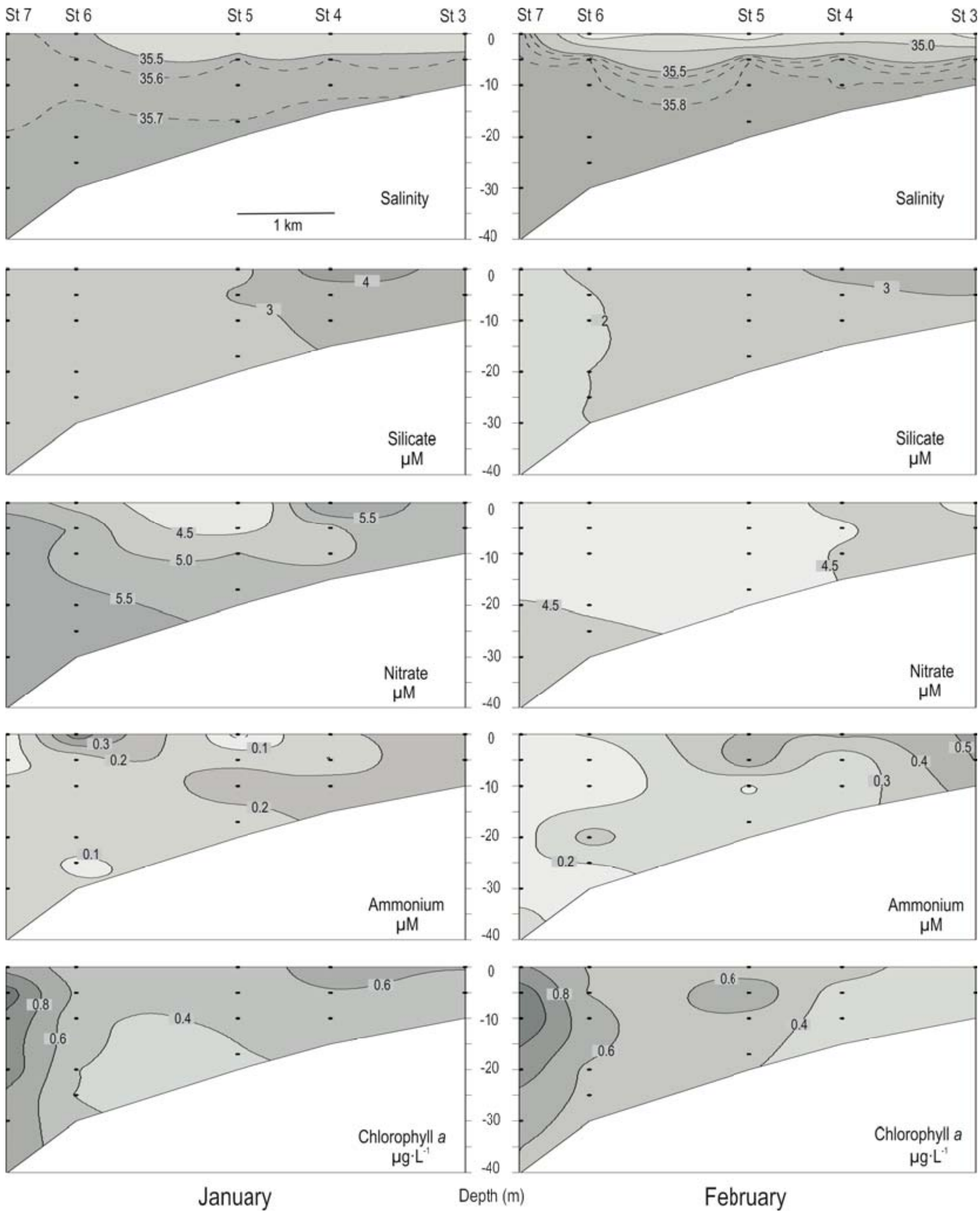


Figure 2.2.3. Contour maps of salinity, dissolved silicate, nitrate, ammonium and chlorophyll-a along the main channel of the Ria of Barqueiro in January (left panel) and February (right panel) 2008. Station positions are indicated in Fig. 2.2.1.a. Black points indicate sampling depths.

upwelling eastward (Viveiro–Barqueiro–Ortigueira) when TS profiles are compared with the values of ENACW (station D, E and F; Fig. 2.2.4).

Taking into account temperature and salinity values of the upwelled seawater in February inside the northern rias it is possible to ensure that this water can not

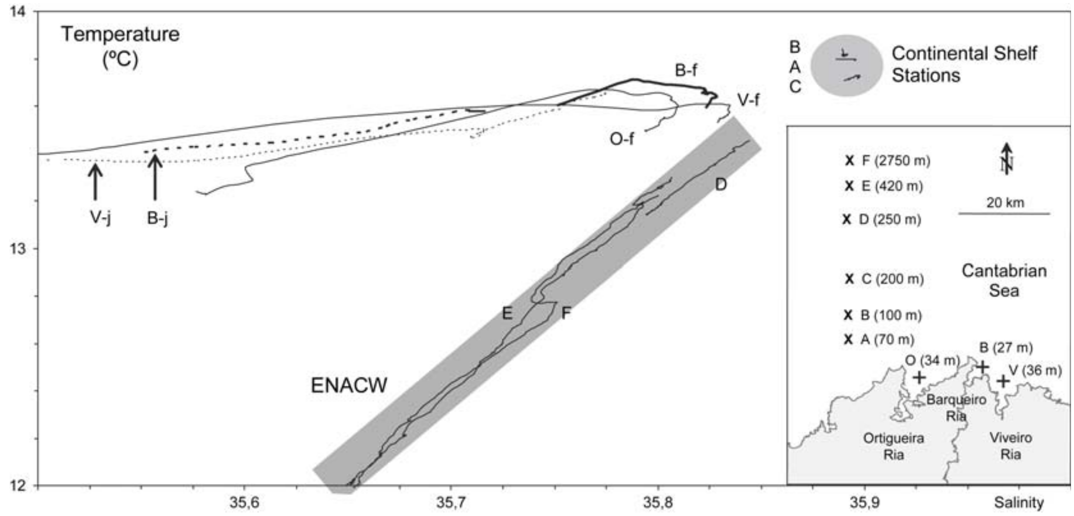


Figure 2.2.4. TS diagram corresponding to the stations located at the mouth of the northern rias (station 6 in Fig. 2.2.1.a) of Ortigueira (O), Barqueiro (B) and Viveiro (V) in January (-j) and February (-f). Stations along the 8 W meridian (A-F) are also included to show the Eastern North Atlantic CentralWater (ENACW grey band using D-F data from 150 to 300m depth) and the continental shelf pattern (A-C). The stations position is shown in the map of lower-right corner with depth indicated between brackets.

be associated with ENACW (Fig. 2.2.4) or IPC (water transported by the Iberian Poleward Current; Frouin et al., 1990; Alvarez et al., 2003; Gil, 2003; Prego et al., 2007), but to shelf bottom water. This situation is in agreement with previous studies which showed that north of Cape Finisterre these water bodies keep distant from the coast, near the shelf break (Prego and Bao, 1997; Bao et al., 1997). Thus, a stronger meteorological forcing would be necessary to observe ENACW (Botas et al., 1990) or IPC (Gonzalez-Pola et al., 2005) inside the Northern Galician Rias.

The salinity decrease observed near surface in January at the inner part of the ria due to river outflow (average flow of sampling date and the five previous days: 21.4 ± 5.0 m·s^{-1}) showed a fluvial contribution of nutrients (station 3, 4; Fig. 2.2.3). There was up to 4.9 µm of silicate, 5.6 µm of nitrate and 0.28 µm of ammonium inside the ria (Fig. 2.2.3). A slight increase of nitrate was detected at the external part of the ria (station 7; Fig. 2.2.3). Dissolved oxygen (not shown) showed a small variation ranging from 98% to 102% of saturation percentage indicating well oxygenated waters. Phosphate and nitrite (not shown) presented homogeneous concentrations of 0.3 µm and 0.26 µm respectively along the ria channel. Chlorophyll-*a* distribution (Fig. 2.2.3) showed low values around 0.5 mg·L^{-1} at the inner part increasing up to 1 m·s^{-1} at the external part of the ria (Fig. 2.2.3).

In February, biogeochemical parameters (Fig. 2.2.3) showed different patterns to the ones described for the previous cruise. Silicate and ammonium decreased seaward with maxima at the inner part of the ria near surface (station 3; Fig. 2.2.3) (3.1 and 0.5 µm respectively), and minima at the external part (station 6; Fig. 2.2.3) (2 and 0.2 µm respectively). Nitrate displayed the opposite behaviour with the lowest concentrations at the inner part near surface (3.9 µm) and the highest ones at the ria mouth near bed (4.6 µm). Dissolved oxygen percentage (not shown) was homogeneous throughout the whole water column, corresponding to 99–101%

of saturation while phosphate and nitrite (not shown) presented nearly uniform concentrations (0.2–0.3µm) all along the ria. Chlorophyll-*a* showed lower concentrations at the inner part of the ria near surface, around 0.3 mg·L^{-1}, and higher ones at the external part (station 7) about 10m depth, with values of 1.2 mg·L^{-1} (Fig. 2.2.3).

Nutrient salts distribution in the Ria of Barqueiro (Fig. 2.2.3), with a January small-concentration increase in the inner ria as result of a higher river flow, also suggested the presence of seawater from subsurface origin because (1) the nutrient concentrations were half of the typical ENACW in the continental border (Fraga, 1981; Prego et al., 1999a), and (2) these concentrations did not varied significantly with regard to January levels (Fig. 2.2.3), i.e. nitrate similar to those forecasted from water temperature of the winter mixing in this marine area (Prego et al., 1999a). However, winter upwelling events have been observed to increase the ria-ocean exchange both in the western and in the Northern Galician Rias. As a result, the surface outflow caused in the Ria of Barqueiro a salinity vertical gradient and chlorophyll-*a* poverty in surface water, as previously observed in the Pontevedra Ria (Prego et al., 2007).

Values of particulate material throughout the water column were also analysed in January (Table 2.2.1) at station 5 (Fig. 2.2.1.a). Integrated chlorophyll-*a* was low, around 8 mg·m^{-2} as well as the primary production, about 0.3 gC·m^{-2}·d^{-1}. The sunny hours and solar radiation were 6.0 ± 2.5 (h) and 820 ± 200 (10 kJ·m^{-2}), respectively (average of sampling date and the five previous days, Viveiro Meteorological station). Particulate organic carbon (POC) and nitrogen (PON) were around 1100 and 130 mg·m^{-2} respectively, with a C/N ratio of particulate organic matter (POM) of 10 (Table 2.2.1).

The mean abundances of phytoplankton measured at station 5 (Table 2.2.2, January) were dominated by naked flagellates with mean abundances of 150 cells·mL^{-1}. Larger phytoplankton showed a predominance of diatoms, with *Navicula cf transitans, Nitzschia longissima* and *Pseudonitzschia cf australis* as dominant species. Dinoflagellates were very scarce and *Amphidinium flagellans* was the characteristic species. Other groups displayed negligible abundances. Planktonic ciliates showed low abundances, around 4 cells·mL^{-1}. Species of Genus *Lohmaniella* and *Myrionecta rubra* were the dominant taxa. Microzooplankton abundance was low, around 600 indiv·m^{-3} and dominated by bivalve's larva. Meso- zooplankton was also low with around 100 indiv·m^{-3}, with *Braquiura larva, Acartia clausi* and copepodits as the main taxa (Table 2.2.2, January).

Taking into account the fluxes of particulate material collected in

Table 2.2.1. Values of particulate material throughout the water column and fluxes to sediment measured at the Ria of Barqueiro (station 5) in January and February 2008

	January	February	Unit
Water column			
Chl *a*	7.8	9.8	mg·m^{-2}
POC	1130	1355	mgC·m^{-2}
PON	136	189	mgN·m^{-2}
C/N	10.03	8.54	mol/mol
PP	0.31	0.14	gC·m^{-2}·d^{-1}
Sediment trap			
Chl *a*	0.96	0.67	mg·m^{2}·d^{-1}
POC	445	503	mgC·m^{2}·d^{-1}
PON	41	47	mgN·m^{2}·d^{-1}
C/N	12.63	12.48	mol/mol

Chl *a*: chlorophyll-*a*; POC: particulate organic carbon; PON: particulate organic nitrogen; C/N: carbon/nitrogen ratio; PP: primary production.

sediment traps (station 5), the flux of chlorophyll-*a* to near bed was around 1 mg Chl-*a*·m^{-2}·d^{-1} (Table 2.2.1, January) representing approximately 10% of the water column stock. POC flux was higher than 400 mgC·m^{-2}·d^{-1} and accounted for 39% of stock throughout the water column. The C/N ratio of the particulate material was about 12.

Fluxes of planktonic material showed that diatoms dominated the large phytoplankton in the trap samples (Table 2.2.3, January). Copepods fecal pellets were also frequent while dinoflagellates were extremely scarce and represented by small unidentified species.

In February, values of particulate material throughout the water column at station 5 (Table 2.2.1) showed that the integrated chlorophyll-*a* was around 10 mg·m^{-2}. Primary production was low, about 0.15 gC·m^{-2}·d-1. The sunny hours and solar radiation were 5.2 ± 2.7 (h) and 940 ± 310 (10 kJ·m^{-2}), respectively (average of sampling date and the five previous days, Viveiro Meteorological station). POC and PON were around 1300 and 190 mg·m^{-2} respectively, with a C/N ratio of particulate organic matter (POM) of 8.5 (Table 2.2.1).

Table 2.2.2. Mean abundance of phytoplankton (cells mL^{-1}), planktonic ciliates (cells mL^{-1}), microzoo and mesozooplankton (in individuals m^{-3}) at the Ria of Barqueiro (station 5) in January and February 2008

Phytoplankton group	January	February
(a) Dinoflagellate		
Amphidinium flagellans	0.4	2.8
Heterocapsa niei	0.0	1.3
Prorocentrum minimum	0.0	2.4
Scrippsiella trochoidea	0.0	1.6
Total dinoflagellate	0.6	9.6
(b) Diatoms		
Chaetoceros curvisetus	0.0	0.6
Chaetoceros dydimus	0.0	2.3
Chaetoceros gracilis	0.0	0.4
Chaetoceros spp	0.0	3.0
Chaetoeros debilis	0.0	1.1
Corethron hystrix	0.9	0.0
Lauderia annulata	0.0	0.7
Navicula cf *transitans*	3.7	0.4
Nitzschia longissima	1.7	3.3
Nitzschia longissima small	5.8	0.9
Pseudonitzschia cf *australis*	1.5	1.7
Rhizosolenia setigera	0.0	2.7
Thalassionema nitzschioides	0.0	0.7
Thalassiosira nana	1.1	0.0
Thalassiosira rotula	0.7	0.0
Thalassiosira subtilis	0.7	0.0
Total diatoms	18.0	19.0
(c) Flagellates		
Flagellates 3-10µm	151.5	348.8
(d) Chrysophyceans		
Dctyocha speculum	0.0	21.7

(e) Planktonic ciliates		
Lohmaniella ovalis	1.4	0.5
Lohmaniella oviformis	0.7	1.3
Myrionecta rubra	0.7	2.4
Srombidium epidemum	0.1	0.7
Strombidium acutum	0.3	0.4
Strombidium conicum	0.2	0.0
Strombidium dalum	0.1	0.4
Strombilidoium neptuni	0.0	0.2
Total ciliates	4.1	6.5
(f) Microzooplankton (40-200 µm)		
Bivalves larvae	446	48
Nauplii copepods larvae	110	2356
Apendicularia	9	785
Total microzooplankton	604	3590
(g) Mesozooplankton >200 µm		
Braquiura zoea	35	26
Acartia clausi	27	421
Acartia clausi juveniles	4	832
Acartia discaudata	0	308
Calocalanus stylimeris	0	3
Clausocalanus spp.	12	21
Ctenocalanus vanus	5	24
Copepodits	21	42
Isias clavipes	0	253
Oithona similis	9	82
Total mesozooplankton	130	2232

Mean abundances of phytoplankton measured in February throughout the water column Table 2.2.2) revealed that small flagellates were the most abundant component of phytoplankton, with abundances higher tan 300 cells·mL^{-1}. Phytoplankton species composition of larger phytoplankton showed a dominance of diatoms. In addition to the species found in January, *Chaetoceros* and *Rhizosolenia* species were the most representative of this group. However, the dominant species of large phytoplankton was the Chrysophycean *Dictyocha speculum,* with abundances higher than 20 cells·mL^{-1}. Dinoflagellates increased with regard to January, reaching abundances around 9 cells·mL^{-1}. *Heterocapsa niei, Prorocentrum minimum* and *Scrippsiella trochoidea* were the dominant species. In any case, low phytoplankton abundances were observed both, on January and February. Planktonic ciliates were slightly higher than in January, with abundances around 6 cells·mL^{-1}. In addition to the taxa present in January, several species of *Strombidium* appeared as dominant in this date. Microzooplankton abundance highly increased with reference to the January sampling reaching more than 3500 indiv·m^{-3}, with copepods nauplii larva dominating. Mesozooplankton dramatically increased compared to values observed in January, with mean abundances higher than 2000 indiv·m^{-3}. Two species of genus *Acartia* dominated with values of 70% in the zooplankton community (Table 2.2.2, February).

The analysis of sediment traps at station 5 in February (Table 2.2.1) demonstrated that the flux of chlorophyll-*a* to near bed was 0.67 mg Chl-*a* m^{-2}·d^{-1}, representing approximately 7% of the water

Table 2.2.3. Fluxes of planktonic material (cells or particles 10^6 m^{-2} d^{-1}) collected in sediment traps in the Ria of Barqueiro in January and February 2008

Phytoplankton group	**January**	**February**
(a) Dinoflagellates		
Heterocapsa niei	0.0	12.8
Prorocentrum minimum	0.0	12.8
Scrippsiella trochoidea	0.0	6.6
Total dinoflagellates	38.46	70.87
(b) Diatoms		
Chaetoceros curvisetus	0.00	6.19
Chaetoceros dyadema	0.00	3.09
Chaetoceros spp	3.09	3.09
Dimmerogramma spp	0.00	12.82
Navicula cf *transitans*	11.05	14.15
Nitschia punctata	0.00	6.63
Nitzschia longissima	5.75	15.03
Nitzschia longissima small	12.82	9.73
Rhizosolenia pungens	0.00	7.96
Thalassiosira levanderi	3.27	0.00
Total diatoms	79.00	88.11
(c) Flagellates		
Flagellates 3-10 µm	239.62	416.01
(d) Chrysophyceae		
Dictyocha speculum	0.00	3.09
(e) Other components		
Fecal pellets Copepods	4.86	26.97
Total planktonic components	**443.42**	**632.86**

column stock. POC flux was 500 mgC·m^{-2}·d^{-1} and accounted for 37% of water stock, with a C/N ratio for the trap (POM) of about 12.

Fluxes of planktonic material collected in sediment traps showed that in February small flagellates were the more abundant taxa (Table 2.2.3). Diatoms dominated the larger phytoplankton. Dinoflagellates and Chrysophyceans also showed significant fluxes to near bed, and fecal pellets accounted for an important fraction of the collected material in the traps.

Taking into account the previous obtained distribution of planktonic material it is possible to observe that phytoplankton biomass (chlorophyll-*a*), like the solar radiation, did not show any relevant change from January to February (Fig. 2.2.3, Table 2.2.3), however allocthonous transport from neighbouring shelf (Crespo et al., 2006; Varela et al., 2005). Thus, the high increase of this group from January to February in the Ria of Barqueiro seems to indicate the existence of intrusion of shelf-waters into the ria. These facts suggest qualitative changes related to the development of spring conditions in February. Moreover, changes in water column are also reflected in the composition of particulate material recovered in the traps. Planktonic ciliates abundances also support the idea of environmental changes in February with a 50% increase of abundances and a shift in species composition (Table 2.2.2). However, the micro and zooplankton components were the best tracers of changing conditions in February with regard to January. Both increased their abundances in one order of magnitude. Most of organisms were copepods larva, suggesting active reproduction of zooplankton. In addition, copepods fecal pellets were an important component of particulate sedimented material. Most species observed in February were typical of spring (Valdes et al., 1991; Bode and Alvarez-Ossorio, 2004; Bode et al., 2005) and some of them like *Calocalanus styliremis* and *Pleuromamma gracilis* are indicative of deep shelf-waters (Corral and Alvarez-Ossorio, 1978). In addition, *Ctenocalanus vanus* is a bathypelagic species of cold waters (Corral, 1970) suggesting the intrusion of allocthonous material into the ria, as in the case of dinoflagellates. In summary, plankton showed the existence of spring conditions in February and an intrusion of shelf-waters into the ria. In the Galician coast, both events are related to north-eastern upwelling favourable winds, which, in turn, are coincident with sunny days, characteristics of spring. What we found is the so called “Prebloom” or winter bloom, a phenomenon already reported in other Galician Rias (Varela et al., 2008).

Winter induced-upwelling conditions

At the western coast, south of Cape Finisterre, there is a high probability of upwelling events during summer which have been extensively studied (Fraga, 1981; Blanton et al., 1987; Alvarez-Salgado et al., 2000; Prego et al., 2001; Alvarez et al., 2005a; Alvarez- Salgado et al., 2006; Gomez-Gesteira et al., 2006; Prego et al., 2007; Alvarez et al., 2008), although recent studies have also shown the existence of upwelling events during winter (Alvarez et al., 2003; deCastro et al., 2006; deCastro et al., 2008). At the north-western coast, a summer upwelling event has been described in the Laxe Ria (Varela et al., 2005), north of Cape Finisterre. This summer upwelling does not reach the Rias of the Artabro Gulf due to the presence of the Gulf which generates an ‘upwelling shadow’ (Prego and Varela, 1998). Note that the coast orientation changes abruptly between Cape Finisterre and Cape Ortegal (Fig. 2.2.1.b), which has a double effect on the upwelling patterns. On the one hand, wind intensity and magnitude are modulated by changes in coastal orientation, especially for areas placed in the lee of the coast. On the other hand, the upwelling favourable conditions change with the coastal orientation, since northerly winds are upwelling favourable along the western coast and easterly winds along the northern coast.

To characterize the winter upwelling recurrence at the northern Galician coast, upwelling favourable conditions were analysed by means of the number of days with UI > 16 $m^3 \cdot s^{-1} \cdot km^{-1}$ per month from 1967 to 2007 at the control point (45.5°N, 7.5°W) using data from the PFEL (Fig. 2.2.5). Note that the threshold (16 $m^3 \cdot s^{-1} \cdot km^{-1}$) corresponds to winds with intensity less than 1 $m \cdot s^{-1}$ to discard calms. The highest number of days under favourable conditions was observed during the spring– summer months with 12–14 days per month. During autumn–winter, the number of days under favourable

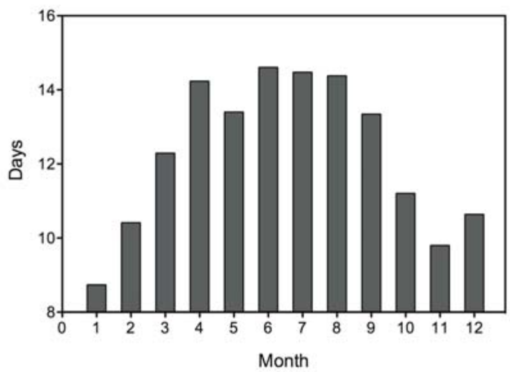


Figure 2.2.5. Number of days with UI>16m^3 $s^{-1} \cdot km^{-1}$ per month, averaged from 1967 to 2007 at the control point 45.5°N, 7.5°W (black square in Fig. 2.2.1.b).

conditions was between 8 and 10 days per month making not negligible (≈30%) the possibility of observing upwelling events in winter. This behaviour was also observed in previous studies. Gomez-Gesteira et al. (2006), analysed Ekman transport close to the northern Galician coast using forecasted winds from November 2001 to October 2004 and they observed that the transport in northward direction is not negligible during the wet season. These results were corroborated by Alvarez et al. (2008) using QuikSCAT satellite data from November 1999 to October 2005.

Upwelling duration was also studied at the same control point. Figure 2.2.6 shows the probability of finding consecutive days under upwelling favourable conditions (UI > 16 $m^3 \cdot s^{-1} \cdot km^{-1}$) during the winter period (January–March) from 1967 to 2007. Obviously, the probability decreases when the number of consecutive days under favourable conditions increases. Upwelling favourable conditions with duration of at least 1 day was ≈35%, decreasing to ≈12% when events of at least 5 days were considered. Nevertheless, the probability of obtaining upwelling favourable conditions during at least three days was still on the order of 20%. Previous findings at the western Galician coast prove that upwelled water can be easily identified when upwelling favourable conditions persist for more than three days (Alvarez- Salgado et al., 2000; Alvarez et al., 2005a; Alvarez-Salgado et al., 2006.

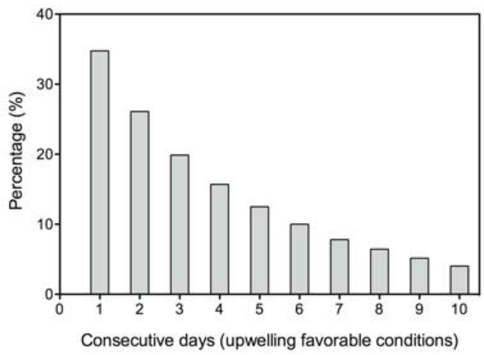


Figure 2.2.6. Probability of finding consecutive days under upwelling favourable conditions (UI>16m^3 $s^{-1} \cdot km^{-1}$) during the winter period (January–March) from 1967 to 2007 at the control point 45.5°N, 7.5°W (black square in Fig. 2.2.1.b).

2.3. Influence of warm water masses in the Northern Galician shelf

Introduction

Several water masses have been identified around the northwestern continental margin of the Iberian Peninsula. From spring to summer, Eastern North Atlantic Central Water (ENACW) is present near the coast (Rios et al., 1992; Prego et al., 1999a) while during late autumn and winter the Galician offshore seawaters are under the influence of a northward surface current, which flows over 1500 km along the Iberian margin (Frouin et al., 1990; Haynes and Barton, 1990). This current, known as the Iberian Poleward Current (IPC), is a layer of 25-40 km wide and about 200 m deep.

The spatial importance and variability of intrusions of ENACW along the Galician shelf has been extensively studied (Wooster et al., 1976; Rios et al., 1992; Alvarez et al., 2005a) especially at the western Galician Rias Baixas and its neighbouring sea area due to the regular occurrence of upwelling events. The different orientations of the Galician coastline influence upwelling frequency and intensity and as a result, upwelling favourable conditions are prevalent in spring-summer along the western Galician coast but not along the northern one (Gomez-Gesteira et al., 2006; Alvarez et al., 2009). Therefore, upwelling research has been mainly focused south of Cape Finisterre and it has been considered a typical spring-summer process driving ENACW into the estuaries (Prego et al., 1999a; Alvarez et al., 2005a). However, this phenomenon can also be observed in fall-winter under northerly winds blowing at the shelf. These winter upwelling events can pump inside the estuaries seawater associated with ENACW (deCastro et al., 2006; deCastro et al., 2008) or driven by the IPC (Alvarez et al., 2003; Prego et al., 2007). Because of the occurrence and intensity of the IPC varies between years (Pingree and LeCann, 1990; Garcia-Soto et al., 2002) the intrusion of this water mass inside the estuaries is not a well studied phenomenon. Thus, the influence of the IPC has been investigated mainly along the Galician shelf in relation to plankton distribution (Fernandez et al., 1993; Huskin et al., 2003; Cabal et al., 2008).

From Cape Finisterre to Cape Ortegal (Fig. 2.3.1) upwelling events associated with the presence of ENACW have been also observed in summer at the Artabro Gulf (Prego and Varela, 1998) although these events are less common than along the western Galician coast and generally restricted to a band near the edge of the continental shelf (Prego and Bao, 1997; Varela et al., 2005). Eastward of Cape Ortegal there is no information about wind induced events except a recent characterisation of a winter (February 2008) upwelling event which introduced shelf bottom seawater inside the northern Galician rias (Alvarez et al., 2009).

The present section aims to contribute to the knowledge of the processes which affect the northern Galician coast in terms of water masses and wind induced phenomena. On the one hand, the presence of a warm water mass related to the IPC at the northern Galician shelf in November 2008 will be characterized by means of Sea Surface Temperature and wind data. On the other hand, the influence of this water mass on the chemical and biological patterns will be analysed inside the northern Galician rias.

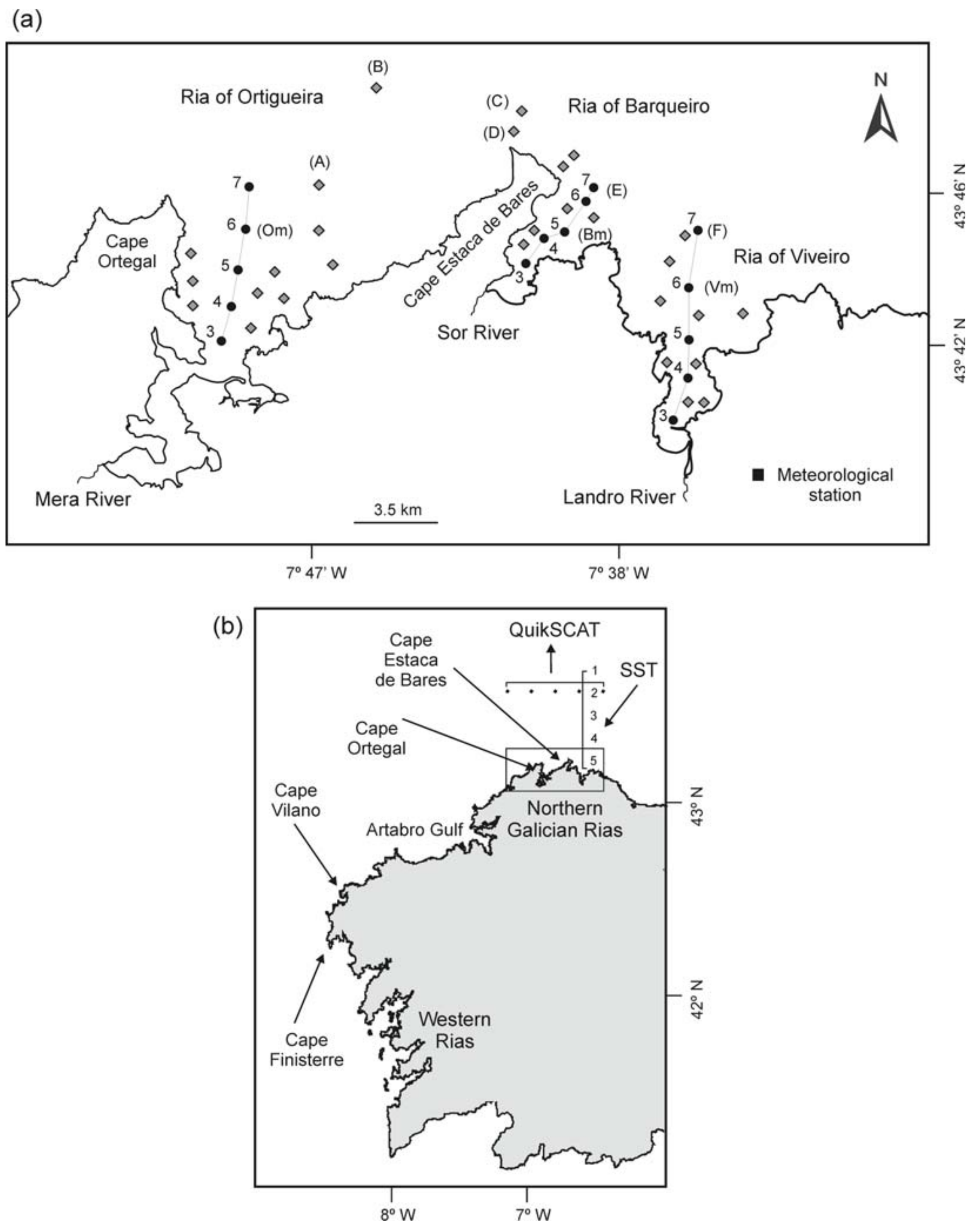


Figure 2.3.1. (a) Map of the Northern Galician Rias showing the sampling hydrographic stations (black circles and gray polygons). Letters refer to the selected stations to analyse the TS diagram of the water column (Fig. 2.3.3). (b) Black dots represent the 5 control points considered to analyse wind data provided by the QuikSCAT. Numbers represent the 5 control points located in front of the Northern Galician Rias to analyse the SST data.

Materials and Methods

Atmospheric variables

Surface wind fields during November 2008 for the Northern Galician Rias were provided by the QuikSCAT satellite (http://podaac.jpl.nasa.gov/DATA_CATALOG/quikscatinfo.html). The data set consists of global grid values of meridional and zonal components of wind measured twice daily on an approximately 0.25×0.25° grid. An average between both measurements was considered. Wind speed measurements range from 3 to 20 m s^{-1} (accuracy: 2 m s^{-1} and 20° in direction) and the reference height of wind data is 10 m. In addition, wind data close to the coast (≈25 km) are not available due to the existence of a small coast mask. However, previous studies have shown that QuikSCAT data are comparable to modelled data in this area (Gomez-Gesteira et al., 2006).

Ekman transport was calculated using wind data and was analysed along the whole Galician coast and at five control points considered along the northern coast at the latitude 44.25°N (black dots, Fig. 2.3.1.b). The obtained discrete series covers from 8.25°W to 7.25°W. Data were averaged for the two previous days to each date under study. This average was considered because atmosphere-ocean interactions take place on a wide range of spatial and temporal scales and the effect of the wind pushing on the ocean surface does not have an immediate response.

Sea Surface Temperature (SST) data were obtained from the National Centre for Ocean Forecasting (NCOF) (http://www.ncof.co.uk/) by means of the Operational Sea Surface Temperature and Sea Ice Analysis (OSTIA) system. OSTIA uses satellite data provided by the GHRSST project (http://ghrsst.jpl.nasa.gov/), together with in-situ observations to determine the sea surface temperature for the global ocean with a resolution of approximately 5 km. SST images were analysed around the Galician coast. In addition, five control points were considered in front of the northern Galician rias in a perpendicular section at approximately 7.7°W (numbers, Fig. 2.3.1.b).

Hydrographical and biogeochemical measurements

A cruise was carried out at the Northern Galician Rias onboard the *RV Mitylus* in November 18th, 2008. Vertical profiles of salinity, temperature and chlorophyll-*a* were measured with a CTD sounder Sea-Bird 25 in several stations placed inside the rias of Ortigueira, Barqueiro and Viveiro and their adjacent shelf (gray polygons in Fig. 2.3.1.a). Moreover, one section with five stations located along the main channel of each ria was considered (St.3 to 7, black dots in Fig. 2.3.1.a). The water column was sampled at 0, 5, 10, 20, 30, 40, 50 m depth using General Oceanic 10 L bottles by means of a General Oceanic Rosette. Dissolved oxygen, nutrient salts and chlorophyll-a sub-samples were taken for analysis.

Daily river flows of the main rivers running into the three northern rias during November 2008 were supplied by the *Aguas de Galicia* company. Moreover, a telescopic pole with a bottle holder was used to collect water samples in these three rivers at the fluvial end-limit of estuaries in November 17, 2008. Salinity and temperature were measured using WTW Multiline P4 sounder and dissolved oxygen, nutrient salts and chlorophyll-*a* sub-samples were taken for analysis.

Daily air temperature was supplied by the Regional Weather Forecast Agency (METEOGALICIA). Data were measured at the meteorological station located 43.66°N and 7.56°W (black square in Fig. 2.3.1.a).

Dissolved oxygen, nutrient salts and Chlorophyll-*a* samples were processed and analysed according to Chapter 1, *Section*

Materials and Methods. From the chlorophyll-*a* result along the sections, CTD fluorometer was calibrated.

Results and Discussion

Sea surface temperature conditions and Ekman transport patterns

SST images were considered around the Galician coast during the previous days of the cruise carried out on November 18 (colour maps in Fig. 2.3.2) to analyse the intrusion process of warm seawater at the northern Galician shelf and rias. SST image corresponding to November 14 showed the presence of a warm superficial water mass near the Galician coast with temperatures around 14.8-15.5°C in front of the northern Galician rias (Fig. 2.3.2.a) and around 16°C near the continental slope of the western

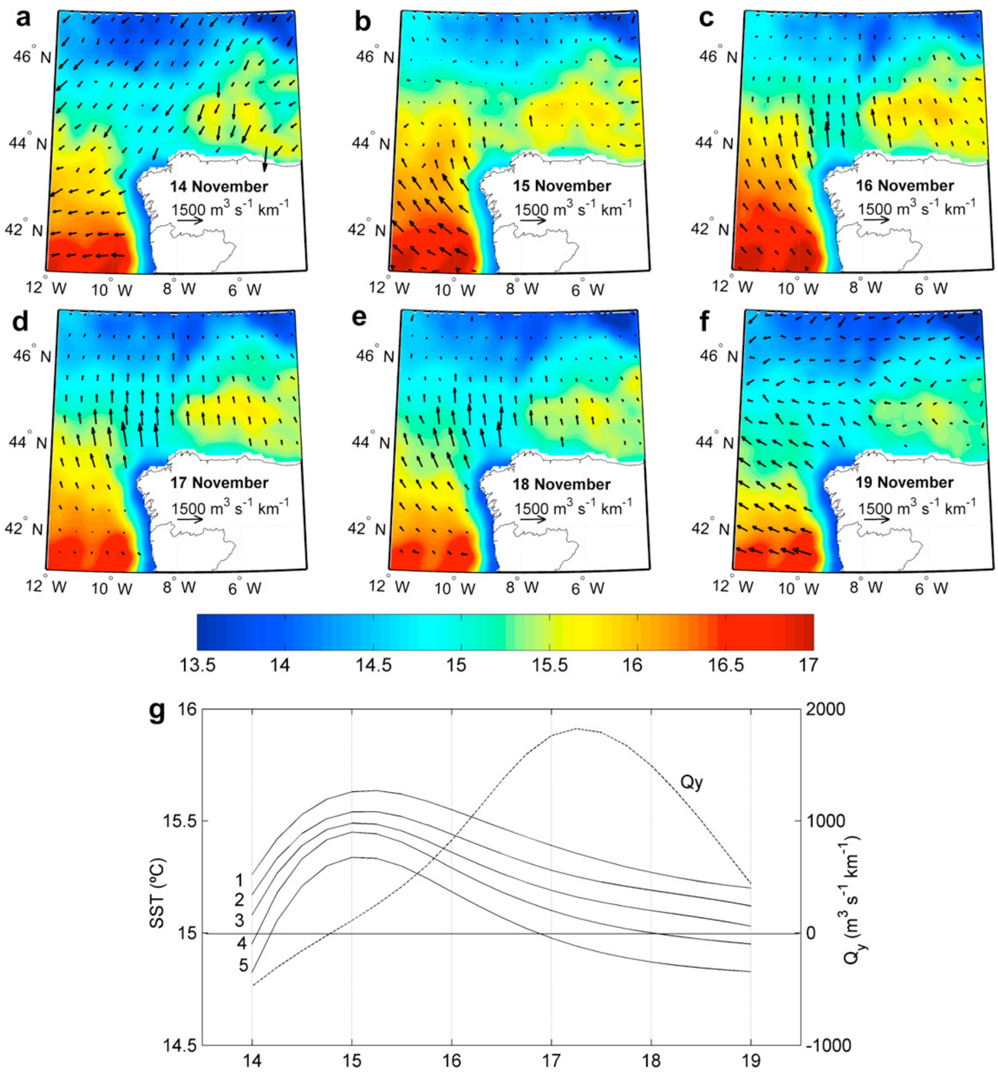


Figure 2.3.2. (a-f) SST images (color maps) and Ekman transport patterns (black arrows) along the Galician coast from November 14-19. SST images correspond to the date shown in each frame. (g) Evolution of SST data in front of the northern Galician coast (black squares, Fig. 2.3.1.b) and meridional component of Ekman transport (Q_y) (dashed line) from November 14-19. Q_y was calculated by averaging data at the 5 control points located along the northern Galician coast (black dots, Fig. 2.3.1.b). Ekman transport was calculated by averaging transport data for the two previous days to the date shown in each frame.

Galician shore. This water mass can be associated with the IPC, which runs from the south of Portugal to the north of the Bay of Biscay (Frouin et al., 1990; Haynes and Barton, 1990) and can be identified by a signal warmer than the surrounding ones (Garcia-Soto et al., 2002) as shown in Fig. 2.3.2. IPC presence was discontinuous along the Galician coast showing a break between Cape Vilano and Cape Ortegal with temperature values around 14.5-15.0°C. On November 15 (Fig. 2.3.2.b), this gap almost disappeared and temperature increased to 15.5-16.0°C. During the next few days (Fig. 2.3.2.c-f) the break was re-established and the gap between offshore areas of the western and northern Galician rias appeared again with a temperature decrease to 14-15°C.

The observed trend of the IPC evolution along the Galician coast may be explained in terms of meteorological forcing considering Ekman transport patterns (arrows in Fig. 2.3.2). On November 14th (Fig. 2.3.2.a) transport was mainly directed southward piling surface waters up onto coast and creating downwelling conditions along the northern Galician shelf. The next day (Fig. 2.3.2.b), negligible values of Ekman transport were measured along the northern coast without any prevailing direction. This situation agreed with a temperature increase at the area between Cape Vilano and Cape Ortegal showing an almost continuous temperature signal along the Galician coast. From November 16 on (Fig. 2.3.2.c-f), northeasterly winds prevailed along the Galician coast (upwelling favourable conditions). The above mentioned gap with lower temperature values between capes at the northern shelf appeared again and a continuous SST decrease was observed at the Galician shelf showing the weakening of the temperature signal.

Previous studies have indicated the importance of wind forcing in controlling the IPC intrusion at the adjacent shelf. So, Gonzalez-Pola et al. (2005) found that downwelling pulses can reinforce the observed IPC signal at the western Cantabrian coast. Therefore, years of sustained and frequent downwelling events can be apparently related to intense penetration of the IPC. On the contrary, during upwelling events the IPC might loose its surface expression and become displaced offshore (Peliz et al., 2005) and the entrance in the Cantabrian coast can even stop (Ruiz-Villareal et al., 2006). In a short time scale, e.g. six days, this trend has been highlighted in the northern Galician shelf by means of the meridional component of Ekman transport (Q_y) and SST data measured near the northern Galician rias (Fig. 2.3.2.g). A period of positive Q_y values (upwelling favourable) was observed during the three days previous to the cruise under study (18 November) agreeing with a decrease of surface water temperature that pointed out a relaxation of the poleward intrusion.

Influence of the IPC on the Northern Galician Rias

The general view offered in the previous section about the poleward evolution along the northern Galician region using satellite images and wind data, was also analysed *in situ* by means of an oceanographic cruise carried out inside the rias. Surface isotherms (1m deep) from CTD data (Fig. 2.3.3.a) indicated an offshore temperature gradient ranging from 13.7°C at the innermost zone of Ria of Ortigueira to 15.4°C at the adjacent shelf around Cape Estaca de Bares. Close to this cape the surface thermocline was observed: 1°C (14.2-15.2°C) in 1.4km of distance. According to the previous discussion on SST maps, the observed surface temperature distribution was established by the IPC influence.

A three-dimensional drawing of the intrusion was provided by means of TS diagrams of the water column

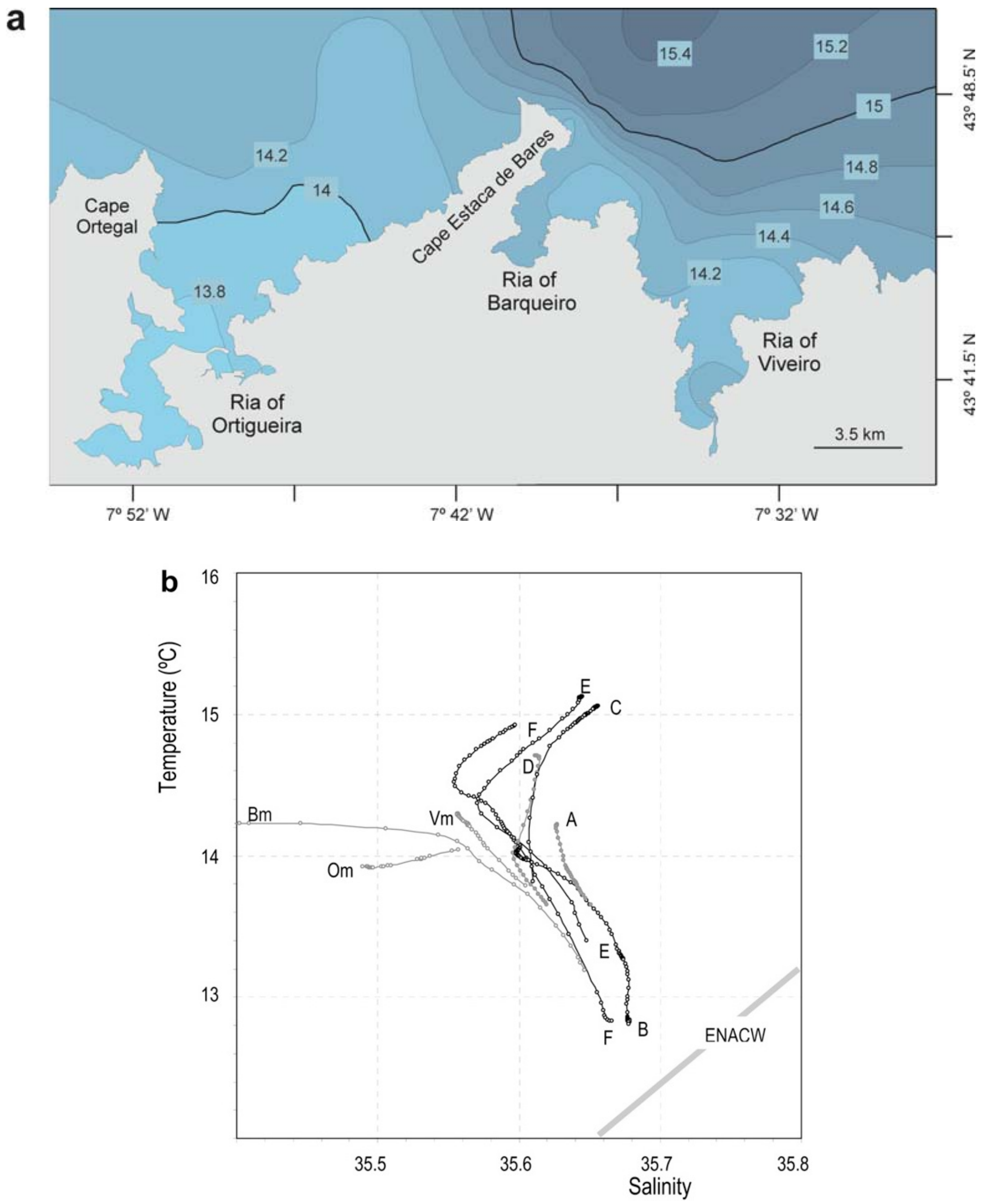


Figure 2.3.3. (a) Temperature distribution at the surface layer (1 m depth) measured at all the sampling stations shown in Fig. 2.3.1.a on November 18. (b) TS diagram of the water column corresponding to inshore and offshore areas (Fig. 2.3.1.a). Ria-mouth stations were named: Om, Bm and Vm (referred to rias of Ortigueira, Barqueiro and Viveiro, respectively) and offshore stations: A, B, E and F. Two stations located at the adjacent shelf around Cape Estaca de Bares (st. C and D) were also considered.

corresponding to inshore and offshore areas of the Northern Galician Rias (Fig. 2.3.3.b). A quasi-linear mixing was observed at the mouth of the three rias (Om, Bm and Vm, Fig. 2.3.1.a) resulting from the fluvial influence, highlighted by the high flow of the Sor River (Table 2.3.1) in the case of Bm station. Taking into account that at the northern Galician region upwelling favourable conditions were established four days before November 19 (Fig.2.3.2), thermohaline variables at these stations could indicate the presence of upwelled water. Nevertheless, TS profiles showed that this water could not be associated with ENACW or IPC. Previous studies indicated that at the western Galician coast upwelled water (ENACW or IPC) can be identified inside the estuaries when favourable conditions persist at least that number of days (Alvarez-Salgado et al., 2000; Alvarez et al., 2005a). At the northern Galician coast, Alvarez et al. (2009) pointed out an upwelling event after nine days of favourable winds although upwelled water corresponded to shelf bottom water which was not associated with ENACW or IPC.

Off the rias of Viveiro and Barqueiro (st. E and F, Fig. 2.3.1.a) the presence of a warm and saline water mass with values around 15°C and 35.60-35.65 was observed in the upper layers of the water column. These conditions were also observed around Cape Estaca de Bares (st. C and D, Fig. 2.3.1.a) while off the Ria of Ortigueira surface temperature values were lower (14°C) (st. A and B, Fig. 2.3.1.a). These high water temperature values are similar to the ones observed for a summer situation due to solar heating (Alvarez et al., 2003; Alvarez et al., 2005a), however, air temperature during the previous days of the cruise under study (November 18) never surpassed 10°C. Therefore, these conditions can only be related to the IPC influence.

Several studies (Frouin et al., 1990; Haynes and Barton, 1990) have found that around the western Galician margin, IPC can be identified by means of thermohaline measurements as a high salinity water body located along the shelf break. The highest salinity values (≈35.9) can be measured around 100m deep decreasing upward where the maximum temperature values (≈16.5°C) can be found. Recently, Huskin et al. (2003) and Torres and Barton (2006) characterized a poleward intrusion in October-November 1999 at the shelf break off Galician coast (between 8.5-9.5°W). IPC salinity and temperature values at surface layers were very similar to the ones observed in November 2008 at the northern Galician shelf.

The hydrographical and biogeochemical patterns were also analysed along the main channel of the northern Rias (st. 3 to st. 7, Fig. 2.3.1.a) to better characterize the influence of the IPC. Only the Ria of Barqueiro is shown (Fig. 2.3.4). The highest salinity (35.6) and temperature (15°C) values were observed close to the mouth of the ria (st. 7, Fig. 2.3.4) decreasing inward and showing that IPC is only present at the external part. The same pattern was also observed at the Ria of Viveiro (not shown). This situation can be explained due to the influence of river discharge at the inner part of the rias, which contributes to prevent the IPC

Table 2.3.1. Discharge and chemical concentrations for the rivers running into the Northern Galician Rias on November 17, one day before the sea cruise

Ria	River	Flow ($m^3 \cdot s^{-1}$)	Temp. (°C)	O_2 (µM)	O_2 (%)	Nitrate (µM)	Nitrite (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	Chlorophyll ($\mu g \cdot L^{-1}$)
Ortigueira	Mera	4.05	12.1	323	96	79.7	0.3	3.4	0.11	156	0.4
Barqueiro	Sor	12.33	12.3	329	98	41.5	0.0	0.2	0.15	91	0.1
Viveiro	Landro	7.68	12.0	320	95	76.4	0.1	0.8	0.14	142	0.4

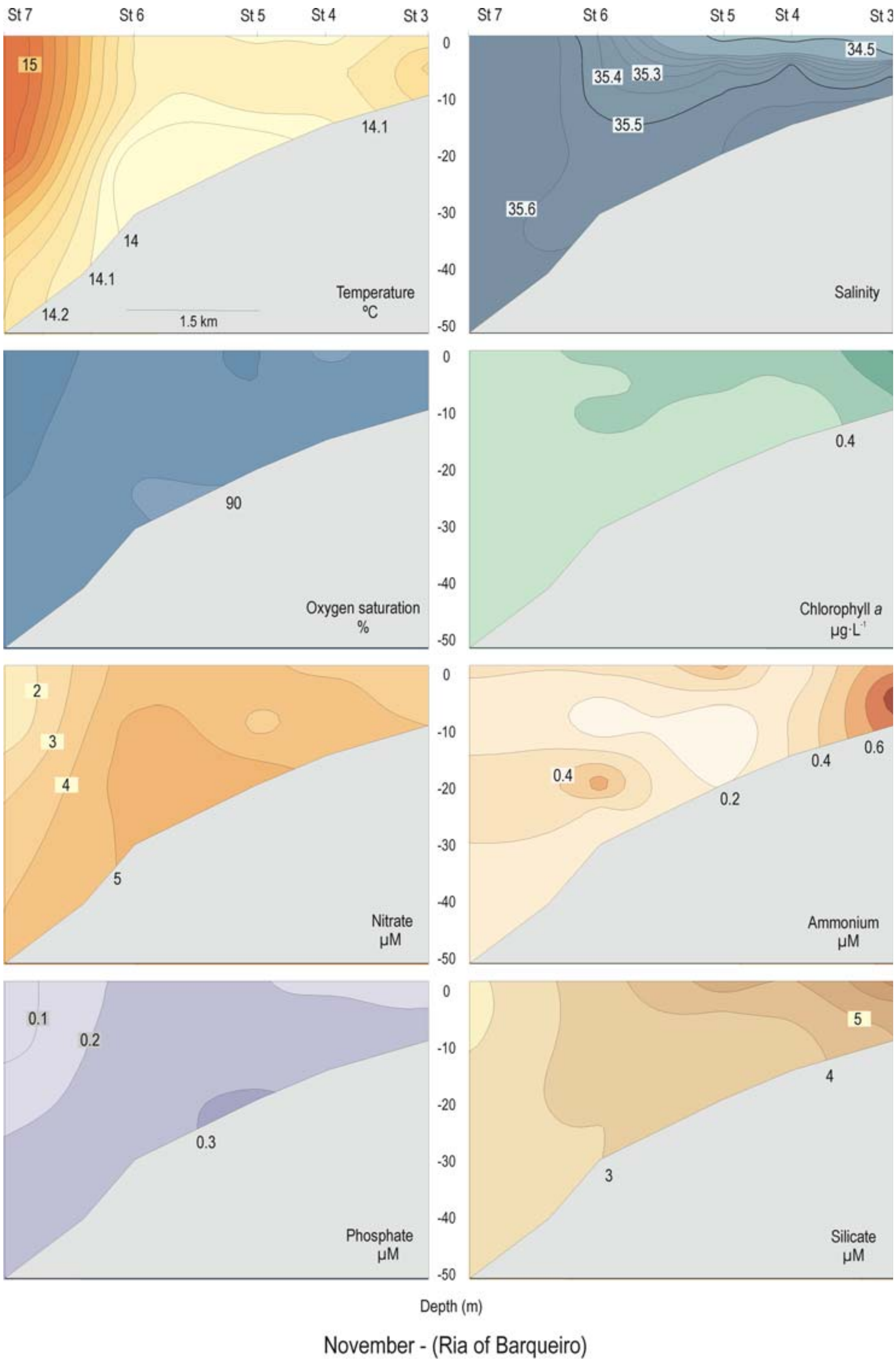


Figure 2.3.4. Contour maps of temperature, salinity, oxygen, chlorophyll and nutrient salts along the main channel of the Ria of Barqueiro corresponding to the cruise carried out in November 18th.

penetration inside them. In fact, river discharge at the Ria of Barqueiro measured the day before the cruise (Table 2.3.1) was two times higher than the annual average flow of about 6 m^3 s^{-1}. A similar situation was previously described at the western

Galician rias where the river runoff originates a low salinity water plume which contributes to the formation of the Western Iberia Buoyant Plume (WIBP, Peliz et al., 2002). This buoyancy plume extends along the coast and under upwelling favourable conditions is advected offshore and can block the entrance of seawater throughout surface layers. Although the cruise at the northern Galician rias (November 18) was carried out after four consecutive days of upwelling favourable conditions, the effect of the river plume was only observed inside the rias (Fig. 2.3.4). It is necessary to take into account that the freshwater input at the western Galician rias (total annual average flow ≈134 $m^3 \cdot s^{-1}$) is higher than at the northern ones (total annual average flow ≈17 $m^3 \cdot s^{-1}$).

IPC also affect the biogeochemical properties. Southward of Cape Estaca de Bares, inside the rias of Barqueiro and Viveiro, a river-ocean gradient of nutrient salts resulting from fluvial contributions (Table 2.3.1) was observed and exemplified by the Ria of Barqueiro (Fig. 2.3.4). A little biological activity was found near surface (Varela et al., 2005), as shown in the chlorophyll concentrations. At the ria mouth bottom, close to the thermohaline gradient resulting from IPC influence, there was a small dissolved oxygen depletion (90% of oxygen saturation) and a light increase of nitrate and phosphate concentrations while the ammonium maximum was observed at 15-20m deep. This situation corresponds to the typical “en echelon” distribution of organic matter remineralization in rias (Prego et al., 1999a). Offshore the ria, near Cape Estaca de Bares, nutrient salts decreased (Fig. 2.3.4). The water mass was poor in nitrate (<2 μM), phosphate (<0.1 μM) and silicate (<2 μM) as it was already observed by Prego et al. (2007) during an IPC intrusion in the western Galician shelf. In the Northern Rias of Barqueiro and Viveiro biogeochemical patterns were disturbed by IPC influence while westward of Cape Estaca de Bares (Ria of Ortigueira) this situation was not observed.

Acknowledgements

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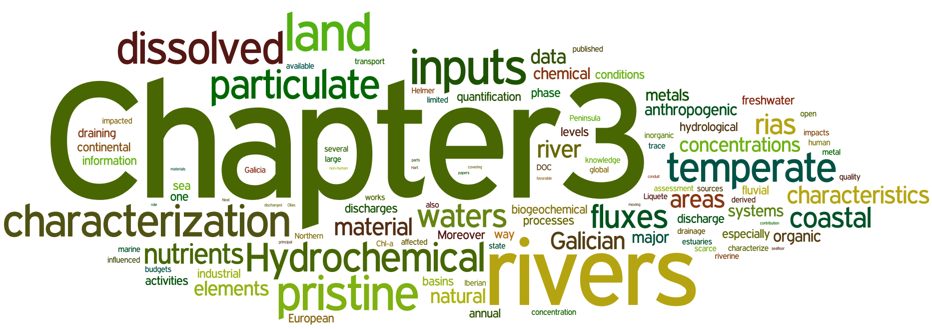

Chapter3
rivers
characterization
Hydrochemical
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dissolved
land
particulate
inputs
temperate
fluxes
waters
nutrients
material
elements
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concentrations
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natural
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Chapter 3

Hydrochemical composition of fluvial waters and river inputs to the Northern Galician Rias

3.1 Hydrochemical composition of fluvial waters and river inputs to the Northern Galician Rias

Introduction

River discharges are one of the prime sources of nutrients for estuaries and rias, coastal waters and offshore waters, and also serve as a major conduit for the introduction of pollutants, both in the dissolved or particulate phases, into the ocean. Moreover, continental inputs could become dominant in large drainage basins dedicated to intensive agriculture and farming, where rivers play a major role in the transference of materials from land to sea and influence significantly the biogeochemical processes in coastal waters. Coastal areas experience complex interactions between continental influences, marine processes and direct and indirect anthropogenic impacts, especially in densely populated areas. In this way, one of the major parts of the anthropogenic chemical load to the sea is derived from urban and industrial developments along the rivers and estuaries. For this reason, it is difficult to find rivers not influenced by human activities and industrial impacts, within Europe.

To date there are reliable published data on trace metal levels and elements concentrations in the dissolved and particulate phase for freshwater systems. Concentration of dissolved and particulate metals, organic material and inorganic nutrients found in rivers are derived from a variety of anthropogenic (Nedwell et al. 2002; Monet 2004; Masson et al. 2007) and natural sources (Meybeck and Helmer 1989; Zhang and Huang 1992; Hart and Hines 1995; Elbaz-Poulichet et al. (1999); Gaillardet et al 2005; Liquete et al. 2010).

Although fluvial transport is a major mechanism for removing metals and nutrients from continental land masses to coastal areas, shelves and open oceans, scarce information is available regarding how trace-metal concentrations vary with fluvial characteristics such as discharge and suspended-sediment concentration (Meybeck 1977). Moreover, little information is available on how the characteristics of various landmasses covering the river basins influences the dissolved and particulate composition of river waters, especially in pristine regions. In this way, a knowledge of metal concentrations in the dissolved and particulate phase, organic carbon, chlorophyll-*a* and nutrients content and transport mechanisms is needed to characterize chemical elements cycling and bioavailability in receiving waters, such as Galician rias.

The quantification of the land-based fluxes of different chemical constituents is a key factor to ascertain the extent those budgets can impact the natural biogeochemical processes and fertilisation, and to detect ecotoxicological risks in coastal systems. This is especially critical for those coastal areas where the riverine/ land based inputs are discharged into enclosed embayments, such as the Galician Rias. Nowadays, the quantification of fluxes -including contaminants, organic material and nutrients-, between land and sea at a regional and a global scale is important. Moreover, there is a lack of knowledge of these fluxes in pristine European rivers, because these data are usually fragmented and not complete for each river. Only the works of Martin and Meybeck (1979); Meybeck and Helmer (1989) and Gaillardet et al. (2005) presented a global database of concentrations and fluxes of dissolved trace elements in rivers. Water quality in European rivers is far from favourable; most of the data is focused on large rivers with high drainage basins and are strongly impacted by pollution. However, no work in small European rivers -from non-industrialised and non-human impacted areas to determine their natural background state has been undertaken.

Several studies shown that human activities as well as changes in fluvial discharge, can modify the biogeochemical conditions of the marine coastal waters (Avilés and Niell 2007) and the accumulation of seafloor sediments (Gao and Ping Wang 2008; Liquete et al. 2010). In this way, ria areas are affected by continentally-derived discharges, that depend on the physiographic conditions of the adjacent coastal zone, the hydrological regime and the oceanographic setup in the open seas. There is only some limited data on metals, DOC, Chl-*a* and nutrients analysis in freshwater systems for dissolved and particulate species (Neal and Robson 2000; Gaillardet et al. 2005). In the Iberian Peninsula research on river water quality is limited (Olías et al. 2006; Avilés and Niell 2007; Falco et al. 2010). Specifically, previous hydrological and budget data on the Galician rias are scarce. Some hydrologic parameters are published by Río-Barja and Rodríguez-Lestegás (1992) and dispersed scientific papers (Ríos et al. 1992; Pérez-Arlucea et al. 2001; Pérez-Arlucea et al. 2005) and nowadays by the state council 'Augas de Galicia'. On the other hand, the characteristics of the dissolved and particulate material moving with the river flow and budgets of this organic and inorganic material draining the Galician rias are very restricted (Vergara and Prego 1997; Cobelo-García and Prego 2003; Cobelo-García et al. 2004; Gago et al. 2005; Filgueiras and Prego 2007; Santos-Echeandía et al. 2008). This lack of information about the nutrient levels and metals supply and fluxes from catchments to a ria system in this geographical region is one of the reasons of this research.

This chapter investigates the characteristics of three natural rivers (Sor, Mera and Landro Rivers, NW Iberian

Peninsula) draining to Northern Galician Rias, in terms of river discharges and hydrochemical and biological conditions, across an annual cycle. The principal goal of this chapter is to establish baseline levels for elements in both the dissolved and particulate phase for riverine waters flowing into the northern rias of Galicia. This chapter deals also with several specific topics: (i) the characterisation of the dissolved material transported by the rivers and the quantification of their annual fluxes, (ii) the assessment of the sediment discharge, annual fluxes and the characteristics of the particulate material and (iii) the evaluation of the importance of this fluxes on the primary productivity in the rias.

Materials and Methods

Sampling and survey program: Samples treatment and analytical methods

Hydrological and hydrochemical sampling of the three largest rivers Sor, Mera and Landro draining the Northern Galician Rias was carried out fortnightly during 2008. In January and February 2009 sampling was also under taken at the mouth these rivers, but out of the tidal influence (Fig. 3.1.1). Daily river flow data of the main rivers running into the three Northern Galician Rias were supplied by the *Aguas de Galicia* company dependent on the 'Consellería de Medio Ambiente' of the *Xunta de Galicia*. River flow for each river was obtained during the sampling period from a scale in a gauging station out of the tidal influence managed by Augas de Galicia. In the Mera River the station is called 443 (Sta. Maria de Mera, Long: 588131, Lat: 4832652, gauged area 102.2 km^2). Station 440 is named for Sor River (Pte. Segade, Long: 602149, Lat: 4742257, gauged area 66.5 km^2). For the Landro River, gauging station is called Station 438 (Chavín, Long: 613794, Lat: 4830628; gauged area 198 km^2). Daily flows were area corrected considering the whole river basin area: 127, 202, 270 km^2, for Mera, Sor and Landro Rivers, respectively. The relatively low-gauged area for the Sor River could lead to an overestimation of the river flow during high precipitation events. However, flood episodes are of low duration and occurred rarely during the sampling period, and therefore, overestimation is negligible.

Air temperature (°C) and daily rainfall (L·m^{-2}) were obtained from the meteorological station Penedo do Galo located at 43.66°N and 7.56°W and supplied by the Regional Weather Forecast Agency (METEOGALICIA). Salinity was measured using a WTW MultiLine F/Set-3 (error range: ±0.1).

Samples of dissolved oxygen, nutrient salts samples, chlorophyll-*a*, particulate organic carbon (POC) and nitrogen (PON) and dissolved organic carbon (DOC) and metals were processed and analysed as was detailed in Chapter 1: *Materials and methods.* Concentrations of Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, and V were determined in the dissolved and particulate phase from the Sor, Mera and Landro Rivers, based on a biweekly sampling from January 2008 to February 2009.

Calculation of fluxes

Dissolved and particulate chemical species in the rivers draining the Northern Galician Rias were estimated from daily discharge and dissolved and particulate elements concentrations. In theory, the total flux over a given period of time is the integration of instantaneous fluxes, which would require continuous determination of discharge, SPM and trace element concentrations (Quémarais et al. 1999). Moreover, the quantification of the annual contribution of the chemical substances from each source could be based on the annual average flow and the annual average concentration of each element, but

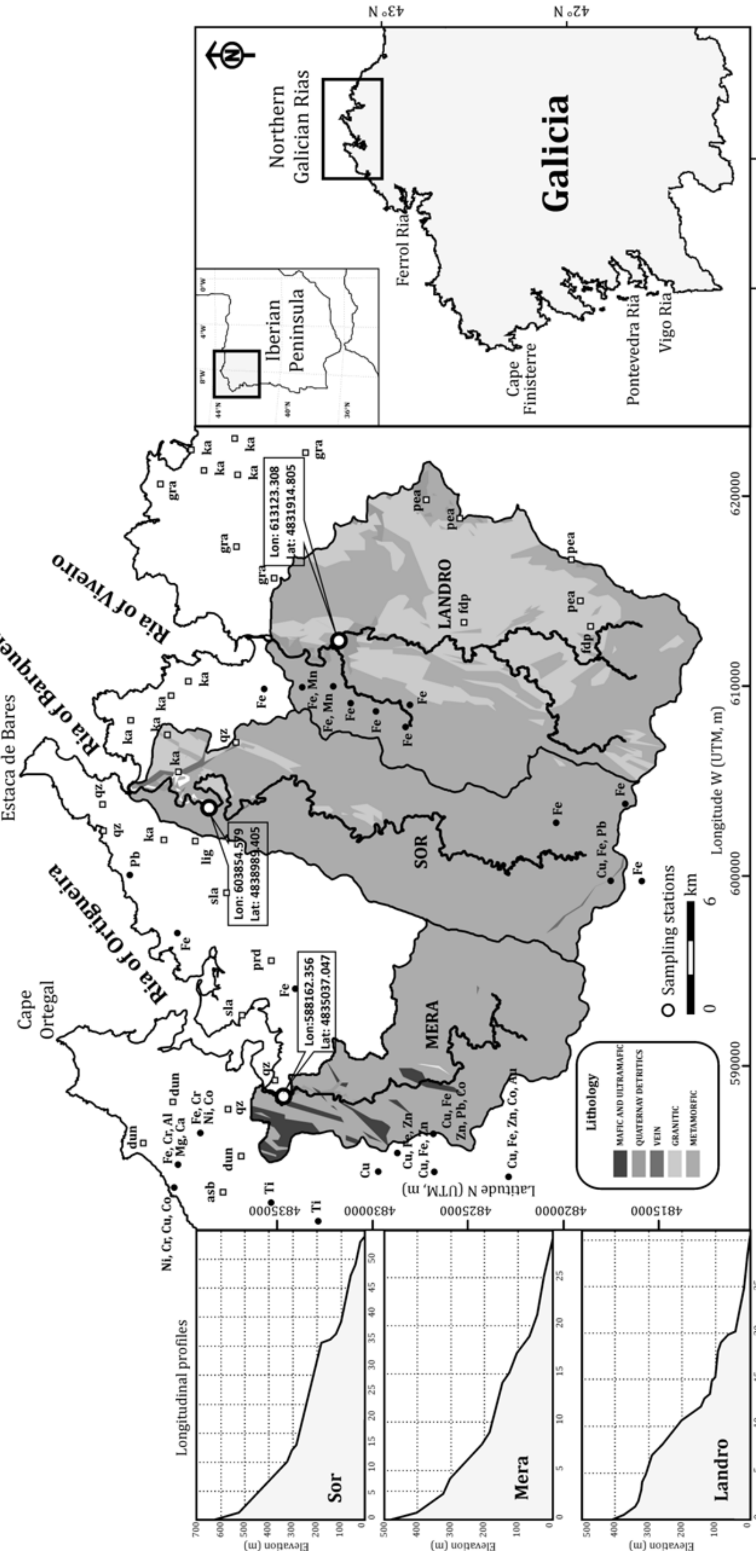


Figure 3.1.1. Geographic situation and hydrological characteristics of the study area. The schematic diagram shows the main riverine basins and rivers draining the rias of Ortigueira, Barqueiro and Viveiro. Data for riverine basins and lithology maps was available from the Spatial Data Infrastructure of Galicia http://sitga.xunta.es/sitganet/index.aspx?lang=gl and from feldspars.

it is suppose a rough estimation because in most of the cases the material flux does not have a lineal relationship with the flow. However, as several chemical species concentrations can hardly be measured continuously, element flux estimates presented in this paper are based upon adapted algorithms recommended by Meybeck et al. (1992). In this way, the transport of dissolved and particulate substances and metals in the Sor, Mera and Landro Rivers has been estimated by means of the classical way to calculate the chemical discharge from the river flow and concentration relationship. Using the exponential CQ (concentration-flow) equation employed by Meybeck et al. (1992), which has been used extensively (e.g. Webb et al. 1997, 2000; Quilbé et al. 2006; Johnes 2007). This relationship is applied to the high frequency discharge record in order to generate a high frequency concentration time-series. Therefore, it can be combined with the discharge series to calculate the total load over the required period of time (Webb et al. 1997) because flow and load were assumed to be described by a bivariate lognormal distribution (Preston et al. 1989).

$$F = \sum_{i=1}^{i=n} Q_i C_i \qquad (3.1.1)$$

Where Q_i is the daily flow (data from *Aguas de Galicia*) and C_i is the daily concentration of chemical substance or metal obtained from the equation (Table 3.1.1):

$$C_i = aQ_i^b \qquad (3.1.2)$$

Annual fluxes (in kg yr^{-1} or t yr^{-1}) were calculated as the sum of daily fluxes over the entire year.

As a fortnightly sampling during most of a year period was applied, the CQ equations obtained are considered appropriates when the critical value of the correlation coefficient (r in Table 3.1.1) is higher than 0.472 (1-tailed testing of 0.01 to n=24).

Mean annual flux was also estimated and was based on an average of the fluxes over the year (Table 3.1.2). When was r<0.472 (Table 3.1.1) the flux (F) was approximately estimated by multiplying the annual average flow of river by the average concentration on each element or substance (F in bold and italics, Table 3.1.2).

$$F = \overline{Q}\overline{C} \qquad (3.1.3)$$

Comparison quantified using Eq. 3.1.1 or Eq. 3.1.3 for r>0.472 results in a difference in QC of 1.4 ± 0.6 times higher than from average values.

The hydrologic situation as 'flood' when discharge is 5 times higher than the mean annual value representative of the observation period has been considered. These periods are short in duration and they do not have a high significant influence on estimated fluxes.

Results and Discussion

Hydrological and meteorological conditions

Daily water discharges for Sor, Mera and Landro River 2008, as well as precipitation and air temperature in the area are shown in Fig. 3.1.2. During year 2008 daily variations in the discharge flux are closely related to variation in the precipitation. This close coupling between discharge and rainfall results from the high impermeable, of the catchment area. Consequently, the sampling stations reflect variations in the precipitation. The discharge of these rivers is related to the natural hydrology of the whole drainage basins (e.g. wet/dry years, local events of high discharge, etc.), and as consequence, fluxes of water and SPM show high temporal variability. Air temperature during 2008 was also lower (10.1 °C) compared to 'normal' year (14°C) (Fig. 3.1.2).

Table 3.1.1. Concentration-flow equations ($C = a \cdot Q^b$) for the main rivers flowing into the Northern Galician Rias

	Sor			Mera			Landro		
	a	b	*r*	a	b	*r*	a	b	*r*
Nitrate	60	-0.194	0.52	50	0.038	0.20	41	0.080	0.24
Nitrite	0.62	-0.80	0.75	0.190	-0.23	0.65	0.34	-0.48	0.80
Ammonium	0.86	-0.21	0.17	0.45	-0.42	0.46	1.21	-0.27	0.23
Phosphate	0.23	-0.36	0.50	0.154	-0.166	0.60	0.28	-0.35	0.67
Silicate	133	-0.165	0.81	192	-0.144	0.86	197	-0.173	0.73
DOC	225	-0.24	0.63	122	-0.088	0.46	187	-0.066	0.22
D-Al	717	0.40	0.65	527	0.188	0.73	1590	0.25	0.60
D-As	16.2	-0.61	0.78	4.27	-0.178	0.85	3.41	-0.27	0.74
D-Cd	0.0164	0.78	0.67	0.058	0.46	0.50	0.049	0.60	0.58
D-Co	0.45	0.75	0.78	1.56	0.115	0.37	0.54	0.82	0.75
D-Cu	0.23	0.57	0.78	2.71	0.28	0.73	0.48	0.40	0.59
D-Fe	1716	-0.64	0.62	650	-0.32	0.78	1790	-0.45	0.67
D-Mn	13.2	0.75	0.78	51	0.077	0.29	67	0.51	0.79
D-Mo	1.36	-0.59	0.68	0.67	-0.27	0.27	0.56	-0.63	0.75
D-Ni	2.55	0.58	0.95	11.8	0.164	0.59	6.71	0.56	0.95
D-Pb	0.20	0.22	0.26	0.36	0.183	0.25	0.046	0.70	0.45
D-V	23.0	-0.65	0.63	12.1	-0.32	0.82	17.1	-0.51	0.61
D-U	0.0061	0.74	0.62	0.0082	0.82	0.87	0.182	0.38	0.82
D-Zn	11.1	0.37	0.75	23.7	0.101	0.41	20.0	0.23	0.47
SPM	0.45	0.25	0.44	1.05	0.45	0.69	0.63	0.64	0.74
POC	3.80	0.45	0.79	12.2	0.26	0.84	8.61	0.57	0.83
PON	1.33	-0.100	0.15	1.08	0.110	0.18	1.26	0.102	0.16
Chlorophyll-*a*	0.23	-0.105	0.10	0.30	-0.080	0.13	0.49	-0.121	0.15
P- Al	0.27	0.48	0.76	1390	0.52	0.85	0.50	0.90	0.83
P- Cd	0.21	-0.26	0.29	0.0167	0.25	0.66	0.0151	0.24	0.26
P- Co	0.44	-0.045	0.10	0.73	0.51	0.81	0.23	0.61	0.67
P- Cr	0.70	0.46	0.59	4.29	0.32	0.72	0.63	0.89	0.70
P- Cu	0.62	0.040	0.06	0.84	0.87	0.86	0.57	0.25	0.33
P- Fe	0.91	-0.029	0.04	1650	0.26	0.72	1.13	0.33	0.48
P- Ni	0.31	0.047	0.08	2.51	0.41	0.80	0.36	0.66	0.64
P- Pb	0.138	0.147	0.18	0.144	0.49	0.87	0.135	0.65	0.81
P- V	0.40	0.32	0.46	2.46	0.42	0.85	0.82	0.42	0.65
P- Zn	0.83	0.24	0.27	4.14	0.35	0.60	1.45	0.63	0.65

Q is the freshwater flow in $m^3 \cdot s^{-1}$; C is the substance concentration in nM except for nutrients and organics µM), suspended particulate matter (SPM, $mg \cdot L^{-1}$) and chlorophyll-*a* ($\mu g \cdot L^{-1}$). r corresponds to the regression coefficient.

At the Northern Galician Rias, the drainage basins received abundant rain during 2008 (annual 2008 average, 2.97 $L \cdot m^{-2}$) with low duration peaks of 61 $L \cdot m^{-2}$, which produces a large flow per basin area. Moreover, the drainage index for the studied rivers is high (Río-Barja and Rodríguez-Lestegás 1992) indicating that the rainfall drives the river flow (Fig. 3.1.2). In this way, mean annual river flow variation in the Sor River during year 2008 was 19.3 m^3 s^{-1}, with maximum values of 205 m^3 $s^{-1}$and minimum of 4.3 m^3 s^{-1}. This average value was higher than mean value obtained for several years (mean 1996-2010: 15.2 m^3 s^{-1}, Augas de Galicia 2011). The opposite occurred in the Mera River, with mean values of 5.97 m^3 s^{-1} during 2008, whereas average value was 6.0 m^3 s^1 (mean 1970-2010, Augas de Galicia 2011). This was also observed in the Landro River, where mean flow during 2008 was 10.1 m^3 s^{-1} in contrast with 9.3 m^3 s^{-1} as a general average (mean 1975-2010, Augas de Galicia 2011).

Table 3.1.2. Chemical contributions of dissolved (D) and particulate (P) phases during 2008 by the rivers flowing into the Northern Galician Rias. Comparison with other coastal areas in the world

	Sor	Mera	Landro	Other studies	unit
Q_r	610	189	319		$10^3 \cdot t \cdot yr^{-1}$
SPM	664	661	1331		$t \cdot yr^{-1}$
Chl-*a*	***149***	***95***	***153***		$kg \cdot yr^{-1}$
DIN	274	***149***	***234***	158[a]	$t \cdot yr^{-1}$
PON	***11***	***3.9***	***9.6***	15.6[a]; 110[f]	“
HPO_4^{2-}	1.36	0.61	1.13	7.89 [a]; 0, 12, 38[c]	“
H_4SiO_4	1319	726	1118	601[a]; 3910,1955, 4106[c]	“
DOC	750	***249***	***784***	629[a]	“
POC	143	54	175	97[a]; 1200[f]	“
D- Al	50	4.3	28		“
P- Al	26	29	67	419[f]	“
D- As	111	40	40		$kg \cdot yr^{-1}$
D- Cd	21.9	4.2	10.3	13[f*]	“
P- Cd	***0.4***	0.7	***0.4***		“
D- Co	278	***16***	121		“
P- Co	***13***	32	26		“
P- Cr	119	97	158		“
D- Cu	74	67	31	514[d]; 231[e]; 3400[f*]	“
P- Cu	***32***	122	***26***	119[e]	“
D- Fe	8.0	3.3	10.2	8.57[b]	$t \cdot yr^{-1}$
P- Fe	***34***	34	51	39[b]; 271[f]	“
D- Mn	7035	***647***	5160		$kg \cdot yr^{-1}$
D- Mo	12.6	***7.4***	3.7		“
D- Ni	784	198	646		“
P- Ni	***17***	83	44		“
D- Pb	***31***	***11***	***15***	1375[f*]	“
P- Pb	***37***	21	61		“
D- V	84	57	78		“
P- V	39	72	44		“
D- U	14.6	3.8	40.9		“
D- Zn	1675	***391***	***660***	4570[f*]	“
P- Zn	***136***	128	194		“

Italics represent those values calculated using average river flow and average concentration instead of using equations since the regression was poor.
[a]Oitabén River, Ria of Vigo (Gago et al., 2005).
[b]Oitabén River, Ria of Vigo (Filgueiras and Prego, 2007).
[c]Mera, Sor and Landro rivers (Vergara and Prego, 1997).
[d]Lérez River and sewage to the Ria of Pontevedra (Cobelo-García and Prego, 2003).
[e]Rivers to the Ria of Vigo (Santos-Echeandía et al., 2008).
[f]Rivers to the Ria of Ferrol (Cobelo-García et al., 2004).
[f*]Dissolved and Particulate (Cobelo-García et al., 2004).

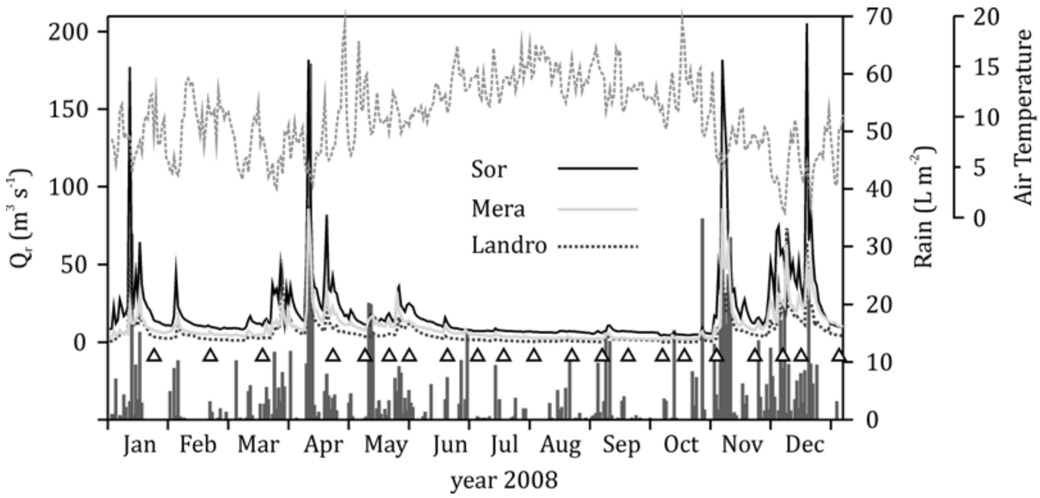


Figure 3.1.2. Plot of the river flow Q_r (lines) of the main three rivers draining the Northern Rias during year 2008, the rain record (grey bars in $L \cdot m^{-2}$) and air temperature (°C) in the meteorological station of Penedo do Galo (43.66° N, 7.56° W) at Viveiro. Data available from the Regional Weather Forecast Agency (METEOGALICIA).

http://www2.meteogalicia.es/galego/observacion/estacions/estacionsHistorico.asp#

Key variables

The mean water temperature was 13.8 °C during 2008 for the Sor River, whereas in the Mera River average water temperature was 13.12°C, and in the Landro River 12.8°C. In the case of salinity, the values are consistently below 1‰ of salinity, which indicates a freshwater input and no tidal influence in the sampling stations.

The pH for the most rivers were neutral, with low pH variations, showing similar values to those found for the rivers draining the Ria of Vigo (Gago et al. 2005; Filgueiras and Prego 2007) and for world global pristine rivers draining granite and gneiss rocks types (Meybeck and Helmer 1989). Mera River is slightly basic with an average pH value of 7.28 and a maximum value of 7.85. Oxygenation in these rivers is always high with mean values near to saturation (93-100%; Fig. 3.1.3). These values are common in the Galician rias, as has been reported in previous papers (Cobelo-Garcia et al. 2004; Gago et al. 2005; Santos-Echeandía et al. 2008).

Characterisation of dissolved material

The extension, characteristics and topography of the drainage basin, the rainfall regime, together with the lithology features and the different land uses (forest, agriculture, industry, urban settlements, occurrence of peat bogs, wetlands and marshes), determine the inorganic and organic loads of a river stream (Meybeck and Helmer 1989; Esser and Kohlmaier 1991). Moreover, characteristics of the dissolved material contained in river waters are highly variable since due to environmental conditions such as basin lithology, the weathering of surface rocks, land use, vegetation and the degradation of terrestrial organic matter and climate (Meybeck and Helmer 1989). However, a vast majority of dissolved elements and species in natural waters are strictly associated with rock weathering, climate characteristics, land use and vegetation alone; other sources such as atmospheric or anthropogenic contributions have an important contribution (Gaillardet et al. 2005).

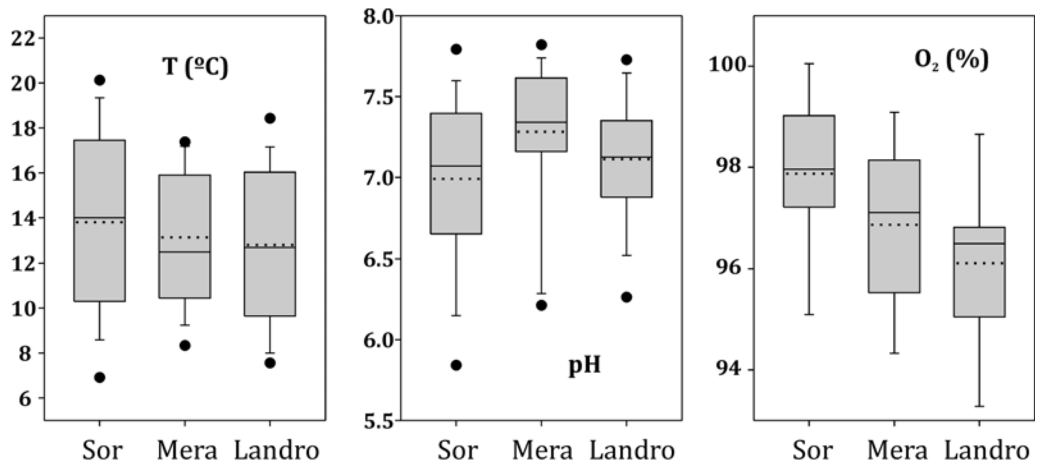


Figure 3.1.3. Box-and-whisker plots key variables, (T, pH and O_2) determined during Jan 2008-Feb 2009 in waters of the rivers draining the area. The length of the box represents the interquartile range containing 50% of the values. Straight horizontal line inside the box indicates the median whereas dotted horizontal line represent mean. The whiskers are lines that extend from the box to the highest and lowest values excluding outliers and extremes. Outliers handling represent the 5 and 95 percentile. Outliers are defined as cases in which the values are between 1.5 and 3 times larger than the length of the box from its upper or lower border; those greater than three times are extremes.

Nutrient concentrations in the three rivers studied were similar for nitrate, nitrite and ammonium (Fig. 3.1.4.a). Nitrate accounted more than 95% of the dissolved inorganic nitrogen (DIN). This is in contrast to the Oitabén River system where nitrate represented 80% of DIN (Gago et al. 2005). Nitrite and ammonium concentrations were very low for all rivers, accounting for less than 5% of DIN. Average values of 0.11 and 0.71 µM for the Sor River, 0.16 and 1.02 µM for the Mera River and 0.16 and 1.09 µM for Landro River, respectively. These features are similar to that found in Galician (Vergara and Prego 1997) and Cantabrian rivers (Prego and Vergara, 1998). These nitrogen compounds are primarily influenced by biological processes (Hart and Hines 1995) but also by anthropogenic sources. The concentrations determined here are in the range for values reported for Galician rivers (18-40 nM; Salminen 2005; De Vos and Tarvainen 2006). This suggest that inputs from nitrogen fertilisers for agricultural activities is minor in these rivers.

Phosphate concentrations were also very low, in comparison with other rivers in the same area (Vergara and Prego 1997; Gago et al. 2005), with a maximum of 0.34 µM and average of 0.11 µM. These values are in accordance with natural levels and suggest little influence from agricultural and urban activities in the area. Moreover, the low population density in basins draining the northern rias of Galicia avoids inputs of detergents, cleansers and industrial chemicals that are phosphate-rich (Esser and Kohlmaier 1991), maintaining the phosphate concentrations in their natural values. Phosphorous appears to be a limiting nutrient in many streams (Correl 1999). However, average values around 0.11 µM in these rivers could indicate that phosphate does not limit biological production in these rivers.

Several differences between rivers were obtained in terms of silicate concentration. Silicate concentrations in the Sor River waters ranged from 64 to 110 µM, whereas for Mera and Landro Rivers average values are of 164.1 and 141.9 µM, respectively

(Fig. 3.1.4.a). Those values are in the range found for rivers draining Galician rias ranging from 60 to 210 µM (Prego et al. 1995; Vergara and Prego 1997). Surprisingly, silicate concentrations in these rivers are even 10 times higher than those obtained for the Oitabén River (Gago et al. 2005) highlighting the importance of keeping the samples preserved at 4°C instead of frozen (Kobayashi 1966). According to the reported data, silicate concentrations in the north of Galicia (Salminen 2005; De Vos and Tarvainen 2006) are ca. 54 nM (SiO_2). Since biological processes may control this chemical species its concentration varies along the studied time-period. However their relation with freshwater flow is high (Table 3.1.2) indicating that hydrological features appear to control its concentration.

All studied rivers exhibit a relatively low concentration of dissolved organic carbon which is typical for rivers draining mid-latitude areas. Dissolved organic carbon concentrations were similar between the Sor and Mera Rivers, with mean values of 121.6 and 109.9 µM, respectively. The Landro River had higher DOC values, with an average concentration of 205.29 µM (Fig. 3.1.4.a). DOC concentrations in rivers of the Galician region are scarce, but previously reported values e.g. Oitabén River draining the Ria of Vigo, range between 60-100 µM, (Salminen 2005; Gago et al. 2005). However, in European rivers, concentrations range between 162 and 1025 µM (Gaillardet et al. 2005). The behaviour of carbon in the dissolved organic form is highly dependent on the biological processes acting in the riverine environment as well as the sources of organic matter to these rivers. Since the river watersheds and soils are relatively rich in organic carbon (1.3-4.1wt%; Salminen 2005; De Vos and Tarvainen 2006) DOC concentrations are noticeable, and suggest that biological processes are of minor importance. Moreover, no evidence of organic carbon point sources from fluvial wastewater has been recorded.

Dissolved Al, Fe and Mn are the most abundant elements, with values ranging from 330 to 5600 nM for Al, 100 to 2500 nM for Fe and 29 to 500 nM for Mn. On average, the Landro River had higher concentration of these three elements because the Fe and Mn exploitations in the Landro watersheds and the content of granites at the catchment (Fig. 3.1.1). Values of dissolved Fe were in the same range or even lower of those obtained for Galician rivers (528-4342 nM; Salminen 2005; De Vos and Tarvainen 2006) and the rivers draining the Ria of Vigo (Filgueiras and Prego 2007), pristine rivers (642 nM; Guieu et al. 1996) but lower than the world rivers average (1181 nM, Gaillardet et al. 2005). Natural abundance of dissolved Al on a global scale is of 1186 nM (Gaillardet et al. 2005), indicating that studied rivers have higher concentrations. This abundance is associated to the lithological characteristics of the river basins, enriched in Al-Si derived minerals as observed for other Galician rivers (1152-3200 nM, Salminen 2005; De Vos and Tarvainen 2006). However, the Mera River always had lower concentrations of Al and Fe (Fig. 3.1.4.a). This fact could be due to the presence of mafic and ultramafic rocks (poor in Al and Fe) in this basin (Fig. 3.1.1). In the case of Mn concentrations in northern Galician rivers were low in comparison with global average (618 nM; Gaillardet et al. 2005) and with other European rivers under the same characteristics (Neal and Robson 2000; Salminen 2005; De Vos and Tarvainen 2006). Mn and Fe are highly dependent upon the redox conditions in the system (Hart and Hines 1995). Moreover, phytoplankton may be effective in Mn deposition (Admiraal et al. 1995) provoking a decreasing concentration in the dissolved phase. In the case of the Galician rivers, Fe^{2+} is the predominant form in the

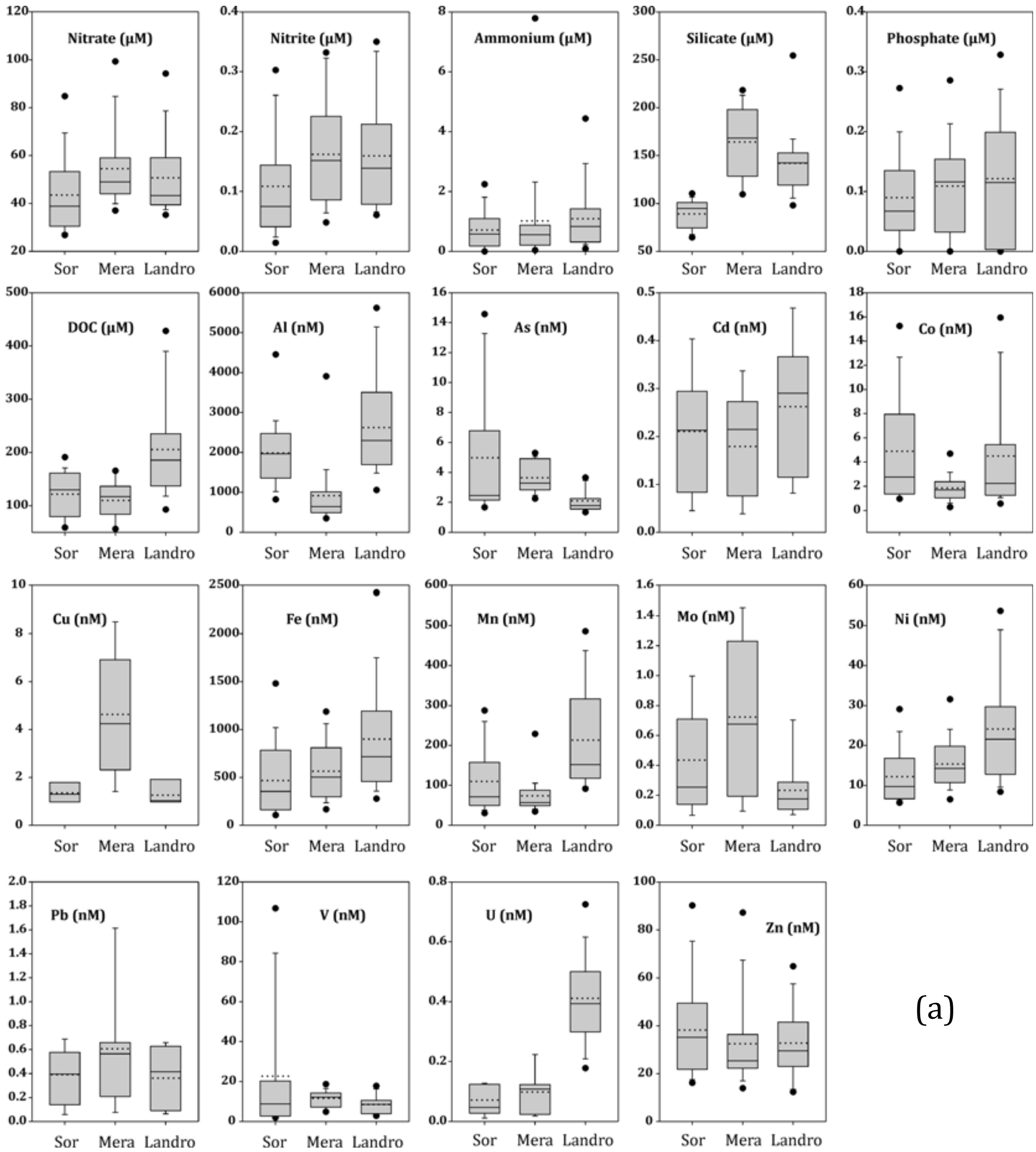
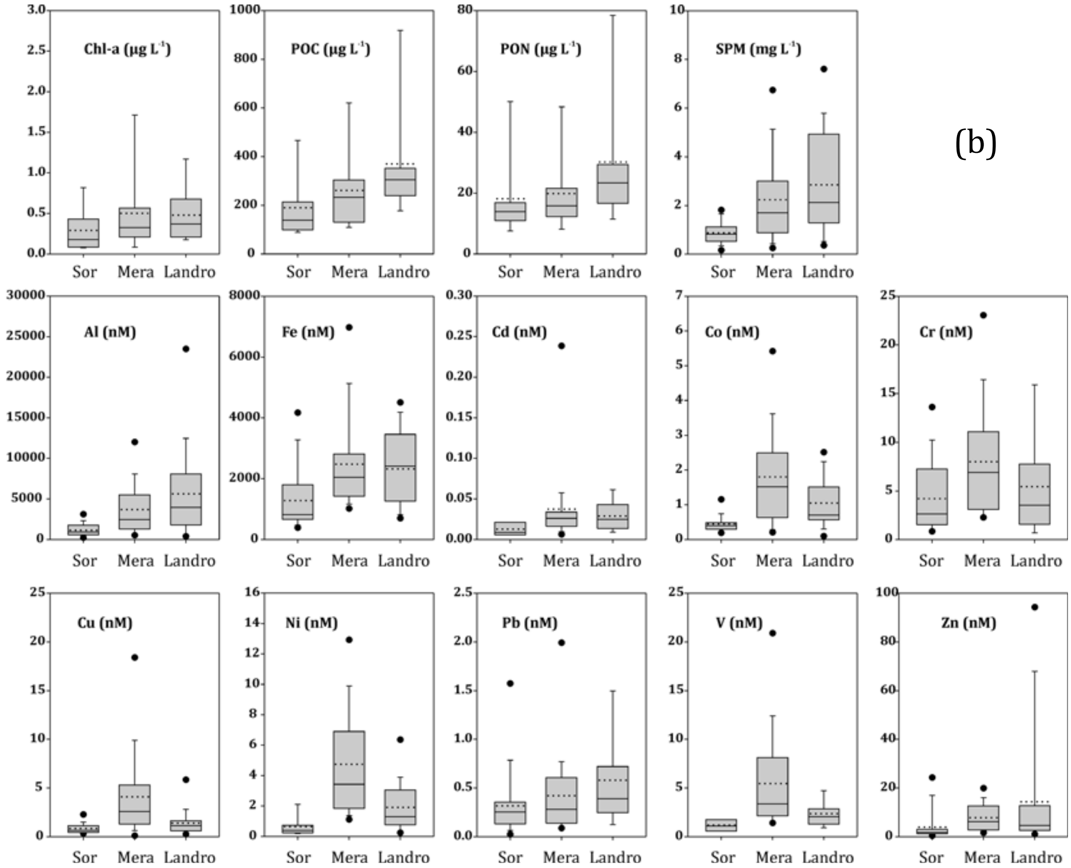


Figure 3.1.4. Box-and-whisker plots of several parameters determined during Jan 2008-Feb 2009 in waters of the rivers draining the area. (a) dissolved phase (b) particulate phase. The length of the box represents the interquartile range containing 50% of the values. Straight horizontal line inside the box indicates the median whereas dotted horizontal line represent mean. The whiskers are lines that extend from the box to the highest and lowest values excluding outliers and extremes. Outliers handling represent the 5 and 95 percentile. Outliers are defined as cases in which the values are between 1.5 and 3 times larger than the length of the box from its upper or lower border; those greater than three times are extremes.



dissolved phase (Salminen 2005; De Vos and Tarvainen 2006).

In the Mera and Sor Rivers, dissolved U average values were 0.07 and 0.10 nM respectively, which are within the range of concentrations reported in stream water of Galicia (ca. 0.12 nM; Salminen 2005; De Vos and Tarvainen 2006). By contrast, high concentrations of U have been measured in the Landro River (0.17-0.75 nM). U concentration in world rivers is 1.56 nM on a global average, but these values can rise up to 20 nM (Moore 1967; Gaillardet et al. 2005). High U values in subsoil (>2.88 mg kg^{-1}) occurred in relation with granitic rocks in Galicia and in this way it can be hypothesised that in the Landro River, which, has a granitic nature (two mica granite; IGME 1982; Fig. 3.1.1), the U dissolved concentrations must be higher.

Vanadium concentrations were similar between studied rivers, with average values ranging between 8.5 and 22.6 nM. Dissolved V concentrations were not reported for rivers draining the Galician Rias, but for world rivers the reported range is between <0.5 and 45 nM depending the lithological characteristics of the river basin catchment (Shiller and Boyle 1987; Shiller and Mao 2000; Salminen 2005; Gaillardet et al. 2005; De Vos and Tarvainen 2006). World global average concentration is 13.9 nM (Gaillardet et al. 2005). Weathering rate and type of source rock appear to be the important factors in determining fluvial dissolved V concentrations (Shiller and Boyle 1987).

Molybdenum concentrations were also low for all rivers ranging from 0.1 to 1.2 nM in comparison with its natural abundance in world rivers (global average 4.37 nM, Gaillardet et al. 2005) but in the same range of the values reported for some European rivers ca. 0.41 nM (Neal and Robson 2000;

Salminen 2005; De Vos and Tarvainen 2006).

Zinc concentrations were very similar to three rivers, with average values around 35 nM. World background concentrations of dissolved Zn (Hart and Hines 1995) were estimated 10 times higher than those reported for these rivers, but according to Gaillardet et al. (2005) world average is 9.17 nM. Dissolved Zn concentrations were in the range of the reported Galician rivers background, which was estimated to be 20-49 nM (Martin et al. 1994; Salminen 2005; De Vos and Tarvainen 2006), but values found for the studied rivers were slightly higher than those found for uncontaminated rivers (1.2 nM; Hart and Hines 1995; Guieu et al. 1996).

Arsenic concentrations were low for all rivers, especially for the Landro (2.10 nM on average) and Mera (3.65 nM). In the Sor River average concentration was 5.0 nM. Those concentrations were extremely lower than those found for highly polluted rivers with this element (Masson et al. 2007), but in the same range of the global average (8.27 nM, Gaillardet et al. 2005) and Galician rivers (4.8-22.95 nM, Salminen 2005; De Vos and Tarvainen 2006).

For Cd and Pb, no significant differences can be found between rivers. Dissolved Pb values for Sor, Mera and Landro Rivers were lower than the range reported for the Galician (Cobelo-García et al. 2004, Salminen 2005; De Vos and Tarvainen 2006) or world rivers (ca. 1 nM Hart and Hines, 1995; 0.2 nM; Guieu et al., 1996). Cd concentration in rivers of the Northern Galician Rias were also an order of magnitude higher than concentrations found for impacted river and streams in the Ria of Ferrol(Cobelo-García et al. 2004) and Oitabén River draining the Ria of Vigo (0.03 nM; Martin et al. 1994) and other Galician rivers (0.001-0.08 nM, Salminen 2005; De Vos and Tarvainen 2006) or even 3 times higher than those found for pristine rivers (0.05 nM, Guieu et al. 1996).

Nickel average values of concentration were 12.19, 15.36 and 24.15 nM for Sor, Mera and Landro Rivers, respectively (Fig. 3.1.4a). These values were close to background limits for world rivers (13.6 nM, Gaillardet et al. 2005). Moreover, Ni concentrations in these rivers were 3-4 times higher than those found in the pristine rivers (4.4 nM; Guieu et al. 1996) but in the same range of other Galician rivers (2.0-13.8 nM, Salminen 2005; De Vos and Tarvainen 2006). An increase in the concentrations of nickel was observed over the twentieth century since it is considered one of the proxies of the anthropogenic influence in the natural systems. In this way, although Ni concentrations in these rivers are low, point diffuse sources may increase their concentrations.

Cobalt average concentrations were similar between Sor and Landro Rivers (4.91 and 4.49 nM respectively), whereas for the Mera River average concentrations were low (1.85 nM). Co world average concentration was 2.51 nM (Gaillardet et al. 2005), however, this value could be also lower in non-polluted systems. In some Galician rivers background values range between 1.2 and 9.0 nM (Salminen 2005; De Vos and Tarvainen 2006), indicating the non-affecting of human polluted activities.

In the Mera River, Cu concentrations were significantly higher (1.15-8.88 nM) than those reported for Sor and Landro, averaging 1.35 and 1.25 nM respectively (Fig. 3.1.4.a). In terms of concentrations determined, dissolved Cu in these major freshwater inputs were found to be within typical values for uncontaminated river waters in the same area (Prego and Cobelo-García 2003; Cobelo-García et al. 2004; Santos-Echeandía et al. 2008; 1.8-10.5 nM Salminen 2005; De Vos and Tarvainen 2006) Moreover, Cu concentrations in these rivers are lower than those found in the pristine rivers (Guieu et al. 1996). Although various sources can contribute to the input of copper to rivers (e.g. industrial and domestic waste-waters or agricultural activities; Monet 2004), the relatively high dissolved concentrations in the Mera River in comparison with the other studied rivers may be explained by Cu mining areas localized in this watershed (IGME 1982; Fig. 3.1.1).

In general, dissolved element concentrations in the major freshwater inputs to the Northern Galician Rias were found to be within typical values for uncontaminated pristine rivers. Moreover, in the dissolved load, the preferential dissolution of the different types of rocks and minerals present may be considered as the main factor that cause large variations in major and minor element abundances in rivers. The composition of the dissolved load of studied rivers reflects the weathering of alumino-silicate rocks present in the watersheds of the Sor, Mera and Landro Rivers (Fig. 3.1.1).

Table 3.1.3. Major and minor element SPM composition of the rivers discharging into the Northern Galician Rias and other world rivers

	POC (%)	PON (%)	Al (%)	Fe (%)	Cd ($\mu g\ g^{-1}$)	Co ($\mu g\ g^{-1}$)	Cr ($\mu g\ g^{-1}$)	Cu ($\mu g\ g^{-1}$)	Ni ($\mu g\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	V ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)
Sor	22 ± 12	1.63 ± 1.37	3.6 ± 2.3	8.8 ± 7.7	2.2 ± 3.2	31 ± 20	282 ± 407	66 ± 46	42 ± 47	71 ± 60	86 ± 64	363 ± 520
Mera	15 ± 10	1.28 ± 1.25	4.0 ± 1.2	8.2 ± 7.1	2.2 ± 2.9	45 ± 13	210 ± 144	109 ± 98	137 ± 91	35 ± 17	105 ± 38	311 ± 342
Landro	14 ± 7	1.23 ± 0.87	4.4 ± 1.8	6.1 ± 5.4	1.1 ± 0.7	24 ± 18	110 ± 101	40 ± 38	41 ± 20	47 ± 37	46 ± 39	358 ± 667
Major World Rivers [a]	-	-	9.1	5.0	-	-	-	83	-	-	-	185
Scheldt River [b]	-	-	4.5	4.6	[12.2]	-	213	-	-	207	-	1039
Vigo Rivers [c]	-	-	-	[4.4-6.2]	-	-	-	-	-	-	-	-
Vigo Rivers [d]	-	-	-	-	-	-	-	[6-62]	-	-	-	-
Ferrol Rivers [e]	[4-17]	[0.2-2.7]	[1.3-4.6]	[0.5-3.0]	[0.22-2.0]	-	-	[24-306]	-	[52-304]	-	[58-340]

SPM characteristics and major elements are in percentage values. Values are given as average ± standard deviation. Values between brackets correspond to the reported range.
[a] Poulton and Raiswell, 2000; [b] Zwolsman and van Eck, 1999; [c] Filgueiras and Prego, 2007; [d] Santos-Echeandía et al., 2008; [e] Cobelo-García et al., 2004

Characterisation of particulate matter

Suspended particulate matter (SPM) was recorded in mean abundances ranging from 0.87 mg·L^{-1} in the Sor River, 2.23 mg·L^{-1} in the Mera River and 2.85 mg·L^{-1} for the Landro River. Variations in particulate matter are noticeable in the Landro riverr, since values reach up to 8.2 mg·L^{-1}. Similar values have been reported by other authors (0.33-18.7 mg·L^{-1}) in the rivers flowing into the Ria of Vigo (Pazos et al. 2000; Santos-Echeandía et al. 2008) and, in other Galician Rias such as the Ferrol, values for rivers (15-20 mg·L^{-1}; Cobelo-Garcia et al. 2004) are obtained.

Chlorophyll-*a* (Chl-*a*) abundance was similar for the Mera and Landro rivers (0.50 and 0.48 µg L^{-1}) and lower for Sor (0.29 µg L^{-1}). In all cases, Chl-*a* concentrations were low since nitrate effluents or phosphate does not enhance primary production. Chl-a concentrations correlated well with POC and PON values, and with SPM as observed in other riverine systems (Neal et al. 2006). The residence time of water in the rivers was low and thus primary production

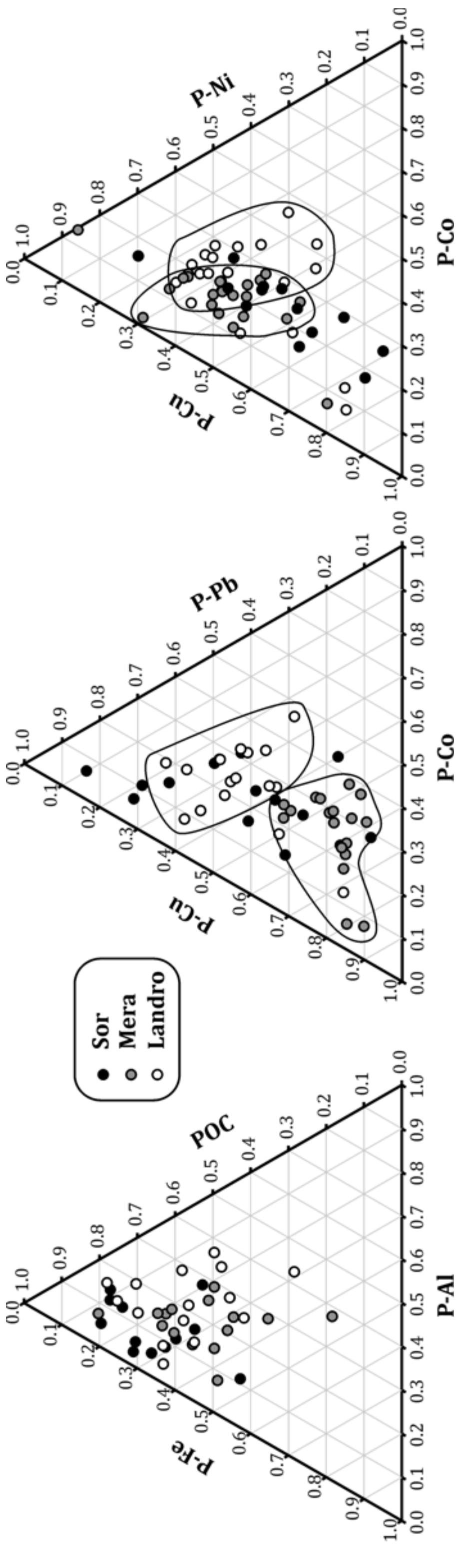


Figure 3.1.5. Ternary diagram showing the contribution of major and minor elements to the SPM for the three studied rivers at the Northern Galician Rias.

was limited and controlled by non-saturated nutrients.

POC and PON follow the same pattern found for SPM concentration and Chl-*a* (Fig. 3.1.4b). The Landro River was richer in POC and PON with values ranging from 170 to 920 µg L^{-1} and 11-106 µg L^{-1} respectively (see Fig. 3.1.1, presence of peat in its watershed), whereas POC mean values for the Sor and Mera rivers were190 and 262 µg L^{-1} and 18.1 and 19.9 µg L^{-1} for PON. SPM was rich in POC and PON, accounting on average 15, 22 and 14% for POC, and 1.28, 1.63 and 1.23% for PON for Mera, Sor and Landro rivers, respectively (Table 3.1.3). Higher percentages of the POC and PON in the SPM occur during with river discharge (Table 3.1.3). The close relationship between SPM and POC indicates that organic carbon in the particulate matter increases with low SPM and low water discharge (Hart and Hines 1995). However, when high discharge occurs and SPM is higher its composition increases in lithogenic material and thus in Al and Fe. Sediments from Galician rivers are rich in organic carbon (1.3-4.1 wt %; Salminen 2005; De Vos and Tarvainen 2006) and thus, most of this carbon passes through the water column in the particulate form, especially when the detrital composition of the SPM is low. Other POC and PON sources are the phytoplankton biomass, but their production is highly dependent on time of travel of the river waters.

According to the dissolved phase, Al and Fe were the most abundant elements in the particulate material. Several differences in the characteristics of the SPM can be found for these rivers. Average concentration of Al was low in the Sor River (1150 nM), with higher values for the Mera River (3680 nM) and the Landro River (5650 nM). Average concentration of Fe was similar for the Mera and Landro rivers (2480 and 2320 nM), but in the Sor River, the values were lower (1280 nM). These concentrations were lower than Fe associated with SPM in the rivers draining the Ria of Vigo (10000 nM-29000 nM; Filgueiras and Prego 2007).

Major elements such as Al or Fe were used to estimate the lithogenic composition of the SPM. On average Al and Fe percentage were 4.4% and 6.1% respectively in the Landro River (Table 3.1.3), indicating that in this river the detrital fraction is higher and highly dependent on the granitic bedrock watershed. Moreover, for the Sor and Mera rivers, the lower SPM detrital composition was mainly due to the higher content of POC (Fig. 3.1.5). This behaviour is confused since POC concentration in Landro River is higher. Moreover, the values of Fe percentage in this river were lower in comparison with Northern Galician rivers but in the same order of magnitude or even lower than others in the same area (Cobelo-García et al. 2004; Filgueiras and Prego 2007). The lower Fe value in the SPM for the Landro River is strange since throughout this river basin Fe veins are abundant (Fig. 3.1.1). Bedrock of this basin must be richer in Si since it is cover by granitic rocks, and thus the SMP composition for this river must be higher in this element. However, Si in the SPM was not analysed ant this hypothesis could not be tested.

The mean particulate Zn concentration is higher in the Landro River (14.29 nM) than in the Sor (3.87 nM) and Mera (7.76 nM) rivers. The mean particulate Pb concentration was also higher in the Landro River, with an average value of 0.58 nM, compared to the mean concentrations for the Sor and Mera rivers mean (0.32 and 0.42 nM, respectively). In contrast, the mean particulate V concentration was 5.45 nM in the Mera River, showing large fluctuations in the values, and it was similar to the Sor (1.20 nM) and Landro (2.35 nM). The Mera River always had higher average concentrations of particulate Co, Cr, Cu and Ni (1.80, 7.98, 4.09 and 4.74 nM respectively), but the Sor River had average concentrations approximately 2-6 times lower (0.45, 4.19, 0.83 and 0.63 nM for Co, Cr, Cu and Ni, respectively). The watershed of the the Mera River appears to have higher concentrations of minerals and rock richer in these mineral assemblage together with Ti, Ni, Mn, Mg, Ca and As (IGME 1982; Guitián-Ojeda 1992; Fig. 3.1.1) since it drains part of the mafic and ultramafic rocks of the Cabo Ortegal complex, leading to an increase of these elements in the particulate material.

No differences in the composition of the SPM, taking into account the major compounds POC (Al and Fe), can be detected for the three studied rivers (Fig. 3.1.5). However, it is easy to discriminate the three rivers on the basis of the relative percentage of minor elements in SPM, as a result of the lithological characteristics of the watersheds (Fig. 3.1.5). In this way, SPM characteristics in the Mera River are controlled by the appearance of Cu and associated metals in the watershed leading to a slight increase in the relative percentage of Co, Cu, Ni and V in the SPM (Table 3.1.3) in comparison with other rivers (Cobelo-García et al. 2004; Santos-Echeandía et al. 2008).

Calibration curves and annual fluxes

The behaviour of dissolved and particulate elements in the riverine waters has been poorly addressed in the literature, together with the total discharge rate into the coastal environment. This behaviour of trace elements and chemical species is difficult to predict, especially in rivers and streams where physical (mainly hydrological), chemical and biological interactions vary (Gaillardet et al. 2005).

The main process controlling the dynamics and variations of chemical elements in the dissolved and particulate form is the river discharge. It has considered the assumption that concentration of various elements and species can be described as a function of stream discharge. In this way, power-law CQ (concentration-flow) calibration equations to predict the daily discharge fluxes were used (Table 3.1.1). The power-law functions were used to calculate the total annual fluxes. Concentration-flux relationships are often described using power-law equations (Vogel et al. 2003; Wheatcroft et al. 2010; Klonsky and Vogel 2011). Some examples of good agreement between concentration and flow were plotted in Fig. 3.1.6.

Dissolved nutrient concentrations decreased exponentially with increasing river water flow, showing a conservative behaviour (Fig. 3.1.6.a,b), with the exception of nitrate in the Sor River. In this way, at low river discharge, nutrient concentrations were high. This fact could be result from increased photosynthetic activity of phytoplankton, increased remineralisation of organic matter, or a higher anthropogenic influence when the water flow is low. This pattern was also observed for DOC, D-As, D-Fe (Fig. 3.1.6.c), D-Mo and D-V (Table 3.1.1). This implies that for these elements the dilution is the main factor controlling their concentration, and biological factors are minor(Hart and Hines 1995). If biogeochemical cycling, exchange with solid phases, changes in temperature or biological activity within the river system takes place, the temporal variations of these elements will not be conservative. In this case, hydrologic events controlled elemental concentrations, but quantitative linkages between these parameters and river discharge and other watershed characteristics have been poorly elucidated.

On the other hand, the dissolved concentration of Al, Cd, Co, Cu, Mn, Ni (shown in Fig. 3.1.6.d), Pb, U and Zn, increased with river discharge. This behaviour is common in some major elements (Gaillardet et al. 2005), and it could be related to an increase in the concentration of SPM due to sediment resuspension associated with high river flow and subsequent desorption from SPM.

This general pattern was not observed for Chl-*a*. Moreover, CQ calibration equation for Chl-*a* does not work since its abundance in river waters is controlled by biological activity instead of river flow. Elements in the particulate form are controlled by the abundance in SPM. POC content in the river waters is also controlled by the abundance of particulate material, organic and non-organic. When riverine discharge is high and particulate material increases (Table 3.1.1), POC content shows an exponential decrease (Fig. 3.1.6.f).

To better understand the influence of small pristine rivers and watersheds on the coastal areas of the Northern Galician Rias, it is important to estimate the total amount of materials discharged. In this way, an estimation of the total annual amounts of the organic and inorganic, dissolved and particulate chemical species was carried out for the rivers draining the Northern Galician Rias (Table 3.1.2). The mean annual river water flux into the Northern Galician Rias observed in 2008 is about 610000 t yr^{-1} for Sor River, and 319000 t yr^{-1} for Landro and 189000 t yr^{-1} for Mera. Based on the whole observation period, the calculated SPM fluxes into the Ria of Ortigueira was 661 t yr^{-1}, which is almost the same for the Ria of Barqueiro (664 t yr^{-1}), but lower than for the Ria of Viveiro (1331 t yr^{-1}). These SPM fluxes were 10 times lower in magnitude than the values cited by Prego et al. (2008). This difference seems to be mainly due to methodology (e.g. considered basin surface, sampling frequency, time-period). However, the high sampling frequency used for this study is supposed to provide reliable data, especially for years with variable or exceptionally high fluxes like 1992.

The annual fluxes estimated here were in the same order of magnitude for other rivers in the study area (Table 3.1.2; Vergara and Prego 1997; Gago et al. 2005; Filgeiras and Prego 2007; Santos-Echeandía et al. 2008), except for human-altered rivers such

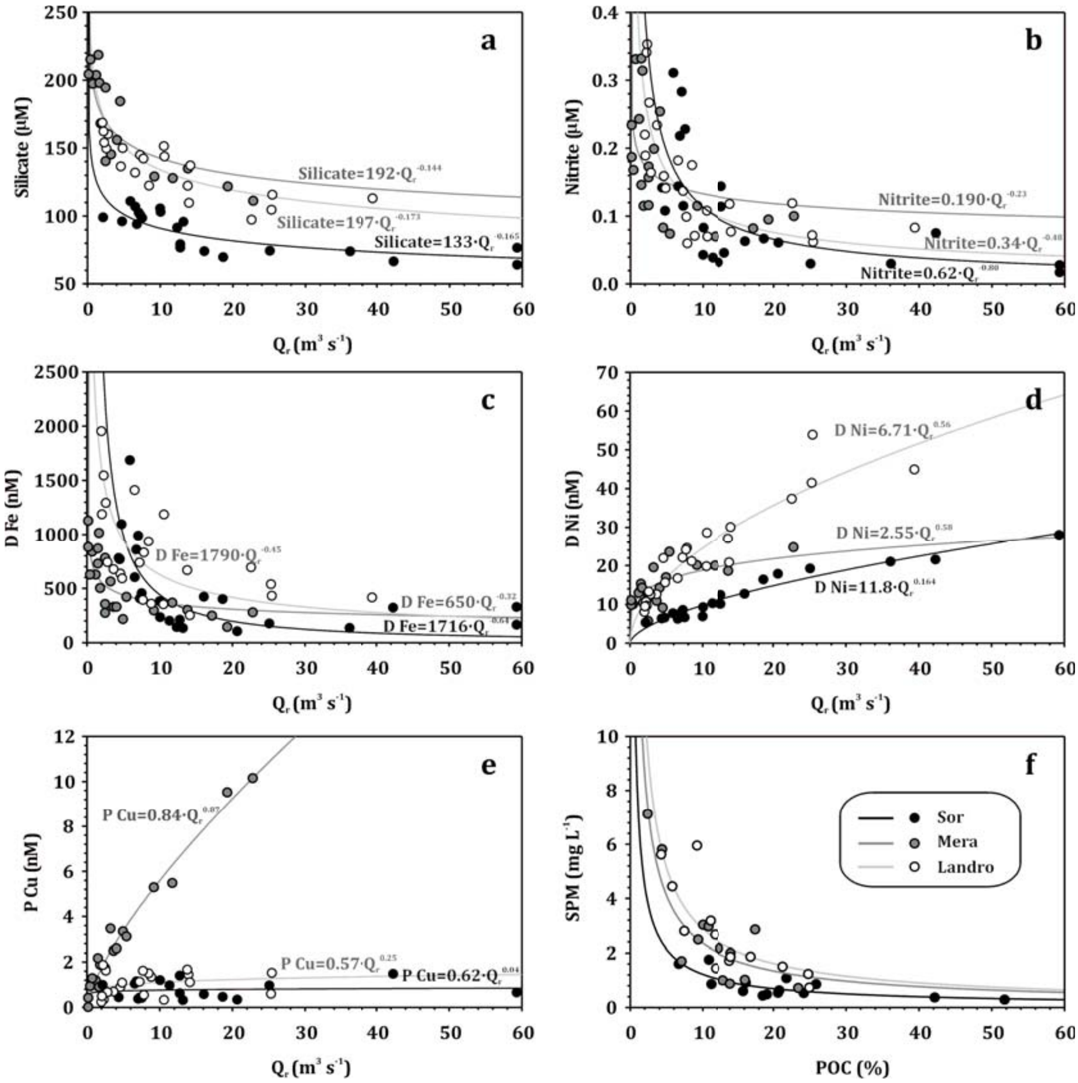


Figure 3.1.6. Examples of concentration-flow equations ($C = a \cdot Q^b$) for the main rivers flowing into the Northern Galician Rias. Q is the freshwater flow in $m^3 \cdot s^{-1}$; C is the substance concentration in nM for metals and µM for nutrients. SPM: Suspended particulate matter ($mg \cdot L^{-1}$); POC: particulate organic carbon (%). r corresponds to the regression coefficient.

as those found in the Ria of Ferrol (Cobelo-García and Prego 2003; Cobelo-García et al. 2004). It is important also to note the higher contributions of DIN in comparison with other pristine rivers with higher flow (e.g., Oitabén, Lérez) in the Galician area. However, for phosphate, silicate, D-Cu, P-Cu, D-Pb and D-Zn annual fluxes are comparatively lower or in the same order of magnitude (DOC, POC, D-Cd, D-Fe, P-Fe).

If considering the ratio between the annual flux and the ria area, results show that for DIN and silicate ratio between flux and area is considerably higher for the Northern Galician Rias compared to the rias of Pontevedra, Vigo and Ferrol. DIN and silicate may also have a coastal fertilising effect and this fact supports the importance of freshwater fertilisation by pristine rivers in small rias. In the case of the Northern Galician Rias, it is important to emphasise that DIN or silicate supply per ria area is between 2-17 times higher than for the Ria of Vigo. In the case of POC and DOC, the supply per ria area is 2-15 times higher than for the Ria of Vigo. Therefore, the increase in nutrient concentration in the innermost part of the northern rias of Galicia (see Chapter 2) during conditions of non-upwelling and high floods could cause an increase in the marine primary production, as observed in other areas (Avilés and Niell, 2007). However, even a large nutrient load per unit area of the ria, the impact of these nutrients loads will also be a function of its residence time within the innermost ria (Nedwell et al. 2002) if the nutrients are flushed rapidly through it.

Only few data about metal inputs from pristine rivers in the Galician rias can be found and it is restricted to dissolved and particulate Cu and Fe. Dissolved and particulate Cu per ria area are of similar magnitude for the Northern Galician Rias than for the rias of Vigo and Pontevedra. Dissolved and particulate Fe influx per area in the Northern Rias was 5-10 times higher than for the Ria of Vigo, indicating than freshwater fertilisation by means of micronutrient is important in these rias.

Dissolved-particulate interactions

A common approach to characterize the partitioning of an element is the use of a coefficient of distribution defined as the ratio between the dissolved and particulate phases (Table 3.1.4).

For the majority elements, results show that Fe was bound to SPM (3-4 times higher in the particulate phase) within the same order of magnitude as for other Galician rivers (Filgueiras and Prego 2007). Fe partitioning could be related to rainfall and high discharge of the resuspension of sediments (Neal and Robson 2000). In relation to the Al, there was a relative equilibrium between two phases, although in the Mera River it seems that Al in the particulate phase was dominant. In the case of organic carbon the dissolved phase had the prevailing abundance, even 6-10 times higher than the particulate one.

Minor elements were mainly bound to the dissolved phase, excepting Pb as observed in other riverine systems (Admiraal et al. 1995). Only in the Sor River (Fig. 3.1.1), Pb in the particulate matter was more abundant due to the presence of Pb mineralization in the watershed (Table 3.1.4). These results are in accordance with the affiliation of lead with the particulate matter, which dominates the partitioning of this metal under typical SPM concentrations, a situation that was observed in the studied rivers and other Galician rivers (Cobelo-García et al. 2004). Cu also had an affiliation with particulate matter and POC, although the concentration in dissolved phase was higher excepting for the Landro River.

Cadmium, Co, Ni, V and Zn always presented affinity with the dissolved phase for all rivers the studied indicating that these metals are initially mobilised by dissolution of solid phases. Moreover, in the Sor River dissolved phase was considerably higher in proportion to particulate phase (K=20.4, Table 3.1.4), suggesting that the affinity of these metals to SPM is lower.

Table 3.1.4. Coefficient of distribution, K =[D]/[P], between the dissolved (D) and particulate (P) concentration of some chemical elements in the main rivers flowing into the Northern Galician Rias

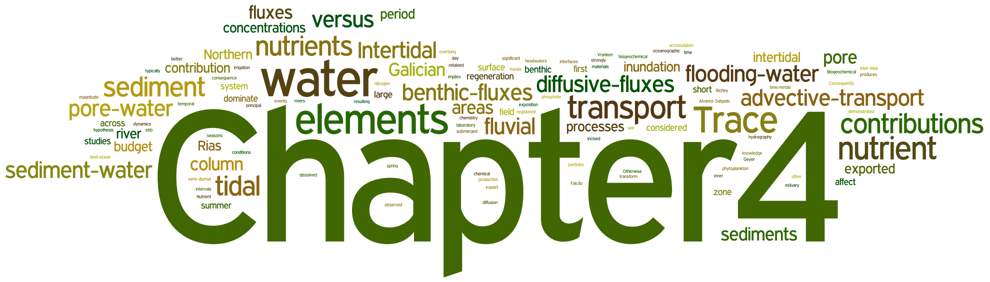
	Sor	Mera	Landro
OC	9.5 ± 4.3	6.1 ± 3.6	6.8 ± 3.1
Al	1.75 ± 0.77	0.34 ± 0.23	1.00 ± 1.17
Cd	8.7 ± 4.0	4.2 ± 3.7	6.1 ± 5.5
Co	17.4 ± 12.5	1.7 ± 1.5	5.0 ± 4.4
Cu	1.12 ± 0.77	1.9 ± 1.4	0.80 ± 0.55
Fe	0.41 ± 0.28	0.32 ± 0.22	0.44 ± 0.34
Ni	24 ± 12	4.7 ± 3.0	16.8 ± 9.5
Pb	1.6 ± 2.4	0.37 ± 0.37	0.30 ± 0.31
V	11.5 ± 8.2	3.7 ± 2.9	3.9 ± 2.5
Zn	20.4 ± 8.2	5.4 ± 3.6	8.2 ± 7.0

OC: Organic Carbon

Acknowledgements

In this chapter, special thanks to 'Meteogalicia' for meteorological data and 'Aguas de Galicia' for river flow; J. Lorenzo (IEO) for the processing and analysis of chlorophyll samples; M.D Doval (INTECMAR) for DOC analyses; A. Rodríguez-Riveiros (CSIC), L. Franco (IEO), G. Ayala (DRNA, Puerto Rico) and A. Vila-Durán for their technical support during sampling; A. Garci (CSIC) and A.V. Filgueiras (CSIC) for their assistance with the analysis of trace elements.

Chapter 4



fluxes
versus
period
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Intertidal
Northern
contribution
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Galician
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Chapter 4

Sediment-water fluxes of nutrients in intertidal ria systems (Northern Galician Rias)

4.1. Sediment-water fluxes of nutrients in intertidal ria systems

Introduction

Physical and biogeochemical processes occur at various temporal and spatial scales in coastal areas (Geyer et al., 2000). Biogeochemical cycling of nutrients in coastal zones under land-ocean interactions is strongly conditioned by fluxes into, through, and out of rivers. The river system store and transforms the elements in transit, such that fluxes and chemical forms of materials finally exported are often quite different from those encountered in the headwaters (Richey, 1983).

In meso and macro tidal ecosystems, the semi-diurnal tidal regime implies that the intertidal zone is alternately covered and uncovered twice a day (Vranken and Oenema, 1990; Portnoy and Giblin, 1997). These periodic covering and uncovering create non-steady state conditions between solids and pore water (Rocha, 1997; Hemmond et al., 2001). When sediments are covered with tidal water, solute transport across the sediment-water interface is driven by different mechanisms, such as diffusion, pore water advection, bioirrigation and bioturbation.

Nutrients fluxes due to diffusion have been quantified in estuarine and coastal areas in several studies (e.g. Callender and Hammond, 1982; Lerat et al., 1990; Gomez-Parra and Forja, 1993; Watson et al., 1993; Caetano et al., 1997; Zabel et al., 1998; Mortimer et al., 1999; Al-Rousan et al., 2004; Serpa et al., 2007). However, nutrient transport associated to dynamic events (i.e. advective transport, resuspension, etc), has been studied to a lesser extent (Huettel, 1998; Jahnke, 2003; Deborde et al., 2008; Ibánhez, 2011).

During the uncovered period, the intertidal sediment, in contrast to subtidal, sediments, is submitted to different conditions of light, temperature and pressure. In addition to this, the flowing water during both flood and ebb tides interact with the sediment pore water (Hemond et al., 1984; Caetano et al., 1997; 2007; Rocha, 1997; Huettel et al., 1998). The way in which water floods the intertidal area is rather complex, and in the first minutes sediment may be resuspended and seawater mixed with pore water of surface sediment layers. The result is the change of water composition achieved during the air-exposed situation (Falcão and Vale, 1998; Huettel et al., 1998; Jahnke, 2003). This change may increase the nutrient exchange, which coupled with benthic regeneration, can support the nutrient demand of primary producers (Nixon et al., 1976; Fisher et al., 1982; Boynton and Kemp, 1985)

This work aimed to quantify the contribution of sediments intertidal sediments to the nutrient budget of two Northern Galician Rias (Iberian Peninsula, SW Europe). These rias are coastal inlets with an external open area dominated by marine processes and a partially enclosed estuarine shallow area (Evans and Prego, 2003). The estuarine area is referred as inner zone and is characterized by large intertidal sedimentary areas. While in winter the strong freshwater inputs dominate the hydrography of these systems (Augas de Galicia, 2011), the oceanographic upwelling-downwelling events dominate in summer (see Chapter 2). Most studies have considered that nutrient regeneration in this area is driven by these processes (Alvarez-

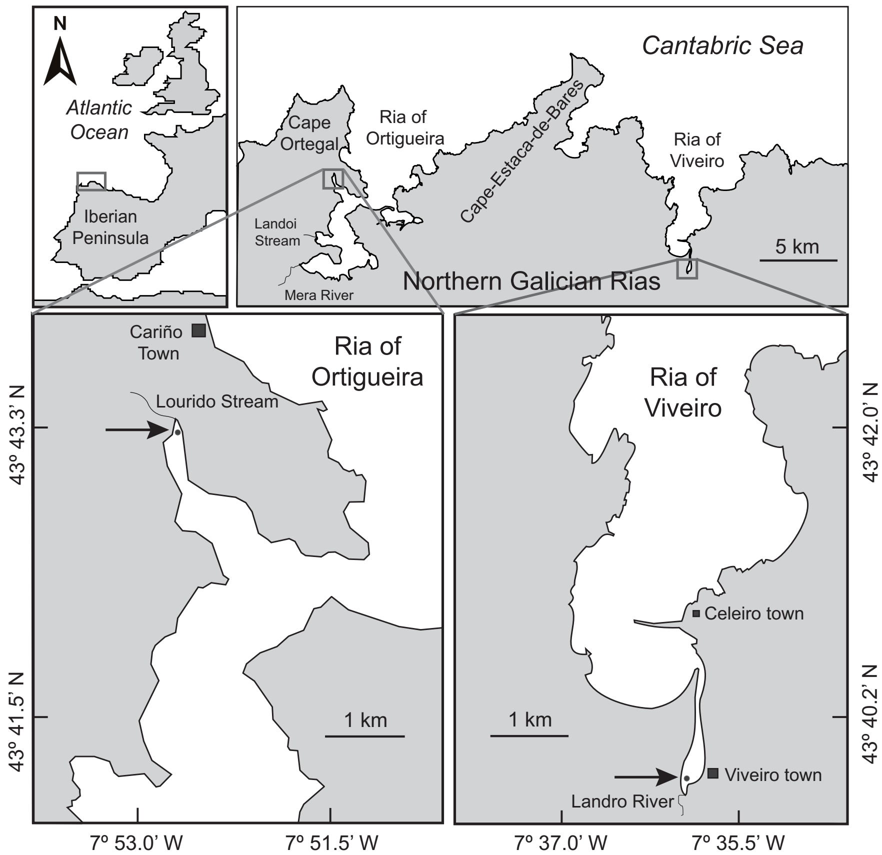


Figure 4.1.1 Map of the Northern Galician Rias, showing study area. Black arrows at the bottom frame (left, right) show the location of sampling stations.

Salgado et al., 1996; Prego et al., 1999; Prego, 2002; Varela et al., 2005).

The extent intertidal sedimentary areas of these rias make them ideal field laboratories to better assess the importance of sediment contribution to the nutrient budget in the water. Sampling was done during the productive seasons, spring and summer of 2008. The study reports concentrations of ammonium, nitrate, nitrite, phosphate and silicate in river water, sediment pore water and overlying water at low tide and in a short period of the tidal inundation over sediments from Ortigueira and Viveiro rias. The nutrient river contribution to the ria was estimated. Additionally, diffusive and advective transport of nutrients across the sediment-water interface of intertidal sediments were calculated. To our knowledge the magnitude of the three contributions to the total nutrient budget in the water column is discussed for the first time in this ria-coastal systems.

Materials and Methods

Sampling of sediment and overlying water in rias

Water and sediment were sampled in spring (9th and 10th April) and summer (21st and 22nd July 2008) in intertidal areas of Ortigueira and Viveiro rias (Fig. 4.1.1). The two sampling periods corresponded to contrasting river discharges (Fig. 4.1.2): 2.6 and 0.1 m3·s-1 for Lourido Stream, and 85 and 5 m3·s-1 for Landro River. At low tide when sediment was exposed to the atmosphere water was collected from the main channel of both rias using acid pre-cleaned syringes with 0.45 µm polycarbonate filter. Around 1 m apart from the water sampling site, sediments were sampled at the Ria of Ortigueira (43°42.82'N-7°52.69'W; Figure 4.1.1) with a methacrylate core (30 cm length, 6 cm diameter) and then quickly sliced in 2 cm layers. Sediment core sections (n=4) were stored in acid pre-cleaned HDPE vials avoiding air presence inside and kept in refrigerated atmosphere until processing at the onshore clean portable-laboratory. At the Ria of Viveiro (43°40.09'N-7°35.66'W; Fig. 4.1.1) topmost (≈3 cm) sandy sediments were collected with pre-cleaned plastic spatula and packed into plastic bags.

When tidal water starts to flood each site, a sample of intertidal sediments and water were collected at each time of inundation: 5, 10, 15, and 20 min. Tidal inundation water, hereafter referred as flooding water, was sampled 1 cm above the sediment surface directly into acid pre-cleaned syringes and filtered with 0.45 µm polycarbonate membranes. Sediments were collected in the same way as in the air-exposed situation. Five sediment cores were sampled at the Ria of Ortigueira, at air-exposed conditions (n=1) and subsequent times (n=4).

Immediately after sampling, the sediment layers were stored into pre-cleaned 50 mL Eppendorf® tubes avoiding the air presence inside. Sampling was done by a team of four people, taking place in less than 3 minutes per core collection. Sediments were centrifuged at the laboratory with a UniCen 15D (Herolab) at 4500 rpm for 5 to 20 minutes at 4°C. No significant changes on redox sensitive elements were found with this sampling procedure (Caetano et al., 1995). After centrifugation, the supernatant, hereafter referred as pore waters, were removed from sediments with plastic syringes, filtered through a polycarbonate filter (0.45 µm) in a laminar flow cabinet (ISO Class 5) and stored in 50 mL polyethylene bottles. All the water samples were preserved under refrigeration until analysis.

Sampling of river waters

Lourido Stream and Landro River were sampled three times, prior to each sampling of sediments and flooding water.

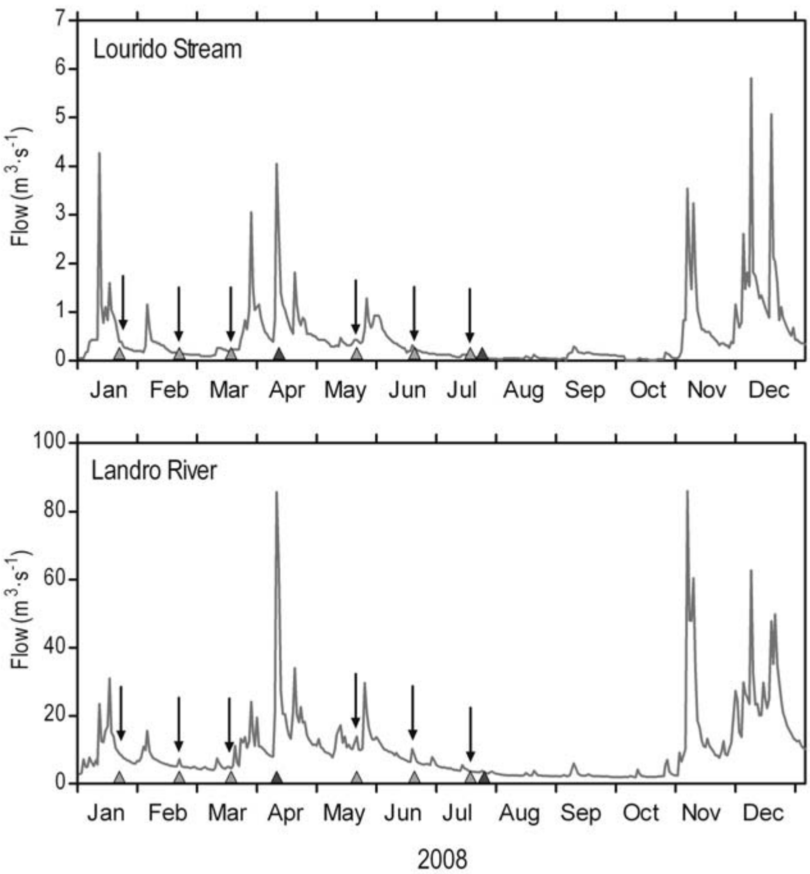


Figure 4.1.2 Daily flow ($m^{-3} \cdot s^{-1}$) of the Lourido Stream and Landro River during 2008. Gray triangles correspond to the sampling dates of rivers and black triangles to the sampling dates of sediments and flooding water.

The rivers were sampled at the same site on January 21st, February 20th, March 17th, May 19th, June 17th and July 15th, 2008. Water was collected into 50 mL polyethylene bottles previously cleaned and washed with HCl acid, and immediately frozen at -20°C to determine nitrate, nitrite, ammonium and phosphate (see Chapter 1: *Materials and Methods*). In order to avoid the formation of polymers in cold fresh water samples (Kobayashi, 1966), silicate samples were taken in 10 mL plastic bottles and preserved at 4°C until analysis.

Analytical determinations

The first two centimetres of the collected sediment cores were dried at 50°C during one week until constant weight and porosity was calculated according to Berner (1980) with the equation:

$$\Phi = \frac{W_{pw}}{W_{pw} + \left(\frac{W_s}{G_s}\right)} \quad (4.1.1)$$

were Φ is the porosity, W_{pw} is the weight of the pore water expressed in grams, W_s is the weight in grams of the dry sediment and G_s is the specific gravity of the sediment, which is assumed as a constant of 2.65 (Vanoni, 2006). The obtained sediment porosity for the rias of Ortigueira and Viveiro was 0.73 and 0.44, respectively. Additional grain-size analyses were performed in superficial sediments from both rias by dry sieving (Retsch AS-200). Sediments were grouped into mud, sand and gravel fractions, following the Udden-Wentworth scale.

Calculations

Diffusive fluxes (DF) across the sediment-water interface were estimated according to Fick's first law of diffusion (Berner, 1980) using the equation:

$$DF = -\Phi^3 \cdot D_0 \left[\frac{C_{pw} - C_{fw}}{\Delta x} \right] \quad (4.1.2)$$

were Φ is the porosity (dimensionless); D_0 is the diffusion coefficient of a solute at a given temperature ($cm^2 \cdot s^{-1}$); C_{pw} is the nutrient concentration (µM) in pore water of the topmost sediment layer at t=20; C_{fw} is the nutrient concentration (µM) in flooding water; and Δx is the thickness of the water-sediment diffusive layer (equal to 1.5 cm in this study which is equivalent to the distance between overlying and pore water). Diffusion coefficients (D_0) for NO_3^-, NO_2^-, NH_4^+ and HPO_4^{2-} and H_4SiO_4 were calculated on the basis of data obtained by Li and Gregory (1974), Lerman and Callender (1979) and Hammond (1982) at 0, 18 and 25°C, by linear interpolation based on known coefficients at a given temperature with the temperature measured in the sampling days.

D_0 values used to calculate diffusive fluxes were: on April (temperature 9.6 ± 0.1 °C), NO_3^- = 13.23 x 10^{-6}, NO_2^- = 10.74 x 10^{-6}, NH_4^+ = 13.58 x 10^{-6}, HPO_4^{2-} = 2.82 x 10^{-6}, and H_4SiO_4 = 3.88 x 10^{-6} $cm^2 \cdot s^{-1}$; and July (temperature 19.0 ± 0.1 °C): NO_3^- = 16.68 x 10^{-6}, NO_2^- = 15.87 x 10^{-6}, NH_4^+ = 17.34 x 10^{-6}, HPO_4^{2-} = 5.59 x 10^{-6}, and H_4SiO_4 = 7.70 x 10^{-6} $cm^2 \cdot s^{-1}$.

Fluxes obtained in Eq. 4.1.2 ($nmol \cdot cm^{-2} \cdot s^{-1}$), were converted to daily fluxes per square centimetre ($nmol \cdot cm^{-2} \cdot d^{-1}$), considering that each day has two dial cycles. Thus the sediment is covered during two periods of the day.

Tidal induced transport (Tt) was estimated based on the following equation (Eq. 4.1.3) that estimate the solute variation during the tidal inundation period (Caetano et al., 2007):

$$T_t = \sum \left[\left(\frac{C_{t2} - C_{t1}}{2} \right) - C_r \right] \cdot (h_{t2} - h_{t1}) \quad (4.1.3)$$

where C_{t2} and C_{t1} are the nutrient concentration in the pore water (µM) at each sampling time (t_1, t_2, t_3, t_n), C_r is the residual concentration in µM (lowest value measured in coastal waters for the sampling area), and h is the water depth (cm) at the same times. Advective transport of nutrients was calculated for the first 20 minutes of inundation. Considering the semidiurnal tidal regime, which implies that nutrients are removed twice a day from the water column, values calculated in Eq. 4.1.3, were multiplied by a factor of two to be expressed as daily fluxes ($nmol \cdot cm^{-2} \cdot d^{-1}$). Positive values indicate a flux from the sediment to the overlying water. Water depth and tide height at the sampling area were determined by barometric difference using data measured with an AQUALogger 520 sensor (Aquatec).

The river flux of nutrients (RF) in the sampling dates was calculated according to expression of Prego and Vergara (1998):

$$RF = Q \cdot C \quad (4.1.4)$$

where Q corresponds to the river flow ($m^3 \cdot s^{-1}$), and C the nutrient concentrations (µM) in the river waters.

Using satellite images and the water velocity of each river in the central channel of the ria ($m \cdot s^{-1}$) a cross–sectional area was calculated. The cross-sectional area is the rivers discharge influence area, defined as the cross section of the river plume in the bay, and it was equivalent to 0.70 and 0.26 km^2 for the Lourido stream and Landro river, respectively. A rough estimation of the flux of nutrients of each river to the ria ($nmol \cdot cm^{-2} \cdot d^{-1}$), was estimated by multiplying the nutrient fluxes obtained in Eq. 4.1.4 (converted to $nmol \cdot d^{-1}$) by the cross–sectional area (converted to cm^{-2}). Surface water velocity ($m \cdot s^{-1}$) was monitored with a Valeport 808 electromagnetic current meter throughout 2008 (n=48). Daily river flows (Q) were provided by *Aguas de Galicia* (Consellería de Medio Ambiente-*Xunta de Galicia*), and corrected for the total river basin (Fig. 4.1.2).

Statistics

Differences in nutrient concentration between river samples were checked using a two-tailed t-test and nutrient variability during sampling periods by means of an F-test. A non-parametric Wilcoxon-Mann-Whitney analysis (Ott and Longnecker, 2008) was used to evaluate differences between nutrient concentration and fluxes in flooding and pore waters during the sampling dates. All the statistical analyses were carried out using GraphPad Prism 4.0 for Mac OS-X (GraphPad Software Inc, 2004).

Results

Nutrient contributions from rivers

Table 4.1.1 gives the ranges of nitrate, nitrite, ammonium, phosphate and silicate concentrations in waters of Landro River and Lourido Stream. Significant differences in concentration of nitrate (t-test: $t = 2.76$, $df = 9$, $p < 0.05$) and silicate (t-test: $t = 3.96$, $df = 4$, $p < 0.05$) were observed between the Lourido Stream and Landro River. Nitrite and nitrate concentrations for each river were relatively constant during the two studied periods. One of the most remarkable aspects was that Lourido Stream showed no significant differences in silicate concentrations between periods, while enhanced silicate values were observed in the period May-July for the Landro River (up to 246 μM) as shown in Table 4.1.1.

Nutrient contributions from sediments

Muddy sediments (Ria of Ortigueira)

Sediments from the inner part of the ria were characterized by high mud content (≈99% grain size <63 μm). The depth profiles of nutrients in pore waters of air-exposed sediments in the two sampling dates showed similar trends. Concentrations increased with the depth and reached the highest values at 6-8 cm depth (Fig. 4.1.3). Nutrients concentrations in flooding water and sediment pore water were, in general, higher in spring than in summer, with the exception of the phosphate (Fig. 4.1.4.a). The lowest levels of phosphate were found in April (water temperature: 9.6°C) and the highest in July (water temperature: 19.0°C).

Differences in nutrient levels in pore water between April and July were significant at $p < 0.05$ (Mann-Whitney test) for ammonium and phosphate.

The pattern of concentration in flooding water and pore water was different for each nutrient as shown in Fig. 4.1.4.a. Nitrate +nitrite displayed higher values in the flooding water (April: 26-74 μM, July: 0.8-10 μM) than in the pore water (April: 1.7-9.2 μM, July: 1.4-2.0 μM). This difference was up to thirty times higher in April than in July. An opposite behaviour was observed for ammonium (flooding water, April: 3-18 μM, July: 1-2 μM; pore water, April: 55 to 113 μM, July: 20 to 50 μM) and phosphate (flooding water, April: 0.2-0.8 μM, July: 0.3-0.6 μM; pore water, April: 0.2-1.4 μM, July: 3.0-6.2 μM) with the highest concentrations in the pore water for both sampling dates. Silicate in flooding (74-128 μM) and pore waters (49-71 μM) followed a similar pattern to nitrate+nitrite in spring, with higher values in the flooding water. Conversely, this pattern changed in summer (flooding water: 15-61 μM; pore water: 59-78 μM) since silicate concentrations in the flooding water decreased

Table 4.1.1. Average nutrient concentrations of the Lourido Stream and Landro River

Nutrient concentration (µM)	Lourido Stream		Landro River	
	January-March	May-July	January-March	May-July
NO_3^-	59 (48-67)	51 (46-60)	47 (38-53)	37 (35-41)
NO_2^-	0.10 (0.06-0.15)	0.16 (0.06-0.25)	0.12 (0.07-1.16)	0.18 (0.12-0.23)
NH_4^+	0.19 (0.07-0.39)	1.46 (0.26-2.81)	0.19 (0.05-0.28)	0.63 (0.37-0.89)
HPO_4^{-2}	0.11 (<DL-0.30)	0.21 (<DL-0.43)	0.11 (<DL-0.34)	0.06 (<DL-0.11)
H_4SiO_4	263 (256-270)	269 (263-275)	141 (136-145)	165 (110-246)

Average nutrient concentrations correspond to the three months prior to the sampling of sediments and flooding water, and are given as average with the range in parentheses for the two sampling periods (January 21 to March 17; May 19 to July 15). DL means detection limit.

During spring, nitrate+nitrite in flooding water increased sharply in the first 5 minutes of inundation remaining high for 5 more minutes (74 µM). Conversely, levels in pore water decreased three folds during the first 5 minutes of inundation. In contrast, concentrations of ammonium in flooding waters decreased in the first 5 minutes of inundation while those of pore water increased in the same period from 55 to 112 µM. Afterwards levels decreased gradually to values close to the initial time. Phosphate in flooding and pore water decreased within the first 5 minutes of inundation and remained relatively constant (≈3 µM) for the remaining 20 min of flooding. Maximum silicate concentration in flooding water was found at t=5 (128 µM), preceded by a sharp rise. A decline of 42% in silicate concentrations was observed 5 and 15 minutes after inundation followed by a new increase in silicate levels (up to 115 µM). In pore water silicate had a similar trend, although with attenuated variations and a peak concentration of 71 µM at 10 minutes of inundation.

During summer, nitrate+nitrite in flooding water decreased 12 times after 20 minutes of inundation. In pore waters, levels were constant around 1.8 µM. As observed in April, concentrations of ammonium were higher in pore waters than in flooding waters. Ammonium levels in flooding water were low (≈2 µM) and slightly variable. Unlike in April, levels in pore waters decreased at the beginning of inundation from 39 to 20 µM increasing again to 38 µM at 15 minutes. Concentrations of phosphate in pore water increased during the first 15 minutes (up to 6.2 µM) decreasing afterwards to values similar with those observed before the tidal inundation. Levels in flooding water were low and relatively constant (0.3-0.6 µM) with time. Silicate in flooding and pore water had similar concentrations before the arrival of the tide (≈66 µM). However, concentrations in pore water remained relatively constant, while in flooding water decreased gradually to 23 µM.

Sandy sediments (Ria of Viveiro)

Vertical core samples were not taken in the Ria of Viveiro because of difficulty in collecting cores in sandy sediments. Sediments from the inner part of the ria corresponded 96% to sand (grain size >63µm).

Therefore temporal differences of nutrient concentrations in pore water represent just the first 3-cm sediment layer. Nutrient levels in flooding and pore water at the Ria of Viveiro were mostly elevated in spring than summer, although silicate showed an inverse behaviour (Fig. 4.1.4.b). Nitrate+nitrite, phosphate and silicate in pore water presented values significantly different between April and July (Wilcoxon-Mann Whitney test, $p < 0.05$).

Nitrate+nitrite displayed minor differences in mean concentrations

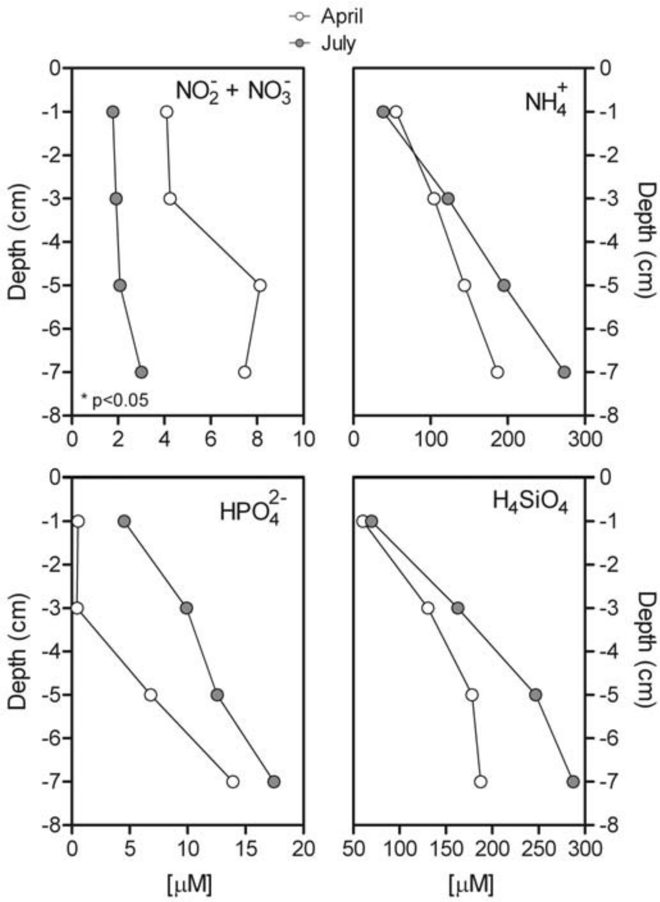
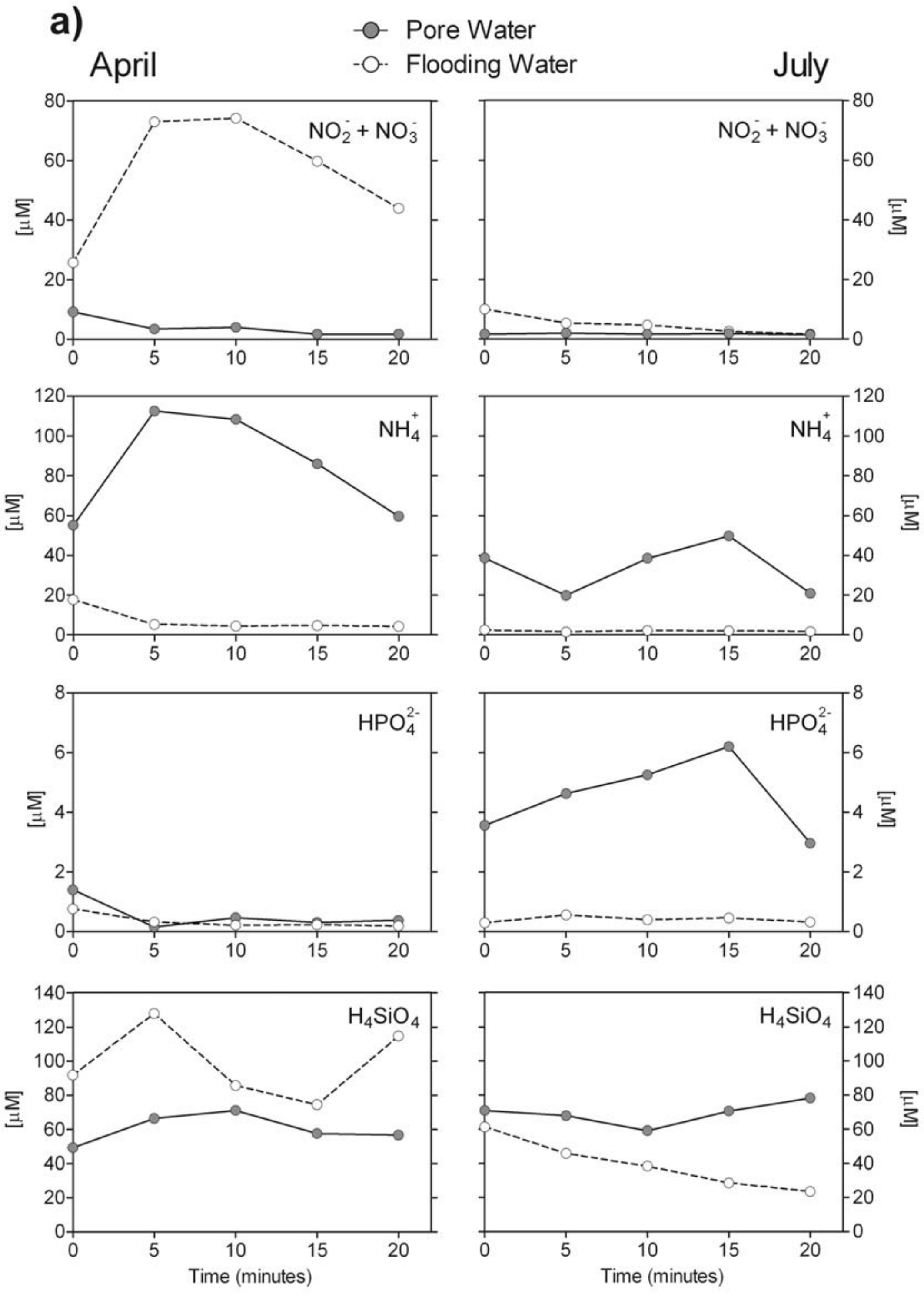


Figure 4.1.3 Vertical profiles of nutrient concentrations (μM) in sediment pore waters at air-exposed conditions at the Ria of Ortigueira during April and July 2008. p-value at the bottom-left corner of the frame indicates significant differences between samplings (Wilcoxon-Mann Whitney test).

between flooding and pore water (April, flooding water: 15-40 μM, pore water: 34-58 μM; July, flooding water: 14-24 μM, pore water: 6-18 μM). Ammonium in flooding and pore water behaved quite differently in spring and summer: levels in flooding water ranged between 17 and 26 μM in April and between 4 and 9 μM in July; and in pore water between 9 and 24 μM in April and 4 and 13 μM in July. Phosphate in pore water was higher than flooding water in both sampling dates (April, flooding water: 0.2-0.5 μM, pore water: 2.8-8.2 μM; July, flooding water: 0.3-0.8 μM, pore water: 1.1-2.0 μM). However, this difference was only four times in the summer in contrast with the fifteen in spring. Time variation patterns of silicate concentrations in flooding water were different between sampling dates. During spring, values were slightly higher in pore water (flooding water: 0.4-2.4 μM, pore water: 2.4-3.4 μM), but in summer, it was presented an inverse behaviour (flooding water: 38-68 μM, pore water: 6-11 μM), with values six times higher in flooding water.

In spring, opposite temporal variation patterns were found for nitrate+nitrite levels in flooding water and pore water. Concentration increase in flooding waters corresponds to the decrease in pore waters. After 5 minutes of inundation values reached 36 μM, remaining relatively constant (34 to 43 μM) during the studied period. Ammonium in flooding water increased 53% during the first 5 minutes of inundation decreasing gradually thereafter, re-establishing concentrations measured at t=0. The time course evolution of ammonium in pore water was irregular. Values decreased between the 5 and 15 minutes of inundation (up to 9 μM) followed by an increase at the end of inundation. Phosphate concentrations in flooding water were relatively constant (0.2 to 0.5 μM), whereas in pore water values decreased gradually from 8.2 μM to 2.8 μM. Silicate values in both flooding water and pore water showed a minor variation being on


a)
April
July
Pore Water
Flooding Water
$NO_2^- + NO_3^-$
NH_4^+
HPO_4^{2-}
H_4SiO_4
[μM]
Time (minutes)

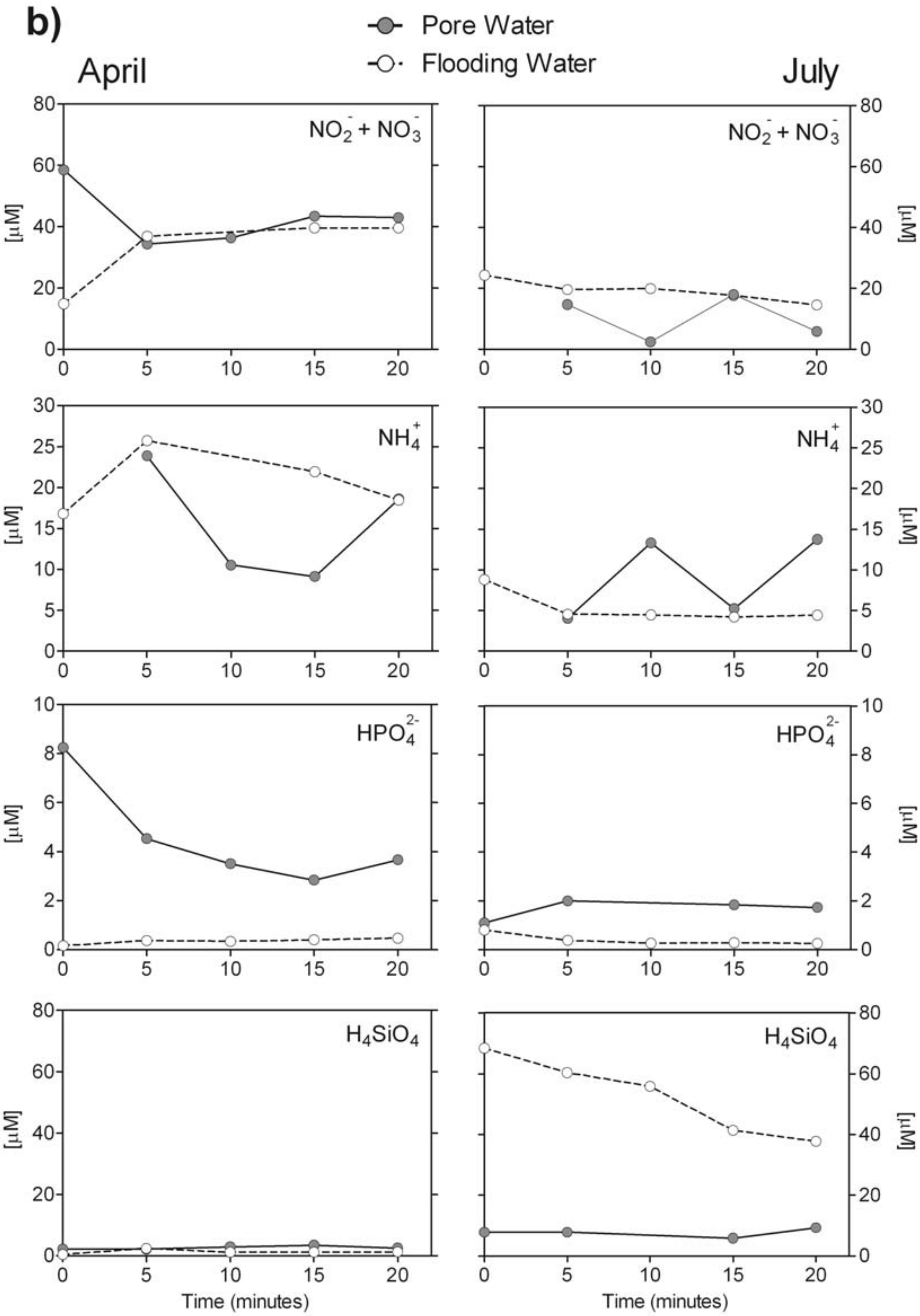


Figure 4.1.4 Nutrient concentrations (µM) in flooding and pore waters during the first 20 min of tidal inundation at the Ria of Ortigueira (a) and the Ria of Viveiro (b) in April and July 2008. Missing points correspond to samples where the volume extracted after centrifugation was not enough for analysis.

average 1.3 and 2.6 µM, respectively.

In summer, nitrate+nitrite in flooding water was kept around 1.3 µM, while in pore water irregular changes were observed, with the minimum concentration at 10 minutes of inundation (2.4 µM). Ammonium levels in flooding water declined 49% during the first 5 minutes of inundation, followed by slight variations around 4.4 µM. In pore water, maximum ammonium concentrations (13 µM) corresponded to the lowest nitrate+nitrite values, as observed in the Ria of Ortigueira. As phosphate levels decreased in flooding water (up to 0.39 µM) there was an increase in pore water concentrations (up to 2.0) shortly after the beginning of inundation (5 minutes). Silicate in flooding water decreased gradually with the arrival of the seawater, reaching its lowest concentration (38 µM) after 20 minutes of inundation.

Discussion

Freshwater nutrient fluxes

On the basis of river flow and nutrient concentrations in freshwater end members of both rias, nutrient loads were estimated in two seasonal periods (Table 4.1.2). Nutrients river inputs were generally low compared with other Galician (Prego et al., 1999) and Cantabrian rivers (Prego and Vergara, 1998), and it is explained for the low flow of the studied rivers, whose values during the sampling periods were always lower than those reported in rivers of the Western Galician Rias (Augas de Galicia, 2011). The general trend of nutrient fluxes was $H_4SiO_4 > NO^-_3 > NH^+_4 > HPO_4^{2-} > NO^-_2$ for the Lourido Stream (Ria of Ortigueira) and $H_4SiO_4 > NO^-_3 > NH^+_4 > NO^-_2 > HPO_4^{2-}$ for the Landro River (Ria of Viveiro).

In the Lourido Stream, nutrient discharges showed no significant differences between the periods for almost all nutrients, with the exception of ammonia whose concentration increased seven times (up to 4.16 $nmol·cm^{-2}·d^{-1}$) in summer. Since river flow was similar in both sampling periods the flux enhancement is attributed to ammonium inputs, which may be associated with remineralisation processes due to the organic nitrogen synthesised in summer (Kiefer and Atkinson, 1984; Dafner et al., 2007). In the case of the Landro River, nitrite, ammonium and silicate discharges increased more pronouncedly in May-June (up to 181 $nmol·cm^{-2}·d^{1}$ for NH_4^+). Under exceptional conditions of high river flow, nutrient fluxes may be underestimated. Fluxes may reach values up to 12 times higher than estimated for normal conditions of river flow, but these exceptional conditions represent only 2% over a year.

Nutrient fluxes between sediment and overlying water at submerged period

Transport induced by diffusion of nutrients across the interface during the submerged period, was estimated using concentration gradients between pore water of topmost sediment layer (0-2 cm) and overlying water. In general, higher diffusive fluxes of nutrient were found in the Ria of Viveiro (Table 4.1.3) were the low porosity of the sediment may have favoured the diffusive processes. This is consistent with the findings of Manheim (1970) that showed the variation of the diffusion constant with the porosity in unconsolidated sediments. However, ammonium diffusive fluxes in the Ria of Ortigueira were higher than those estimated in the Ria of Viveiro, presumably due to the sorption of NH_4 to fine sediments. In sediments with higher organic matter content like in the Ria of Ortigueira (up to 6%), ammonium accumulation may be linked to the breakdown of fresh organic matter. Mackin and Aller (1984) showed that absorbed ammonium in marine sediments may be higher in fine-grained sediments rich in silt and clay.

Table 4.1.2. Average nutrient fluxes from freshwater to the sampling areas of the rias of Ortigueira and Viveiro

	Unit	Lourido Stream (Ria of Ortigueira) January-March	Lourido Stream (Ria of Ortigueira) May-July	Landro River (Ria of Viveiro) January-March	Landro River (Ria of Viveiro) May-July
Average flow	($m^3 \cdot s^{-1}$)	0.25	0.23	6.88	8.69
*Nutrient fluxes**					
NO_3^-	($nmol \cdot cm^{-2} \cdot d^{-1}$)	186	146	10670	10830
NO_2^-	($nmol \cdot cm^{-2} \cdot d^{-1}$)	0.32	0.45	28	51
NH_4^+	($nmol \cdot cm^{-2} \cdot d^{-1}$)	0.61	4.16	44	181
HPO_4^{-2}	($nmol \cdot cm^{-2} \cdot d^{-1}$)	0.34	0.59	26	17
H_4SiO_4	($nmol \cdot cm^{-2} \cdot d^{-1}$)	825	767	3210	47700

*Fluxes are given as average values for the two sampling periods (January 21 to March 17; May 19 to July 15).

The negative diffusive fluxes of nitrate, nitrite and silicate in the Ria of Ortigueira in April and July indicate that nutrients were transferred from the water column into sediments.

This trend was also found in July for nitrate, ammonium and silicate in the Ria of Viveiro. The oxygen solubility reduction is directly related to the increase of temperature, as explained by Jørgensen and Revsbech (1985). Low oxygen diffusion into sediments affects the nitrification rates, due to the reduction of nitrate or nitrite to gaseous forms of nitrogen (N_2 or N_2O) (Cartaxana et al., 1999). Under oxygen depletion and nitrate availability, occur that oxygen is replaced by nitrate as electron acceptor in organic matter decomposition (Berner, 1980). These processes may explain the limited availability of pore water nitrates and nitrites, especially during the warmer periods. Nitrate and ammonium fluxes estimated in the Northern Galician Rias were comparable with those calculated by Lerat et al. (1990) in the Bay of Morlaix (France) reporting fluxes from -3.12 to 10 $nmol \cdot cm^{-2} \cdot d^{-1}$ of nitrate and from 27 to 65 $nmol \cdot cm^{-2} \cdot d^{-1}$ of ammonium during spring-summer season.

Phosphate fluxes also showed a contrasting seasonal variation in Ortigueira and Viveiro that may be attributed to sediment type and oxygen penetration depth (Sundby et al., 2003). Sandy sediments, like those from Viveiro, are generally characterized by a thinner iron oxyhydroxide buffer layer (Krom and Berner, 1981) allowing intense exchanges across the sediment-water interface. Otherwise, in the Ria of Ortigueira the thicker oxic-suboxic sediment layer in spring act as retention to the upward diffusive phosphate flux while at summer this layer is reduced due to the increase of organic matter mineralization rates (Ishikawa and Nishimura, 1989; Falcão et al., 2006). Phosphate and silicate diffusive fluxes were low compared with the fluxes of important river-dominated estuaries (Watson et al., 1993; Mortimer et al., 1999), but similar to those found by Al-Rousan et

Table 4.1.3. Diffusive flux and tidal induced transport of nitrate, nitrite, ammonium, phosphate and silicate across the sediment-water interface of the rias of Ortigueira and Viveiro in April and July 2008

	Ria of Ortigueira 10th April	Ria of Ortigueira 21st July	Ria of Viveiro 9th April	Ria of Viveiro 22nd July
Diffusive flux ($nmol \cdot cm^{-2} \cdot d^{-1}$)				
NO_3^-	-5.15	-2.61	+11.6	-9.50
NO_2^-	-0.03	-0.06	+2.10	+0.23
NH_4^+	+30.1	+6.72	+0.73	-1.32
HPO_4^{-2}	-0.01	+0.27	+0.49	+0.15
H_4SiO_4	-2.94	-0.43	+0.22	-13.2
Tidal induced transport ($nmol \cdot cm^{-2} \cdot d^{-1}$)				
NO_3^-	+5010	+146	+1500	+1450
NO_2^-	+12	+1	+5	+13
NH_4^+	+437	+140	+754	+436
HPO_4^{-2}	+28	+28	+14	+22
H_4SiO_4	+10230	+2680	+2	+4050

Positive values indicate a flux from the sediment to the overlying waters.

al. (2004) in coral reef along the Jordanian coast of the Gulf of Aqaba.

Sediment water exchanges associated to tidal flooding

Based on time course evolution of nutrient concentrations during tidal inundation of sandy sediments the transport across the sediment-water interface was calculated. Noteworthy and unlike diffusive fluxes, pore water transport was always positive in both sampling dates for all the nutrients studied. This clearly indicates that tidal excursion causes the export of nutrients from sediment to the water column independently of the season. Similar findings were found by Falcão and Vale (1998) in a SW European coastal lagoon and Cabrita et al.,1999) in the Tagus (Portugal) meso-tidal estuary. Minor seasonal variations were found at the Ria of Viveiro for tidal induced transport of nitrate, nitrite and phosphate (Table 4.1.3), while tidal induced transport of ammonium was almost two times higher in April than in July. In the Ria of Ortigueira, advection is limited due to the cohesive nature of the sediments. However, the time course variation of flooding water showed an intense exchange of nutrients between the sediment surface and the overlying water. The transport/exchange of nutrients may be calculated on the same basis as the advection. This transport was higher in April than in July for nitrate (34 times), nitrite (12 times), ammonium (3 times) and silicate (4 times), while for phosphate values remained constant (28 nmol·cm^{-2}·d^{-1}). The intense exchange of ammonium during the tidal excursion may derived from desorption from sediment particles due to the turbulence induce by this physical process (e.g wind driven sediment disturbances, Corbett, 2010). Gently mixing of sea water in the surface sediment seems to change the reversible adsorption-desorption equilibrium of ammonium in the sediment (Mackin and Aller, 1984) and causes a semi-diurnal supply of ammonium to the water column (Caetano et al., 1997). Similar results were found by Simon (1989) where changes in the sorption equilibrium of ammonium were caused by sediment resuspension induce by wind in shallow areas. The excursion of water during tidal inundation may also mix well-oxygenated water with anoxic sediments inducing chemical in nitrification and Fe chemistry. Kerner and Wallmann (1992), in laboratory

Table 4.1.4. Comparative table of diffusive flux and tidal induced transport of nutrients in some intertidal areas

Flux / Location	NO_3^- + NO_2^-	NH_4^+	HPO_4^{2-}	H_4SiO_4	Reference
Diffusive flux (nmol·cm^{-2}·d^{-1})					
Northern Galician Rias, Spain	-9.3 to 13.7	-1.32 to 30.1	-0.01 to 0.49	-13.2 to 0.2	This study
Ria Formosa, Portugal	nd	0.70 to 162	-0.32 to 9.20	nd	Falçao and Vale, 1998 [a]
Bay of Morlaix, France	-4.6 to 40.1	14.8 to 72.7	nd	-0.96 to 31	Lerat et al., 1990
Gulf of Aqaba, Red Sea	0.1 to 1.1	0.1 to 3.6	0.02 to 0.40	0.5 to 1.4	Al-Rousan et al., 2004
Tamar Estuary, SW England	nd	-57.4 to 409	-18 to 55	-50 to 315	Watson et al., 1993
Humber Estuary, UK	-4450 to 1640	nd	-110 to 220	-510 to 360	Mortimer et al., 1999
Tidal induced transport (nmol·cm^{-2}·d^{-1})					
Northern Galician Rias, Spain	147 to 5030	140 to 754	14 to 28	2 to 10230	This study
Ria Formosa, Portugal	nd	7 to 142	0.20 to 31	nd	Falçao and Vale, 1998 [b]
Island of Giglio, Italy	-71 to 531	-44 to 91	nd	66 to 175	Huettel et al., 1998 [c]

[a] Fluxes calculated from data in Fig. 2 and Fig. 3 in the original reference; [b, c] Fluxes calculated from data in Table 3 in the original reference; nd: no data.
Positive values indicate a flux from the sediment to the overlying waters.

experiments, showed that during percolation of aerobic water in suboxic sediment, in which nitrate, manganese and iron were the main electron acceptors, microbial oxygen reduction starts to be the main catabolic process. Changes in the chemistry of the Fe were also reported during tidal inundation, which may have consequences on the phosphate availability due to the equilibrium with freshly formed Fe oxihydroxides (Falcão and vale, 1990; Caetano et al., 1997; Falcão et al., 2006; Serpa et al., 2007).

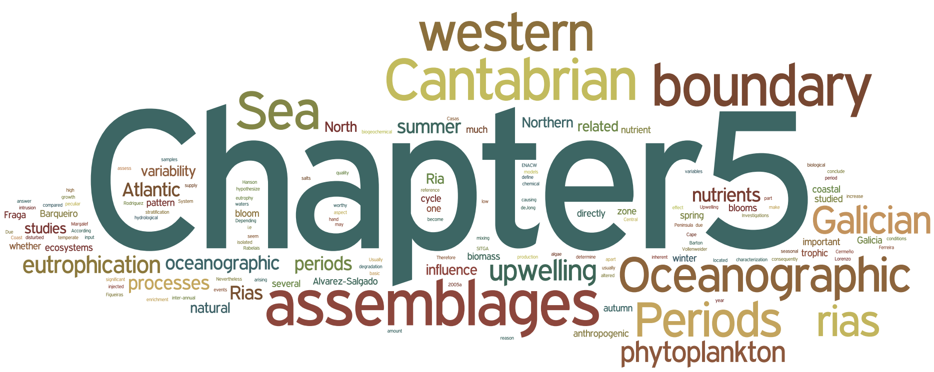
Although favourable conditions of upwelling were found in the Northern Galician Rias during April and July (see Chapter 2), this process does not affect the inner part of the rias and therefore does not influence the sediment-water exchange in the rias of Ortigueira and Viveiro. The high levels of both silicate and ammonium in pore waters (Fig. 4.1.4a) may result from an increased mineralization of algal material (Conley and Johnstone, 1995) rather than fluvial input that was comparable during both sampling periods. The dissolution of the skeletons of diatoms associated with the spring bloom (Fraga, 1981; Bidle and Azam, 1999) could explain the high silica availability.

Comparison of fluvial inputs against diffusive fluxes and tidal induced transport

Tidal induce transport was always greater than diffusive fluxes for all the dissolved nutrients (rias of Ortigueira and Viveiro: Wilcoxon-Mann Whitney test, $p < 0.05$) (Table 4.1.3). The greatest differences were observed for silicate at the Ria of Ortigueira, where tidal transport was four orders of magnitude larger than diffusive fluxes. The above is consistent with other studies that have shown that advection of pore water plays a important role in the water-sediment interchange of solutes, with differences greater than two orders of magnitude between pore water advection and molecular diffusion (Huettel et al., 2003). However, the striking result was that the nutrient transport derived from tidal excursion occurs simultaneously with river inputs. This sediment-water exchange was so intense that it represents 94% of the nutrient budget in the internal part of the Ria of Ortigueira, by considering the fluxes from the Lourido Stream, the diffusive fluxes and tidal induced transport. In contrast, in the Ria of Viveiro the river contribution was more important but this transport account for 33% of nutrient inputs. The morphology and the sandy nature of its watershed make sediments a moderate reservoir of nutrients. In the Northern Galician Rias, the tidal induced transport of nutrients was higher than in other marine and coastal areas (Table 4.1.4), suggesting that these ecosystems are influenced by tidal processes that may determine the availability of nutrients between the sediment-water boundary and their supply to internal parts of rias.

Acknowledgements

In this chapter, special thanks to ‘Aguas de Galicia’ for supply the river gauging data, to the ‘Delegación Territorial de Lugo de la Consellería do Mar (Xunta de Galicia)’ for laboratory facilities in Celeiro Harbour, to J. Raimundo (IPIMAR-Lisbon), R. Cesário (IPIMAR-Lisbon) and A. Rodríguez-Riveiros (CSIC) for their technical assistance in the sampling, analysis and data processing.



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Chapter5
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Chapter 5

Hydrological, chemical and biological interactions in a Northern Galician Ria

5.1 Phytoplankton assemblages and oceanographic periods in the western boundary of Cantabrian Sea

Introduction

Investigations concerning phytoplankton biomass, primary production and nutrients inputs have been carried out in the Galician Rias (NW Iberian Peninsula), mainly in the Western (Margalef et al., 1955; Hanson et al., 1986; Figueiras and Pazos, 1991; Alvarez-Salgado et al., 1993; Prego et al., 1999; Rodriguez et al., 2003; Lorenzo et al., 2005; Cermeño et al., 2006; Prego et al., 2007; Varela et al., 2008) and Middle Rias (Bode et al., 1996; Bode and Varela, 1998; Varela et al., 2001; Varela and Prego, 2003; Bode et al., 2005a,b; Varela et al., 2005). These studies recognised the existence of several oceanographic periods (Casas et al., 1997, 1999), similar for all the rias, with the usual changes related to the inter-annual variability of the ecosystems. The oceanographic cycle of the rias is the typical of temperate zone, with a mixing period in winter, stratification in summer and phytoplankton blooms in the transition periods: mixing-stratification (spring bloom) and stratification-mixing (autumn bloom). Nevertheless, this cycle is altered by the intrusion of Eastern North Atlantic Central Water (ENACW) during summer (Fraga, 1981), which supplies nutrients and allow for phytoplankton summer blooms, as important as those of spring and autumn (Varela et al., 2005, 2008). According to the oceanographical pattern, biogeochemical processes and phytoplankton assemblages, samples studied can be included into one of these periods. Usually, diatoms are dominant throughout the year even in summer due to the continuous upwelling pulses. Only during winter their abundance and biomass are very low.

On the other hand, the Galicia upwelling (Fraga, 1981) is part of the North boundary of the Eastern North Atlantic Upwelling System (Wooster et al., 1976, Barton

1998). The above mentioned studies point out that upwelling may not extend beyond Cape Estaca-de-Bares (as was discussed in Chapter 2). Therefore, one question arising from these studies is how much this boundary extends to the Northern Galician Coast? Depending on the answer to this question we could conclude that the rias eastern to this cape, i.e. the Cantabrian rias of Galicia, would not be under the influence of the oceanographic processes that make the Atlantic Galician Rias so peculiar and extensively studied.

One aspect directly related to the coastal zone where human settlements are important is the eutrophication, which is directly related to nutrient enrichment causing an increase of microalgae biomass (Andersen et al., 2006). Due to the increase of estuarine and coastal degradation in the last years, marine eutrophication has become a basic topic of study (Vidal et al., 1999; Howarth et al., 2000; EEA, 2001; Pinckney et al., 2001; Rabelais and Nixon, 2002; deJong, 2006), and consequently several models and criteria have been developed to assess the trophic state and quality of the waters (Nixon, 1995; Vollenweider et al., 1998; Ferreira, 2000; Bricker et al., 2008; Druon et al., 2004). Atlantic Galician Rias are usually under the effect of a natural eutrophication during the upwelling episodes when a high amount of nutrients are injected through the upwelled seawaters (Alvarez-Salgado et al., 1996; Prego, 2002; Varela and Prego, 2003). Moreover, the Northern Galician Rias seem not to be under a significant influence of anthropic activities (SITGA, 2010). As these rias are not disturbed by natural (upwelling) and non-natural (anthropogenic) eutrophication processes, it can be hypothesise that eutrophy is not inherent to the Northern Galician Rias.

Therefore, it seems to be worthy to define oceanographic periods and trophic status in the Ria of Barqueiro a Northern Galician Ria located in the western Cantabrian Sea, and isolated from natural or anthropogenic eutrophication processes. In this respect, the objectives of this section are:

i) to determine whether upwelling events affect the Ria of Barqueiro and how much influence the nutrients input and the seasonal variability of phytoplankton assemblages.

ii) to resolve whether these rias can be considered apart from the other Galician rias according to their pattern variability of hydrological, chemical and biological variables.

The characterisation of nutrient salts availability and phytoplankton assemblages could be useful as a reference level for the type-ria ecosystems.

Materials and Methods

Water column sampling and analysis

Monthly cruises were carried out onboard the *RV Mytilus* and *RV Lura* from January/08 to January/09 at a fixed station (20 m depth) located in the central part of the Ria of Barqueiro at 43°45.509'N and 07°39.493'W (Fig. 5.1.1). Temperature and salinity profiles were obtained with a General Oceanic Rosette, including a Sea-Bird 25 CTD with PAR (Li-COR) and Fluorescence (SCUFA) sensors. The water column was sampled using General Oceanic (5 or 12 L) bottles. Aliquots were collected at standard depths (0, 5, 10 and 17 m) from surface to near the bottom.

Collected water samples were analysed for: (1) Dissolved oxygen concentration and their saturation percentages, (2) Particulate organic carbon (POC) and nitrogen (PON), (3) Dissolved organic carbon (DOC) and nitrogen (DON), (4) Nutrient salts: nitrate, nitrite, ammonium phosphate and silicate, (5) Chlorophyll-*a*, (6) Phytoplankton abundances and (7) Primary production. A detailed explanation about processing and analysis of the samples is provided in Chapter 1, *Section Materials and Methods*.

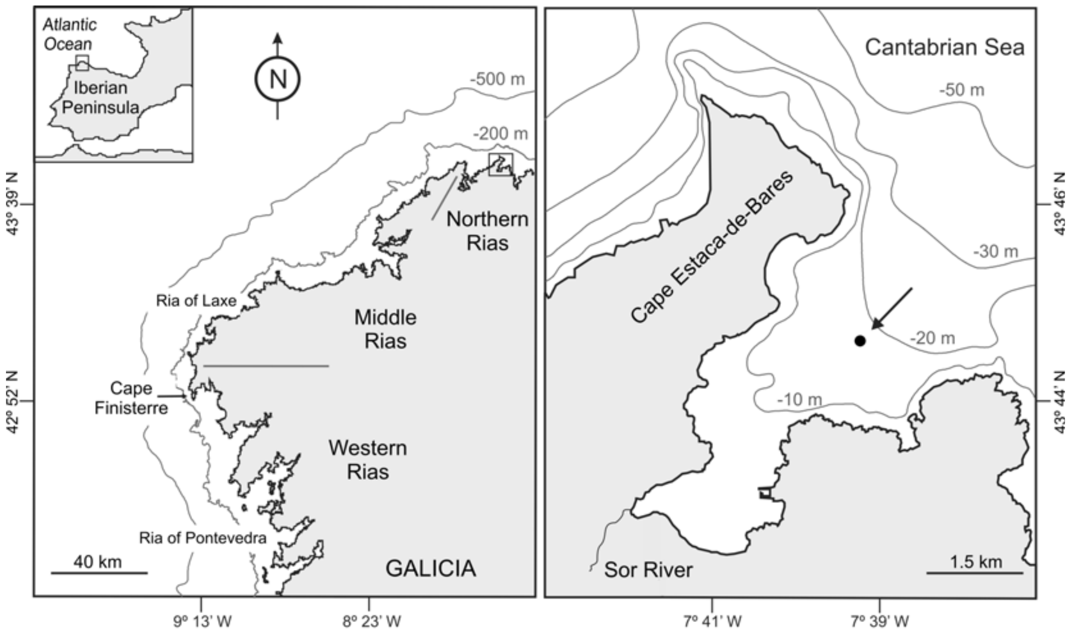

Figure 5.1.1. Map and bathymetry of the Ria of Barqueiro. Black circle on the right frame shows the sampling station.

Meteorological and hydrographic data

Upwelling indices (UI) were estimated at a point located at 43°N and 11°W (Lavin et al. 2000), using daily geostrophic wind speeds estimated from atmospheric surface pressure charts of State Meteorological Agency (AEMET) according to the methodology of Bakun (1973). These values were smoothed by a 7 days mean calculation.

Due to the different orientation of Galician coast according to the location of the various existing type rias, averaged values of the UI for the Northern Galician Rias (UI_N) were used in this study. Taking into account that UI can be defined as the Ekman transport component in the direction perpendicular to the shore-line (Nykjaer and Van Camp, 1994; Gomez-Gesteira et al., 2006), the Qy component of the Ekman transport was utilized as the UI for the Northern Galician Rias (UI_N).

Additionally to the measured variables, daily data of the Sor River flow during 2008 /09 supplied by *Aguas de Galicia* (Consellería de Medio Ambiente-*Xunta de Galicia*) were also studied. Flows were corrected considering the total basin area for the river (202 km^2).

Data analysis

In order to explain the temporal variation of the data among months, a one-way ANOVA followed by post-hoc Tukey (HDS) test was performed (Zar, 1984). Data normality was checked with a K-S test and then transformed using ln (x+1). All statistical analyses were conducted using SPSS 16.0 for Mac OS-X (StatSoft, 2008). Contour plots were generated using the Kriging method with Surfer 9.0 (Golden Software, 2009). The results are expressed as the mean ± standard deviation.

The observed conditions at the Ria of Barqueiro were contrasted with other Middle and Western Galician Rias. Data used correspond to the fixed stations located at: i) the Ria of Laxe from the project Hydrodynamic and hydrochemistry of the Anllons River-Laxe Ria system: seasonal stages (Varela et al. 2005); ii) the Ria of Pontevedra from the project Hydrodynamic and silicon cycle in the Pontevedra Ria (Varela et al., 2008).

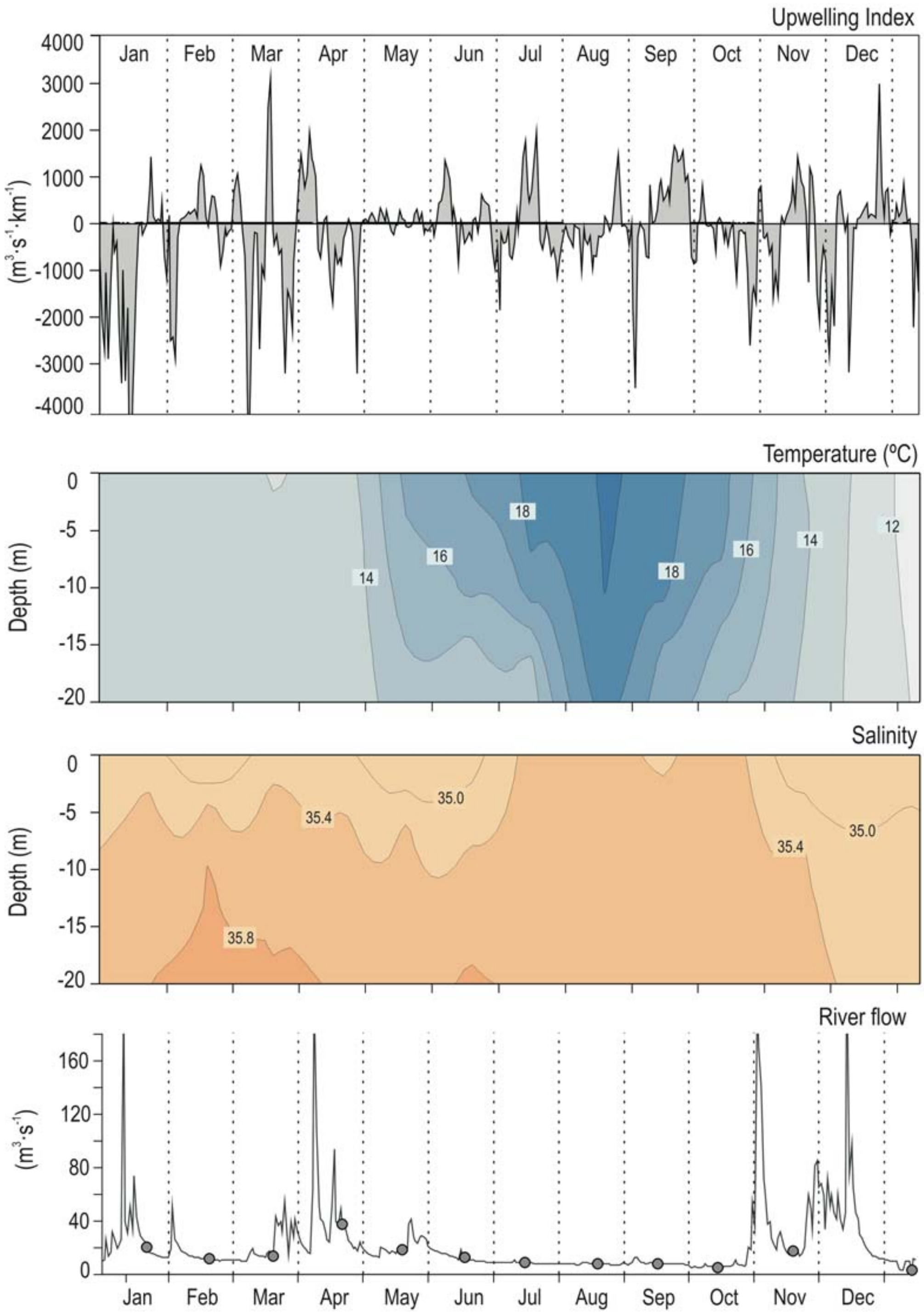

Figure 5.1.2. Temporal evolution of the Upwelling Index ($m^3 \cdot s^{-1} \cdot km^{-1}$) for the Northern Galician Rias (UI_N), water column temperature and salinity at the Ria of Barqueiro, and the Sor River flow ($m^3 \cdot s^{-1}$) during the annual study period (2008). Gray dots correspond to the sampling dates.

Results

Upwelling index, hydrography and river flow

Favourable conditions for upwelling were observed throughout the year. Persistent favourable conditions to upwelling were observed during April (9 days with UI_N of 1028±368 $m^3 \cdot s^{-1} \cdot km^{-1}$), July (9 days with UI_N of 1095 ± 549 $m^3 \cdot s^{-1} \cdot km^{-1}$), and mainly in September (19 days with UI_N of 861 ± 486 $m^3 \cdot s^{-1} \cdot km^{-1}$). Downwelling favourable conditions were also detected during period of study mainly in winter, even though sporadic positive indexes could be noticed (Fig. 5.1.2).

Water temperature showed seasonal differences ($F = 33.02$, $p < 0.001$). The minimum values were observed during December (11.6 ± 0.3°C) and the maximum in August (18.9 ± 0.1°C) (Fig. 5.1.2). Salinity was characterized by a horizontal stratification with values from 34.1 to 35.8, indicating a strong oceanic influence. Stratification was most evident in the first 10 m of depth (Fig. 5.1.2). The mean freshwater discharge was high during November (42.1 $m^3 \cdot s^{-1}$) and December (38.9 $m^3 \cdot s^{-1}$) and low during August (6.5 $m^3 \cdot s \cdot^{-1}$).

Nutrient salts

Temporal variability of nitrate was clear (ANOVA, $F = 29.64$, $p < 0.001$), exhibiting a decreasing trend until the summer, and followed by a gradual increase toward winter. The lowest concentrations of nitrate were observed in August (0.19 ± 0.15 μM) with a reduction throughout the water column (Fig. 5.1.3), and the highest in December (5.82 ± 0.23 μM) associated with the peaks of the river inputs (Fig. 5.1.3). Nitrite also showed seasonal differences (ANOVA, $F = 9.55$, $p < 0.001$) with low concentrations throughout the year, reaching the lowest values in November (0.09 ± 0.03 μM) and the highest in March (0.38 ± 0.06 μM) (Fig. 5.1.3). Ammonium also showed seasonal differences (ANOVA, $F = 46.22$, $p < 0.001$) increasing during June (2.6 ± 0.2 μM).

Silicate was seasonality variable (ANOVA, $F = 7.32$, $p < 0.001$) but low through the year (generally less than 3 μM). Particular exceptions were observed in mid-May and November when the concentrations increased in the surface layers. Concentrations of 4.0 ± 1.1 μM in the first 5 m depth were achieved. Phosphate also presented differences during the year (ANOVA, $F = 27.14$, $p < 0.001$), with the lowest values in May (0.04 ± 0.03 μM) and the highest in December (0.40 ± 0.01 μM).

Oxygen, organic matter and C/N distributions

Water column was very well oxygenated throughout the year with percentages above 90% (Table 5.1.1, Fig. 5.1.4). The higher values were observed in the upper layers with the maximum of over-saturation in April (110 ± 1%).

Temporal patterns in vertical profiles of PON and POC (Fig. 5.1.3 and Fig. 5.1.4) were similar. The highest values of PON and POC were observed at the bottom waters in April (1.5 ± 0.5 and 13.7 ± 3.4 respectively). PON also showed high values in June and October at deep waters. POC displayed high values in summer, and early autumn and winter. Lowest values were measured in late winter and middle summer. C/N mol ratios ranged from 5 to 12 (Fig. 5.1.4), with the maximum ratios in winter and during the spring bloom (>8).

Chlorophyll-a and primary production

Chl-*a* values showed a temporal variability (ANOVA, $F = 5.99$, $p < 0.001$), with January (0.39 ± 0.05 $\mu g \cdot L^{-1}$) and July (0.34 ± 0.08 $\mu g \cdot L^{-1}$) as the months with the lowest values, and April (1.47 ± 0.57 $\mu g \cdot L^{-1}$) and June (1.30 ± 0.74 $\mu g \cdot L^{-1}$) with peaks of maximum concentration. Increases in the Chl-*a* concentration were also detected in

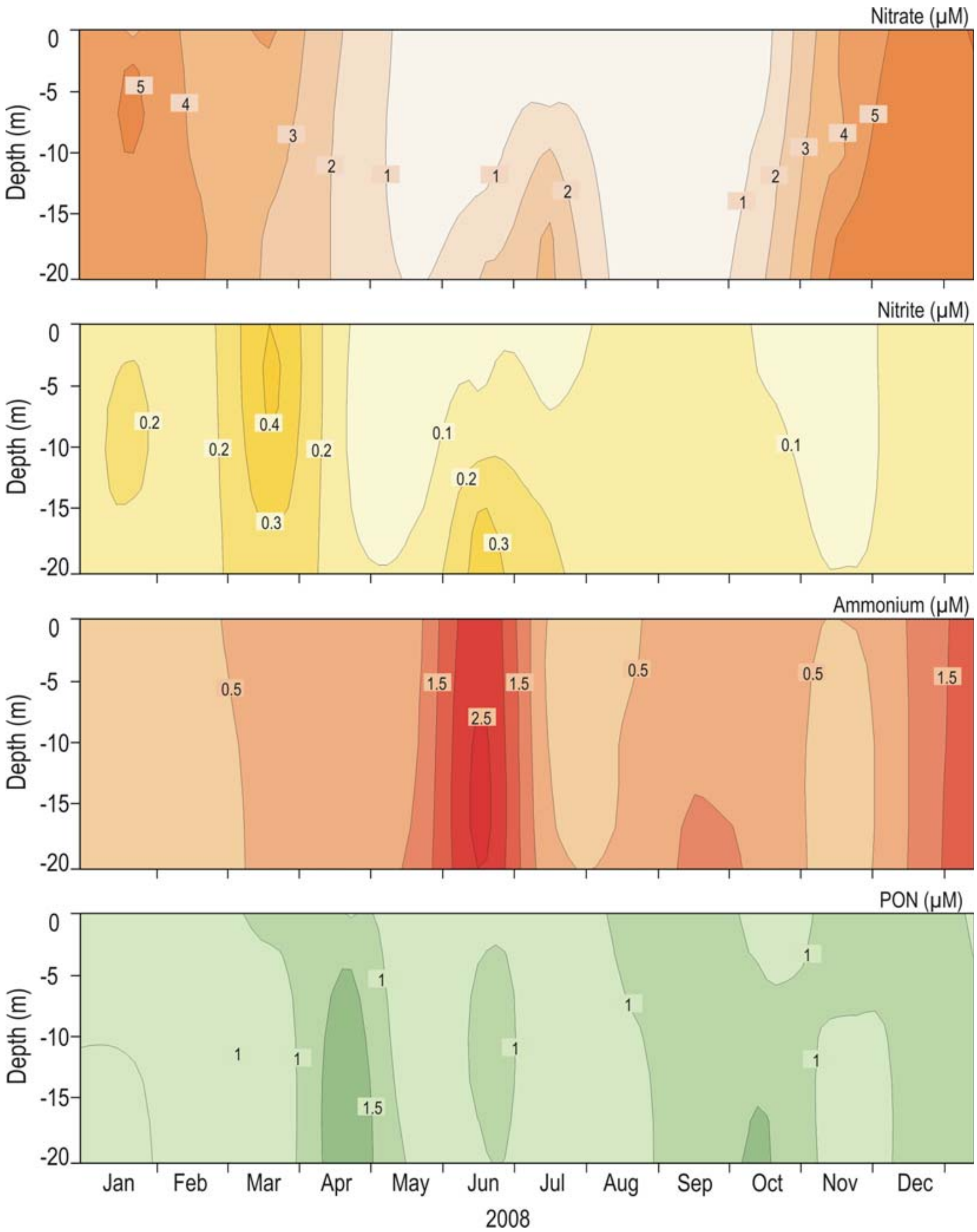

Figure 5.1.3. Contour plots of nitrate, nitrite, ammonium, and particulate organic nitrogen (PON) at the Ria of Barqueiro during the annual study period (2008). All values are expressed in µM.

September (0.86 ± 0.10 µg·L^{-1}) (Fig. 5.1.4). A late spring bloom occurred in April, showing the highest values of the period of study (Table 5.1.1).

Primary production presented significant differences in its distribution (ANOVA, F = 7.93, $p < 0.001$), with three important peaks greater than 12 mgC·m^{-2}·h^{-1} during the

Table 5.1.1. Physical, chemical and biological parameters of the water column found in the oceanographic periods identified at the Ria of Barqueiro during the annual study period

Parameter	Unit	Oceanographic period Spring (4, 5, 6)	Summer Stratification (7, 8, 9)	Autumn (10, 11)	Winter (1, 2, 3, 12)
Salinity	-	35.3 ± 0.4	35.6 ± 0.1	35.4 ± 0.5	35.4 ± 0.5
Temperature	ºC	15.0 ± 1.5	18.0 ± 1.2	15.3 ± 1.5	13.0 ± 0.8
Oxygen saturation	%	103.9 ± 3.11	99.0 ± 3.1	95.8 ± 3.0	99.0 ± 1.7
Nitrate	µM	0.96 ± 0.77	0.56 ± 0.77	2.77 ± 2.05	4.48 ± 1.10
Nitrite	µM	0.10 ± 0.09	0.16 ± 0.04	0.10 ± 0.03	0.22 ± 0.10
Ammonium	µM	1.44 ± 0.85	0.59 ± 0.22	0.59 ± 0.37	0.74 ± 0.68
Phosphate	µM	0.09 ± 0.09	0.10 ± 0.05	0.22 ± 0.05	0.27 ± 0.11
Silicate	µM	1.72 ± 0.94	2.09 ± 0.71	3.27 ± 1.18	2.47 ± 0.72
Chlorophyll-*a*	$\mu g \cdot L^{-1}$	1.07 ± 0.68	0.68 ± 0.15	0.52 ± 0.15	0.56 ± 0.19
Primary production	$(gC \cdot m^{-2} \cdot d^{-1})$	1.3 ± 0.9	8.2 ± 3.1	0.2 ± 0.1	0.3 ± 0.2

Numbers in parentheses correspond to the months of the year. Values are given as the mean ± standard deviation.

spring and late summer season (Fig. 5.1.4). The seasonal pattern was similar to that of chlorophyll, with lower values during winter and middle summer (<5 $mg \cdot C \cdot m^2 \cdot h^{-1}$). Maxima were found in April (12 ± 4 $mg \cdot C \cdot m^2 \cdot h^{-1}$) and later in September (13 ± 5 $mg \cdot C \cdot m^2 \cdot h^{-1}$) during stratification. The main difference between blooms is the sub-superficial location in spring months, while during the stratification period the maximum is at surface. In autumn, values dropped to almost winter levels (Table 5.1.1).

Phytoplankton assemblages

A total of 161 species or taxa were identified during the study. Considering only diatoms and dinoflagellates, the total numbers of taxa were 137, of which 69 corresponded to dinoflagellates and the rest to diatoms. The other species belonged to other groups as *Chrysophyceans, Prymnesophyceans, or Cryptophyceans*, and also to empty diatoms. The empty valves were not included in the tables or figures. However, they were very abundant in some particular periods and were taken into account, because they were indicative of continental runoff or resuspension. Most of species were estuarine benthic, epipelic or epiphytic, but in periods of intensive runoff, the percentage of freshwater species increased.

Small flagellates (<10 µm) were very abundant and showed a clear seasonal cycle with high abundances in early spring, early summer and late at the end of summer (Fig. 5.1.5).

Dinoflagellates followed a similar pattern to that of flagellates, with sub-superficial maxima in late winter-early spring and surface maxima in early and late summer (Fig. 5.1.5). Most species were unidentifiable (Table 5.1.2), but clearly belonged to Genus *Gymnodinium* or *Gyrodinium.* Among the recognised species, *Heterocapsa niei*, showed a constant presence throughout the year, *Lingulodinium polyedrum* during the stratification, *Scripssiella trochoidea* in winter-spring and *Prorocentrum minimum* in winter and early summer stratification.

Diatoms showed their maxima late in June and later in autumn (Fig. 5.1.5). The maxima were always sub-superficial with abundances beyond 300 $cells \cdot mL^{-1}$. Table 5.1.2 shows remarkably high abundances in spring and autumn. Chaetoceros species were present during all periods, but the highest abundances corresponded to spring and autumn. *Lauderia annulata,*

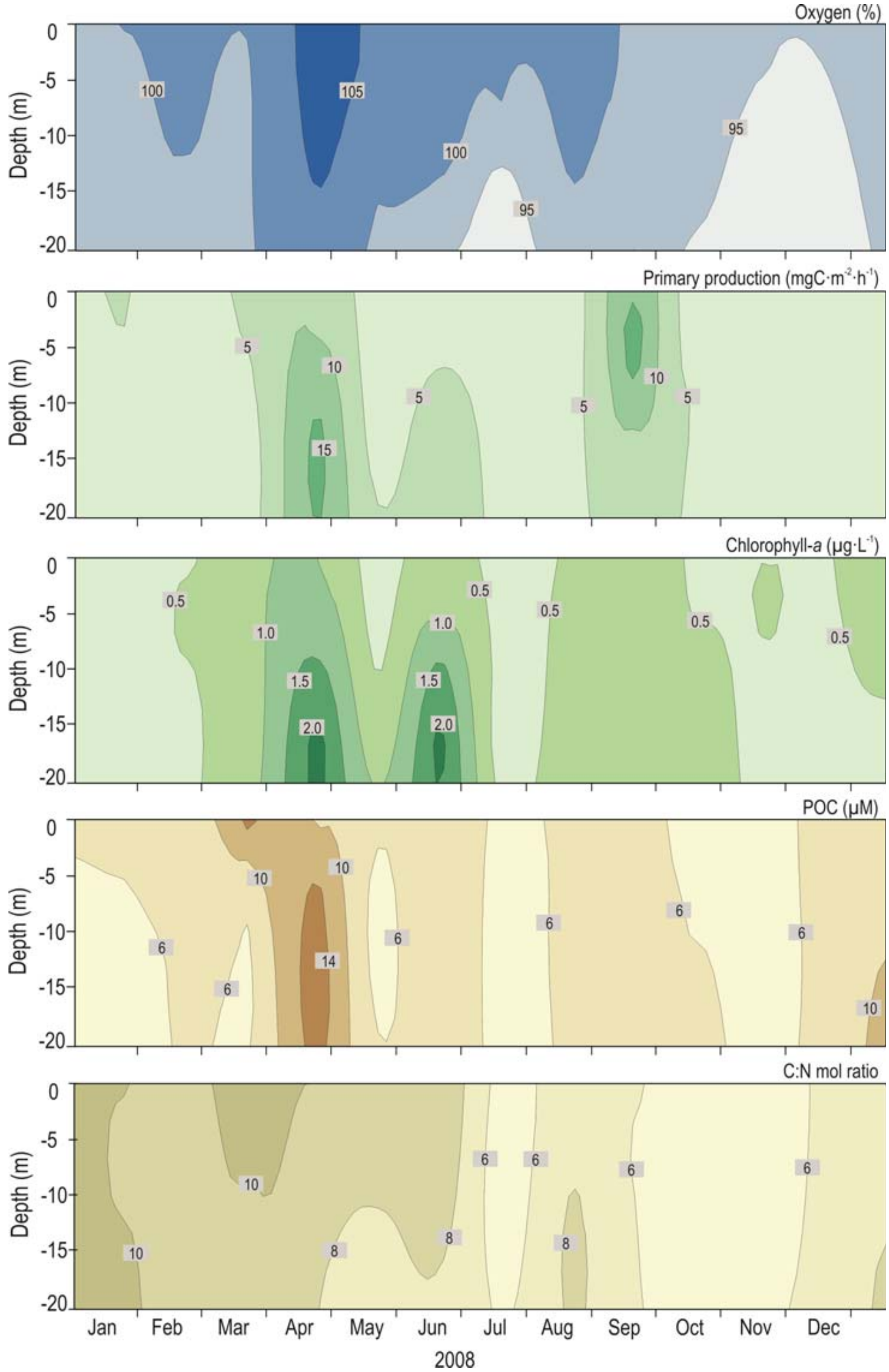

Figure 5.1.4. Contour plots of oxygen saturation (%), primary production (mgC·m^{2}·h^{-1}), chlorophyll-*a* (µg·L^{-1}), particulate organic carbon (POC) (µM) and C/N mol ratio at the Ria of Barqueiro during the annual study period (2008).

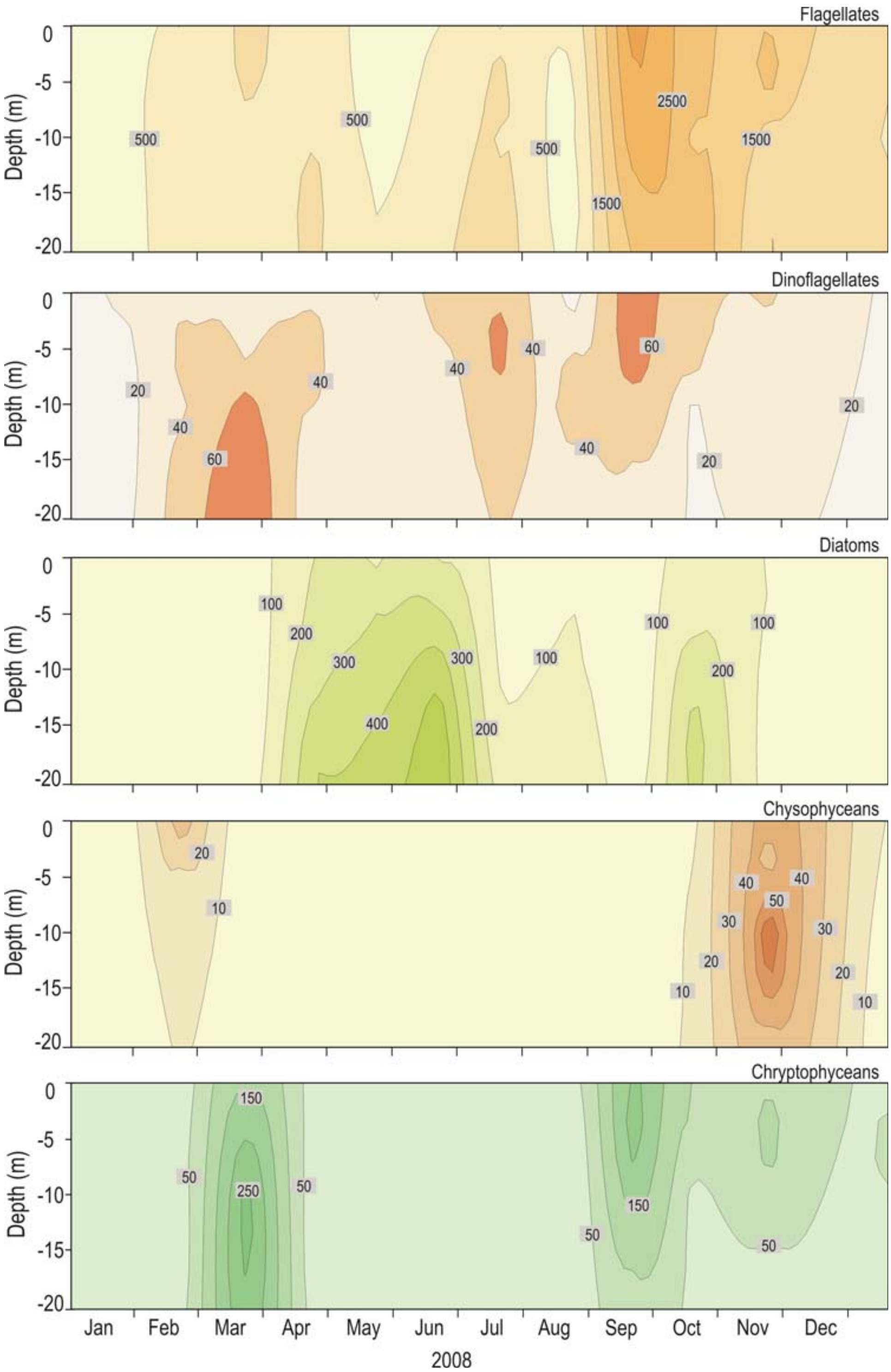

Figure 5.1.5. Contour plots of phytoplankton abundances at the during the annual study period. Values are expressed in cells·mL^{-1}.

Leptocylindrus danicus and *Pseudo-nitzschia delicatissima* were the more abundant taxons and dominant during spring. *Thalassionema nitzschioides* was especially predominant in winter, and some benthic species from Genus *Rhabdonema* were common during summer months.

Chrysophyceans showed a reduced maximum in late winter and almost disappeared until November when they reached the highest abundances (Fig. 5.1.5). The most representative species were *Distephanus speculum,* in winter, and *Rhizomonas setigera* in autumn. Cryptophyceans showed a pattern opposite to that of diatoms and almost identical to that of flagellates and dinoflagellates with clear maxima in late winter-early spring and later during late summer.

Discussion

Seasonal variability of phytoplankton assemblages

Phytoplankton assemblages tightly coupled with oceanographic variability in the Ria of Barqueiro. Hydrography showed a period of mixing in autumn, winter lasting from October to March and summer stratification from July to September. High concentrations of Chl-*a* were observed from April to June, and later there is a little increase during late summer, which is not related to any upwelling event, but with stratification. No autumn blooms were observed and the cycle can be summarised in a single spring bloom of reduced importance although upwelling favourable condition occurred during September.

Seasonal changes in Chl-*a* in the Ria of Barqueiro were different to the typical previously reported for the Atlantic Galician Rias (Mariño et al., 1985; Figueiras and Niell, 1987; Varela et al., 2001, 2008). In the Western and Middle Rias, the oceanographic periods were well defined, with a clear spring bloom and summer upwelling blooms associated to pulses of ENACW (Fraga, 1981); alternating with stratification periods and autumn mixing with light increase of phytoplankton abundances, sometimes associated blooms, and winter mixing with low phytoplankton densities.

The microscopic study of phytoplankton yielded more precise information depicting a seasonal cycle with higher precision of that of chlorophyll, i.e. the chlorophyll solely masks a cycle, which is revealed by phytoplankton abundance and taxonomic composition. In the Ria of Barqueiro, previous to the typical spring bloom dominated by diatoms, bloom of flagellates (micro and nanoflagellates, dinoflagellates, crisoficeans and critoficeans) occurs. This early bloom was not observed in previous studies in the other Galician rias, even though has been described for other areas of the ocean (Heiskanen, 1993; Spilling et al., 2006; Olli and Trunova, 2010). The maximum of dinoflagellates is at the bottom, which suggests the possible importance of resuspension in the development of this group. Many dinoflagellates form cysts (Taylor, 1987) remaining in the sediment until the return of favourable conditions.

The typical spring bloom, dominated by diatoms in the Atlantic rias, occurs late in the Cantabrian, starting in April and extending until June. Such persistent bloom suggests the existence of favourable conditions for blooms during this period alternating with periods of nutrient exhaustion and decreasing biomass of phytoplankton. This fact is in agreement with the taxonomic composition of phytoplankton with typical spring species as *Lauderia annulata* (Varela et al., 2010) and small Chaetoceros resembling C. socialis, a commonly accompanying species of *L. annulata* in April (Varela et al. 2001). On the contrary, in May and June, dominant species, as *Asterionellopsis glacialis, Leptocylindrus danicus Guinardia* *delicatula* or *Pseudo-nitzschia delicatissima*, are more indicative of advanced successional stages, according to available information from other Galician rias (Varela et al., 2001, 2005, 2008). Most of these species are common during upwelling relaxation and stratification, confirming the assumption that May and June are not typical spring months as in the rest of the Galician rias. However, it is difficult to include these samples among those of upwelling or stratification as

Table 5.1.2. Characteristic phytoplankton species for the oceanographic periods identified. Species abundances in cells·mL^{-1}

	Oceanographic Period			
Group / Species	**Spring**	**Summer Stratification**	**Autumn**	**Winter**
Dinoflagellates				
Amphidinium flagellans	0.78	-	1.13	-
Dinoflagellates < 30 µm	12.11	20.25	19.98	51.00
Dinoflagellates> 30 µm	0.46	2.19	1.86	0.63
Exuviaella vaginula	-	-	0.96	0.98
Heterocapsa niei	7.41	12.47	3.49	4.25
Katodinium glaucum	-	3.03	1.50	0.85
Lingulodinium polyedrum	0.31	-	5.69	-
Prorocentrum balticum	0.16	3.14	0.43	0.43
Prorocentrum minimum	2.43	-	2.47	-
Scrippsiella trochoidea	1.27	2.71	1.75	0.25
Diatoms				
Asterionellopsis glacialis	0.94	13.63	-	-
Chaetoceros affinis	1.17	2.41	1.28	1.28
Chaetoceros atlanticus	-	-	0.85	-
Chaetoceros cf. convolutus	-	-	0.95	-
Chaetoceros curvisetus	0.14	-	-	0.85
Chaetoceros densus	0.20	0.42	1.91	-
Chaetoceros diadema	0.85	-	-	-
Chaetoceros didymus	0.66	3.13	-	-
Chaetoceros esporas	-	-	7.25	-
Chaetoceros socialis	1.69	-	-	-
Chaetoceros spp.	1.68	13.47	2.22	
Detonula pumila	-	3.87	0.85	-
Centric diatoms < 30 µm	1.70	6.78	0.21	5.53
Centric diatoms > 30 µm	0.31	-	0.21	-
Pennate diatoms < 30 µm	1.62	7.59	4.25	1.33
Pennate diatoms > 30 µm	0.34	1.36	1.28	1.23
Guinardia delicatula	-	20.6	3.87	0.25
Lauderia annulata	0.32	38.86	-	-
Leptocylindrus danicus	0.28	108.92	1.51	-
Leptocylindrus mediterraneus	-	-	1.39	-
Leptocylindrus minimus	-	26.9	2.88	-
Navicula transitans	1.70	0.91	1.54	-
Nitzschia spp.	-	1.2		0.13
Nitzschia longissima	2.15	4.44	4.43	1.63
Nitzschia longissima petite	3.97	7.44	0.73	-
Paralia sulcata	0.56	-	1.72	-

Pseudo-nitzschia delicatissima	0.78	18.08	5.22	0.63
Pseudo-nitzschia pungens	0.25	6.57	1.28	-
Pseudo-nitzschia spp.	0.64	-	1.76	-
Pseudo-nitzschia subpacifica	0.20	-	1.59	0.75
Rabdonema spp.	-	-	0.85	-
Rhizosolenia imbricata	0.44	0.48	2.89	-
Rhizosolenia setigera	0.93	0.6	0.62	1.13
Skeletonema costatum	0.38	-	-	-
Thalassionema nitzschioides	1.49	3.24	0.93	1.63
Thalassiosira angulata	0.63	2.77	4.36	0.38
Thalassiosira levanderi	4.33	7.46	1.21	-
Thalassiosira nana	0.94	-	2.45	-
Thalassiosira rotula	0.19	-	0.43	-
Thalassiosira spp.	-	-	2.32	-
Cryptophyceans				
Cryptomonas	79.90	85.71	9.99	175.95
Chrysophyceans		0,00		
Dictyocha fibula	0.94	-	-	-
Dinobryon faculiferum		0.63	-	0.85
Distephanus speculum	5.31	0.47	-	0.13
Solenicola setigera	-	-	0.38	1.25
Euglenophyceans				
Eutreptiella	0.46	-	-	-
Primnesophyceae				
Phaeocystis pouchetii	-	-	-	-
Flagellates				
Flagellates < 3 µm	25.31	981.98	18.00	798.75
Flagellates 3-5 µm	36.00	1254.38	326.25	1552.50
Flagellates 5-8 µm	68.23	238.13	73.69	348.75
Flagellates > 8 µm	29.33	21.03	12.33	86.70

upwelling did not occur (Fig. 5.1.2) and stratification had not yet developed.

From July to September, the months when upwelling is an usual feature in the Galician rias (Fraga, 1981) and under favourable conditions during summer 2008, in the Ria of Barqueiro a weak upwelling event has occurred only in July (see Chapter 2). This event differs from that observed in the Atlantic rias, both in terms of phytoplankton biomass, production or abundances. Despite this the taxonomic composition resembles the assemblages found in the rias. Several species of *Chaetoceros, Leptocylindrus, Pseudo-nitzschia, Thalassiosira* and *Rhizosolenia* are characteristics of this period. However, the contribution of diatoms to total phytoplankton carbon is only 44% in the Ria of Barqueiro. It is a very low percentage as compared to that of Atlantic rias where the contributions of diatoms to biomass always exceed 70% and usually reaches almost 100% (Estrada, 1984; Bode et al., 1994). In the Ria of Barqueiro the contribution of dinoflagellates and flagellates to biomass is about 56%. During summer stratification, the differences compared to other rias are also evident. While both, Western and Middle Rias display a mixing of dinoflagellates and diatoms during summer, with oscillating contribution to biomass, according to the frequency of upwelling pulses, in this study we have observed a drop in diatoms abundances to densities lower than in winter. Consequently, the contribution of this group to biomass was less than 10%, and small flagellates and dinoflagellates dominated by far the phytoplankton community.

Autumn coincides with a decrease of groups mentioned above, and the new appearance of diatoms. Chl-*a* is not able to reveal this change in the phytoplankton composition, as the variation with respect to summer is small. However, microscopic observations showed a diatom maximum. The species composition is similar to that observed in previous months, but abundances are clearly higher. The contribution of diatoms to biomass increased up to 40%, and flagellates of different types representing the remainder 60%. The bloom is located near the bottom, just like in the spring bloom. The most striking characteristic of the autumn diatoms bloom is the lack of signal in the Chl-*a* just the opposite when compared to the spring bloom. When autumn phytoplankton was observed under microscope, revealed a poor physiological stage. Cells were smaller than usually observed in other studies in Galicia (Varela et al., 2002, 2010). On the other hand diatoms frustules appeared deformed and weakly silicified and with reduced Chl-*a* content as well. All that suggests that growth is limited by some nutrients. This is supported by the stoichiometric nutrient limitation criterion established by Justic et al. (1995), who defines: N limitation when DIN:P < 10 and Si:DIN > 1, P limitation when Si:P > 22 and DIN:P > 22 and Si limitation when Si:P < 10, Si:DIN < 1. Nutrient ratios show nitrogen as the limiting factor for phytoplankton growth in October, which would explain the poor condition of cells. Nitrogen limitation existed from late spring to autumn, even though it was not so evident under the microscope as in October. Nevertheless, most diatom species from spring to autumn showed small size and a degraded aspect. This may explain the reduced importance of diatoms compared to other phytoplankters of smaller size, more efficient in nutrient uptake, and the persistent presence of dinoflagellates, with most of species having the ability of mixotrophic nutrition (Sanders and Porter, 1988; Moorthi et al., 2009). In winter, diatoms showed a 25% of contribution to phytoplankton biomass. In any case the importance is higher than in summer and this is another characteristic to point out compared to other Galician rias where the contribution of diatoms to biomass in winter is almost negligible (Varela et al., 2001, 2002).

Nutrient quality status and trophic characterisation

The Ria of Barqueiro was characterized by a low concentration of nutrients. Values were in the range of those reported for unpolluted coastal areas (Ketchum, 1969). In general, chlorophyll and primary production were linked to the mixing-stratification cycle of water column, mainly governed by temperature. The role of the river is little relevant, as indicated by the salinity profiles and nutrient concentrations at the studied station. This is just the contrary to that observed in other Galician rias (Prego et al., 1999; deCastro et al., 2006), where a close relationship between nutrients and river flow was found. Chlorophyll and phytoplankton abundances matched well with the POC distribution, especially during spring and late summer. Ammonium increased during June (2.6 ± 0.2 μM), due to remineralisation processes that take place immediately after the spring bloom, and which is consistent with the depletion of nitrate observed in the surface layers in summer.

According to the criteria for assessment of nutrient levels in transitional, coastal and marine waters classification (Crouzet et al., 1999), which only considers the nitrogen and phosphorus as indicators, waters of the Ria of Barqueiro presented a good quality status (mean annual values: $NO_x < 6.5$ μM, $HPO_4 < 0.5$ μM). In order to compare the Barqueiro case with other rias under higher industrial and anthropic pressure, an evaluation for the Ria of Pontevedra and the Ria of Laxe was performed following the same criterion, also resulting in a good level for its water quality. It is important to consider that the categorisation of the trophic state of an ecosystem is not a simple process, particularly because the use of different approaches can result in different categories of eutrophication for the same area (Newton et al., 2003). Low-high concentrations of one variable are not always associated with oligotrophic-eutrophic conditions (Cloern, 2001; Sharp, 2009).

The trophic classification for marine systems has generally been associated with the concept defined by Nixon (1995), which is based on the supply of organic carbon. Following this simple approach and using the primary production as indicator, the Ria of Barqueiro corresponds to a mesotrophic system with a primary production of 280 $gC \cdot m^{-2} \cdot y^{-1}$. In contrast, the Ria of Laxe (1250 $gC \cdot m^{-2} \cdot y^{-1}$, Varela et al. 2005) and the Ria of Pontevedra (600 $gC \cdot m^{-2} \cdot y^{-1}$, Varela et al., 2008) (Fig. 5.1.6) correspond to hypertrophic systems.

Another more detailed criteria, the methodology for the Assessment of Estuarine Trophic Status (ASSETS), developed by the United States National Estuarine Eutrophication Assessment (NEEA) uses a mixture of water quality parameters as Chl-*a*, macroalgae and epiphytes, dissolved oxygen, submerged aquatic vegetation (SAV), nuisance and toxic blooms (Bricker et al., 2003). Following ASSETS (Bricker et al., 2003; NOAA-IMAR, 2008), but only considering the Chl-*a* as parameter, the Ria of Barqueiro is in the "low" eutrophication category (Chl-*a*: 0-5 $\mu g \cdot L^{-1}$), while the Ria of Laxe tended toward the "medium" eutrophication category (Chl-*a*: 5-20 $\mu g \cdot L^{-1}$) (Fig. 5.1.6).

Over the last decade a method to characterize the trophic status of coastal waters, the trophic status index (TRIX), has been widely implemented (EEA, 2001). The

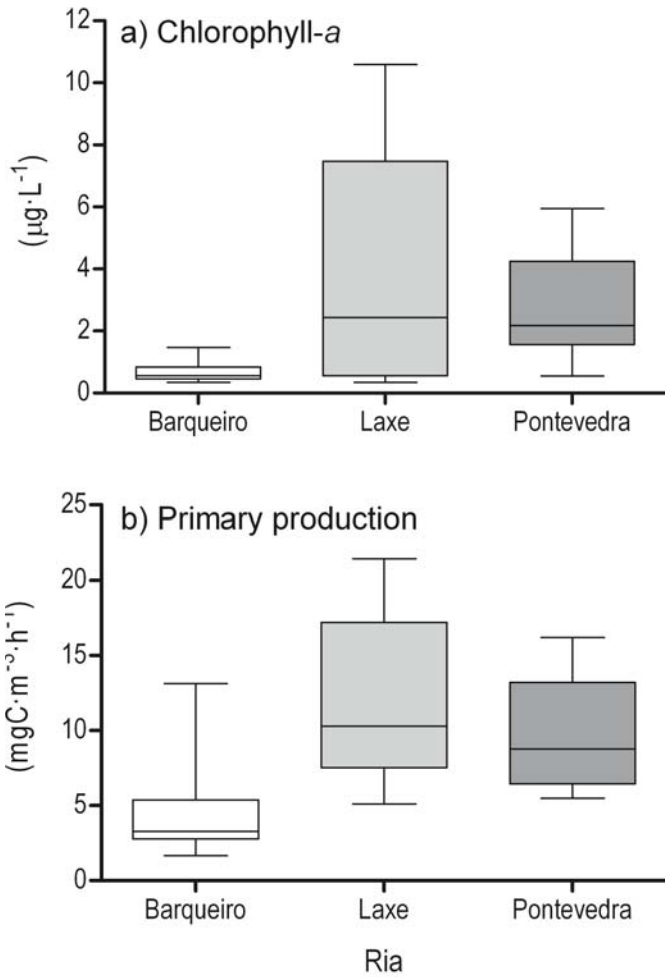

Figure 5.1.6. Box and whisker plots of chlorophyll-*a* (a) and primary production (b) in different Galician Rias. Barqueiro (Northern Rias), Laxe (Middle Rias) and Pontevedra (Western Rias). Horizontal lines correspond to the median and the edges of the box the 25th and 75th percentiles respectively.

TRIX uses as parameters the Chl-*a*, dissolved inorganic nitrogen, dissolved inorganic phosphorus and oxygen saturation (Vollenweider et al., 1998; EEA, 2001). So, monthly data in the rias of Barqueiro and Pontevedra were used to calculate the TRIX according to the algorithm of Vollenweider et al. (1998). Conforming to the classification of TRIX by Penna et al. (2004), the Ria of Barqueiro has a "high"water quality and a low trophic level. Because the TRIX has been developed for Mediterranean waters, the above results should be considered as preliminary. During the last years the applicability of this method has been evaluated in other coastal systems as the Ria Formosa in Portugal (Newton et al., 2003), the Mar Menor lagoon in Spain (Salas et al., 2008) and the Helsinki Sea in Finland (Vascetta et al., 2008), but its use in other European waters still needs to be validated.

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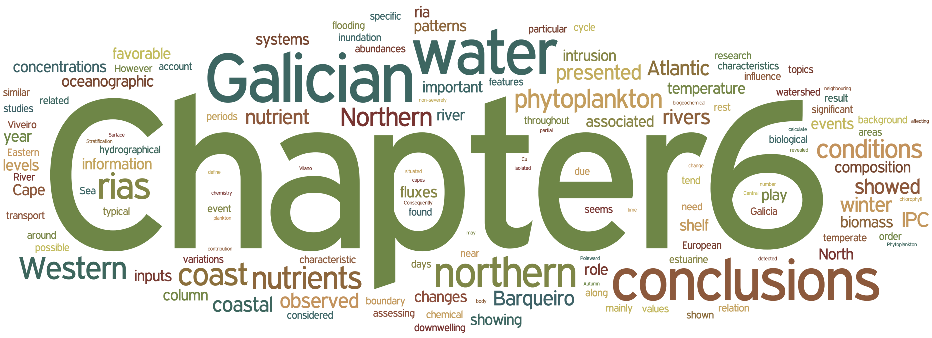
Chapter6
Galician
water
conclusions
northern
Western
rias
coast
nutrients
Northern
phytoplankton
conditions
Atlantic
Barqueiro
coastal
observed
presented
showed
winter
biomass
IPC
shelf
rivers
nutrient
fluxes
concentrations
oceanographic
systems
patterns
intrusion
temperature
important
associated
composition
events
favorable
information
levels
Cape
year
changes
showing
inputs
column
North
ria
river

Chapter 6

Consideraciones finales / Final considerations

6.2. Conclusiones generales / General conclusions

Las cuestiones relacionadas con los patrones oceanográficos de las rías gallegas se derivan principalmente de los primeros estudios realizados sobre los procesos de afloramiento (upwelling) y contra-surgencia (downwelling) en las rías bajas (costa oeste de Galicia). Sin embargo, este enfoque debe ser revisado después de los resultados obtenidos en las rías del norte de Galicia (**Capítulo 2**). En las costas norte de Galicia, bajo condiciones de viento favorables al afloramiento durante el verano, éste se mantuvo fuera de las rías afectando sólo a la plataforma adyacente. Por lo tanto, en ese período de tiempo las rías gallegas del Norte tienden a ser sistemas mesotróficos, como indicaron las concentraciones de nutrientes y clorofila, así como la abundancia de fitoplancton. Por el contrario, bajo condiciones similares, las rías bajas tienden a la eutrofía. Una dirección litoral diferente parece jugar un papel significativo en los patrones hidrográficos, biogeoquímicos y biológicos durante los eventos de surgencia y contra-surgencia.

Se ha demostrado que los eventos de afloramiento invernal no son una característica particular de las rías bajas de Galicia. Un evento similar fue detectado en la ría de Barqueiro en febrero de 2008 bajo condiciones meteorológicas favorables. Sin embargo, la distribución de la salinidad y la temperatura reveló que la masa de agua correspondió a agua sub-superficial aflorada desde la plataforma, en contraste con observado en la costa oeste de Galicia, donde el afloramiento estuvo asociado con la ENACW o con la IPC. Esta significativa diferencia hidrográfica no involucró cambios en las concentraciones de sales nutrientes y en los niveles de nitrato , que fueron principalmente el resultado de la mezcla de invierno a lo largo de la columna de agua. La biomasa del fitoplancton no presentó ningún cambio relevante, pero los flagelados pequeños, los ciliados planctónicos y los dinoflagelados, característicos de aguas abiertas, aumentaron sus abundancias hasta un orden de magnitud , sugiriendo la influencia del agua de la plataforma dentro de la ría. A partir del análisis del transporte Ekman durante los últimos cuarenta años, fue posible calcular el número de días al mes bajo condiciones favorables de afloramiento en invierno para la zona (8-10 días), mostrando cómo la posibilidad de observar eventos de afloramiento en invierno no es insignificante y cómo el evento observado (febrero de 2008) no puede considerarse un episodio aislado.

Por otro lado, imágenes de temperatura superficial del mar (SST) (noviembre de 2008) indicaron que bajo condiciones favorables de afloramiento la presencia de la corriente ibérica que va hacía el polo (IPC) fue discontinua a lo largo de la costa gallega mostrando una diferencia de temperatura entre Cabo Vilano y Cabo Ortegal, y un debilitamiento de la señal de temperatura a lo largo de la costa norte. Además, la IPC se observó cerca de la boca de las rías de Barqueiro y Viveiro, alrededor del Cabo de Estaca de Bares, haciendo el agua pobre en nutrientes. La descarga de los ríos contribuyó a evitar la entrada del IPC y el efecto de la pluma del río sólo se observó en el interior de las rías mostrando una ligera actividad biológica y una estratificación del estuario cerca de la superficie. Teniendo en cuenta los patrones descritos anteriormente, se puede concluir que características particulares de la costa, como cabos y rías, juegan un importante papel oceanográfico en relación con las intrusiones ocasionales desde el margen continental.

Los ríos que desembocan en las rías gallegas del Norte (**Capítulo 3**), suministran la entrada de agua dulce más importante a estas rías templadas, con nutrientes, elementos traza disueltos y particulados, y niveles de carbono dentro de los valores típicos para ríos gallegos y ríos no contaminados a nivel mundial, y por lo tanto reflejando valores de fondo geoquímico. Las descargas de nutrientes de estos ríos revelaron poca influencia de actividad y eutrofización. La variabilidad temporal de los flujos de nutrientes durante todo el año podría desempeñar un papel importante en estos sistemas de ría gallegos que no son severamente afectados por las entradas nutrientes marinos debido al afloramiento.

La composición de los elementos traza de las partículas en suspensión fue similar a la de los ríos que desembocan en el mismo tipo de cuencas, aunque se encontraron varias características especiales (e.g., la influyen en la minería de Cu en el río Mera; las concentraciones de

Al y U en el río Landro, debido a la naturaleza granítica de su cuenca).

La mayoría de los estudios publicados hasta ahora sólo han presentado un conjunto de datos parciales de la composición química del agua del ríos de la zona. El completo estudio presentado en el Capítulo 3 es de gran valor para investigadores medioambientales y administradores que necesiten una gran cantidad de información sobre química del agua y niveles de fondo de ríos prístinos de Europa, y proporciona información útil en el desarrollo de iniciativas europeas y mundiales para evaluar las entradas antropogénicas a los estuarios y zonas costeras y oceánicas.

La contribución de los sedimentos en el balance de nutrientes en las zonas intermareales fue relevante. La influencia de la inundación mareal sobre los sedimentos intermareales de las rías de Ortigueira y Viveiro fue señalada por notables cambios en la concentración de nutrientes en el agua sobrenadante y el agua intersticial, durante cortos periodos de inundación (**Capítulo 4**). El transporte desde los sedimentos a la columna de agua fue tan intenso, que se superpone al aporte de nutrientes de origen continental. Este tipo de flujos se deben tomar en cuenta al evaluar los presupuestos de nutrientes en sistemas costeros macro y meso-mareales. Además, se puede hipotetizar que la inundación de zonas costeras asociada a cambios climáticos, resultaría en flujos adicionales de las zonas intermareales a la columna de agua.

Las variaciones estacionales del fitoplancton en las rías del norte de Galicia (ría de Barqueiro) (**Capítulo 5**) mostraron un ciclo muy diferente al típico de la ría de Laxe (rías medias) y la ría de Pontevedra (rías bajas), ambas bajo la influencia del afloramiento de Cabo Finisterre. Los periodos oceanográficos definidos en ésta ría fueron: Afloramiento de Primavera, Estratificación de Verano, Afloramiento de Otoño y Mezcla Invernal, a diferencia de las otras rías de Galicia, donde la influencia del afloramiento es mucho más relevante. Las diatomeas y dinoflagelados representaron el 85% de las especies de fitoplancton identificadas. Las diatomeas dominaron los ensambles de fitoplancton, especialmente durante el afloramiento de primavera y otoño. En verano, en ausencia de afloramiento, una mezcla de diatomeas y dinoflagelados co-dominó la comunidad de fitoplancton, con una menor contribución de diatomeas, en comparación con el resto de rías gallegas. Los micro y nano-flagelados, aumentaron su contribución relativa a la biomasa durante el verano. Este ciclo puede ser considerado como el típico de mares templados, con una mezcla invernal y estratificación de verano. Los afloramientos de fitoplancton se desarrollaron en los períodos de transición, mezcla-estratificación (afloramiento de primavera) y estratificación-mezcla (afloramiento de otoño).

El nitrógeno fue identificado como el principal factor limitante para el crecimiento del fitoplancton a lo largo de todas las épocas, especialmente durante el otoño. La eutrofización natural/antropogénica reportada en otras rías gallegas no se observó en la ría de Barqueiro, que puede ser catalogada como un área prístina, de acuerdo con el buen estado de calidad de sus aguas. Adicionalmente, el área de estudio puede ser considerado como el límite norte del sistema de afloramiento del Atlántico Nororiental, donde el afloramiento de las aguas del Atlántico Norte es escaso, resultando en un ciclo de plancton característico de zonas templadas.

Toda la información presentada anteriormente en cada uno de los compartimentos: océano (Capítulo 2), río (Capítulo 3), sedimentos (Capítulo 4) y estuario-ria (Capítulo 5), permite concluir que las rías del norte de Galicia presentan características suficientemente diferentes de las otras rías de Galicia para ser consideradas como un grupo aparte. Hay razones hidrográficas, químicas y biológicas implícitas que sustentan la clasificación de las rías gallegas en tres categorías: Bajas, Medias y Altas (rías del norte de Galicia).

General conclusions

The topics related to oceanographic patterns of Galician Rias are mainly derived from the initial studies carried out about upwelling and downwelling in the Western Rias. However, after the results obtained in the Northern Galician Rias these topics need to be revised (**Chapter 2**). In this northern coastline under wind induced upwelling conditions during summer, the upwelling remained out of rias affecting only the neighboring shelf. Therefore, in that time period Northern Rias tend to be mesotrophic systems as indicated by nutrient and chlorophyll concentrations as well as plankton abundances. On the contrary, under similar conditions, the Western Rias tend towards eutrophy. A different shoreline direction seems to play a significant role in the hydrographical, biogeochemical and biological patterns during upwelling and downwelling events.

It has been demonstrated that the winter upwelling events are not a peculiarity of the Western Galician Rias. After favourable meteorological conditions, a similar event was detected in the Northern Galician Ria of Barqueiro in February 2008. However, salinity and temperature distribution revealed that the upwelled water body corresponded to subsurface shelf seawater opposite to that observed in the Western Galician coast where upwelling was associated with Eastern North Atlantic Central Water or the Iberian Poleward Current. This significant hydrographical difference involved no changes in the nutrient salts concentrations , and it was mainly the result of winter mixing throughout the water column. Phytoplankton biomass did not present any relevant change even though small flagellates, planktonic ciliates and dinoflagellates, characteristic of open sea waters, increased their abundances up to one order of magnitude, suggesting the existence of shelf-water influence into the ria.

From the Ekman transport analysis during the last forty years it was possible to calculate the number of days per month under upwelling favourable conditions in winter for the area (8-10 days) showing how the possibility of observing upwelling events in winter is not negligible and how the observed event (February 2008) can not be considered an isolated episode.

Sea Surface Temperature images (November 2008) showed that under upwelling favourable conditions the IPC presence was discontinuous along the Galician coast showing a temperature gap between Cape Vilano and Cape Ortegal and a weakening of the temperature signal along the northern coast. In addition, IPC was observed close to the mouth of the Northern Galician Rias of Barqueiro and Viveiro, around Cape Estaca de Bares. This water was poor in nutrients, with levels typical of the IPC. The river discharge contributed to prevent the IPC entrance and the effect of the river plume was only observed inside the rias showing a slight biological activity and an estuarine stratification near surface. Taking into account the patterns described above, it can be concluded that particular coastal features as capes and rias play an important oceanographic role in relation to the occasional poleward intrusions near this coast.

The rivers draining into the temperate Northern Galician Rias (**Chapter 3**), supply the main freshwater inputs, with nutrients, dissolved and particulate trace metals and carbon levels within typical values for Galician and world-unpolluted rivers and therefore reflecting the geochemical background values. Nutrient loads of these rivers reveal the lack of human influence and eutrophication.

The temporal variability of the nutrients fluxes throughout the year could play an important role in this Galician ria systems non-severely affected by marine nutrients inputs due to the upwelling.

The trace elements composition of suspended particles was similar to that of rivers draining into the same type of watershed, although several specific features were found (e.g. Cu mining influence in the Mera River, Al and U concentrations in the Landro River due to the granitic nature of its watershed).

Most of the studies published so far have only presented a partial dataset of the chemical composition of river water. The comprehensive summary presented in Chapter 3 is of specific value to environmental researchers and managers who need a great quantity of information on the water chemistry and background levels of pristine European rivers. It also provides useful information in the development of European and global initiatives for assessing anthropogenic inputs to estuarine, coastal and open-sea environments.

The contribution of sediments to the budget of nutrients in intertidal areas, was found to be very relevant. The influence of tidal flooding over intertidal sediments of the rias of Ortigueira and Viveiro was pointed out by striking changes of nutrients in flooding and pore water, during short periods of inundation (**Chapter 4**). The transport from sediment to the water column is so intense that it superimposes the contribution of nutrient associated with freshwater end members. This type of fluxes should be taken into account when assessing nutrient budgets in macro- and meso-tidal coastal ecosystems. Furthermore, it can be hypothesized that inundation of coastal areas associated with the global change, will result in additional fluxes from inter-tidal areas to the water column.

Seasonal variations of phytoplankton in the Northern Ria of Barqueiro, (**Chapter 5**) showed a cycle very different to that typical of the Middle Rias (Laxe) and Western Rias (Pontevedra), both under the Finisterre upwelling influence. The oceanographic periods defined in this Northern Ria were: Spring, Summer stratification, Autumn and Winter, in contrast to other Galician Rias, where the influence of summer upwelling is much more relevant. The diatoms and dinoflagellates accounted for 85% of the phytoplankton species identified. Diatoms dominated phytoplankton assemblages especially during spring and autumn blooms. In summer, in absence of upwelling, a mixing of diatoms and dinoflagelllates co-dominated phytoplankton community with a lower contribution of diatoms as compared with the rest of Galician Rias. Micro and nano-flagellates, increased their relative contribution to biomass during summer. This cycle can be considered as the typical of temperate seas, with mixing in winter and stratification in summer. Phytoplankton blooms develop in the transition periods, mixing-stratification (spring bloom) and stratification-mixing (autumn bloom).

Nitrogen was identified as the main limiting factor for phytoplankton growth throughout all periods, especially during autumn. The natural/anthropogenic eutrophication reported for other Galician Rias was not observed in the Ria of Barqueiro, which can be categorised as a pristine area, according to the good quality status of its waters. Values measured can be used as background reference of pristine areas. The area of study can be considered as the Northern boundary of the Eastern North Atlantic Upwelling System, where the upwelling of North Atlantic Waters is scarce, resulting in a plankton cycle characteristic of temperate zones.

All the information presented above in each one of the compartments, ocean (Chapter 2), river (Chapter 3), sediment (Chapter 4) and estuary-ria (Chapter 5), leads to conclude that the Northern Galician Rias show features sufficiently distinct from those of other Galician Rias as to be considered a separate group. There are implicit hydrographic, chemical and biological reasons supporting the classification of the Galician Rias in three categories: Western, Middle and Northern Rias.

6.3. Perspectivas

La estrategia de estudio en esta tesis doctoral consistió en el planteamiento de preguntas clave para cada uno de los compartimientos estudiados (océano, río, sedimento y estuario-ria). En cada capítulo se desarrollaron cuestiones relevantes para responder la pregunta general de investigación planteada, tal y como se presentó en el apartado de Conclusiones.

Sin embargo, los resultados obtenidos han planteado nuevas preguntas, que apuntan al mejor conocimiento de los procesos biogeoquímicos de los sistemas costeros.

Específicamente, se requiere una atención más detallada en el caso de los patrones oceanográficos descritos en los capítulos precedentes (ver Capítulo 2). Debe mejorarse el conocimiento sobre los límites de los sistemas de afloramiento, como en el norte de Galicia (43°N), en cuanto a la frontera este del sistema de afloramiento del Atlántico Norte Central (43°-10°N), y además, establecer la intrusión de masas de agua y los procesos que la generan. También es importante examinar la influencia de los complejos geológicos en la disponibilidad de metales traza en las zonas costeras vecinas. En este sentido, y como consecuencia de los resultados obtenidos en ésta tesis, se está estudiando actualmente la transferencia de REE y metales como Cr y Ni del complejo geológico de Cabo Ortegal hacia las rías del norte de Galicia.

Otro campo, que no fue considerado en la tesis doctoral, es el estudio de las contribuciones atmosféricas de metales traza en las rías, el cual adquiere mayor importancia si se considera el régimen de precipitaciones característico del NO de la Península Ibérica.

Finalmente, el estudio de los flujos de nutrientes en la frontera sedimento-agua abordado en ésta tesis, debería ser ampliado también a los flujos de metales traza, tanto en otras rías del Atlántico Norte como en otros sistemas de ría a nivel mundial i.e. Bretaña en Francia, Devon y Cornwall en las Islas Británicas, Corea, sureste de China y sur de Argentina, con el fin de obtener una imagen más completa de los patrones que rigen este tipo de intercambio en sistemas ampliamente influenciados por la marea.


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Chapter 1

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Appendices
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Appendix I.

Dissemination of results and research stays associated to the thesis

A. Publications in SCI Journals

Alvarez, I., Ospina-Alvarez, N., et al. (2009). A winter upwelling event in the Northern Galician Rias: frequency and oceanographic implications. Estuarine, Coastal and Shelf Science 82: 573–582. DOI: 10.1016/j.ecss.2009.02.023

Ospina-Alvarez, N., Prego, R. et al. (2010). Oceanographical patterns during a summer upwelling-downwelling event in the Northern Galician Rias. Comparison with the whole ria system (NW of Iberian Peninsula). Continental Shelf Research 30:1362–1372. DOI: 10.1016/j.csr.2010.04.018

Alvarez, I., Ospina-Alvarez, N., et al.. (2010). Poleward intrusion in the northern Galician shelf. Estuarine, Coastal and Shelf Science 87: 545-552. DOI: 10.1016/j.ecss.2010.02.009

Bernárdez, P., Ospina-Alvarez, N., et al. Hydrochemical characterisation and land inputs by pristine temperate rivers (SW Europe). Submitted for publication.

Ospina-Alvarez, N., Caetano, M., et al. Exchange of nutrients across the sediment-water interface in intertidal ria systems (SW Europe) Submitted for publication.

Ospina-Alvarez, N., Varela, M., et al. Phytoplankton assemblages and Oceanographic Periods in the western boundary of Cantabrian Sea. Submitted for publication.

B. Conference proceedings

Ospina-Alvarez, N., Caetano, M., et al. (2011). Interchange of dissolved trace metals across sediment water interfaces in a ria-type ecosystem (Ria of Ortigueira, NW Spain). Proceedings of 43rd International Liege Colloquium on Ocean Dynamics. University of Liège, GEOTRACES, IMBER. Liège (Belgium)

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C. Research stays

June-November / 2011

Applied Analytical Chemistry Laboratory, Department of Chemistry, University of Warsaw. Warsaw (Poland).

April-July / 2010

Marine Environment Unit, INRB -IPIMAR/National Institute of Biological Resources.
Lisbon (Portugal).

May-September / 2009

Centre for Chemical and Physical Oceanography, Department of Chemistry, University of Otago. Dunedin (New Zealand).

Appendix II.

Recommended literature as theoretical framework

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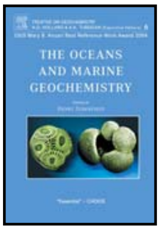

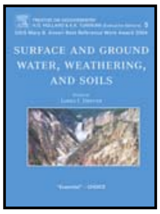

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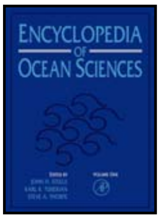

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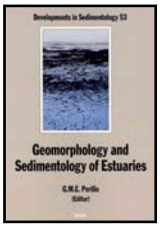

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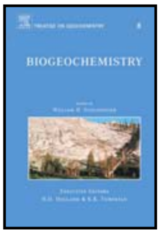

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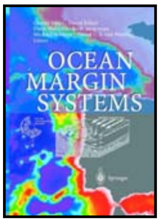

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Appendix III.

Original articles published and submitted

1. **Oceanographical patterns during a summer upwelling-downwelling event in the Northern Galician Rias. Comparison with the whole ria system (NW of Iberian Peninsula).**

Ospina-Alvarez, N.; Prego, R.; Alvarez, I.; deCastro, M.; Alvarez-Ossorio, M.T.; Pazos, Y.; Campos, M.J.; Bernardez, P.; García-Soto, C.; Gómez-Gesteira, M.; Varela, M.

Continental Shelf Research (2010) 30: 1362–1372.

DOI: 10.1016/j.csr.2010.04.018

Impact Factor 2010: 1.928

Abstract

Summer upwelling and downwelling processes were characterized in the Northern Galician Rias during July and August 2008 by means of sampling carried out onboard *R/V Mytilus* (CSIC) and *R/V Lura* (IEO). Thermohaline variables, dissolved oxygen, nutrients, chlorophyll, phytoplankton, ciliates and zooplankton abundances were measured at sections located in the Rias of Viveiro, Barqueiro and Ortigueira and their adjacent shelves. Ekman transport was calculated from QuikSCAT satellite, upwelling intensity estimated with upwelling index from the average daily geostrophic winds, and SST maps obtained from NASA GHRSST satellite. Ekman transport and SST behaviour showed two different patterns: (i) offshore and upwelling favourable conditions on 13-22nd of July; (ii) onshore and downwelling favourable conditions from 23rd July to 19th August). During upwelling, TS diagram showed an intrusion of Eastern North Atlantic Central Water affecting the continental shelf but not the rias. Nutrient salt concentrations increased with depth, reaching their maximum values near the mouth of Ortigueira Ria. During downwelling, coastal water increased its temperature (18.5-19.8ºC) and was retained inside rias; nutrients were nearly depleted, except for the innermost ria (estuarine zone) due to fluvial nutrient inputs. In this inner area, the maximum of chlorophyll-a (Barqueiro Ria) was observed. Low phytoplankton abundances were measured in both cases, even though a short increase in the plankton biomass was observed inside rias during upwelling, while under downwelling a small red tide of *Lingulodinium polyedrum* was detected. During the upwelling period Northern Rias tend to be mesotrophic systems as revealed by nutrient concentrations, chlorophyll levels and plankton abundances. On the contrary, in similar situations, the Western Rias behaves as eutrophics. In the Northern Galician shelf, the average of upwelling (downwelling) was 1.9±0.8 (2.1±1.0) events·yr^{-1} from May to September (1990-2008) considering at least one week with favourable wind conditions and UI averages out of the range of ±500 m^{3}·s^{-1}·km^{-1}.

Resumen

Procesos de afloramiento (upwelling) y contra-surgencia (downwelling) de verano en las rías del norte de Galicia se caracterizaron durante julio y agosto de 2008, en campañas de muestreo realizadas a bordo del *B/I Mytilus* (CSIC) y *B/I Lura* (IEO). Las variables termohalinas, oxígeno disuelto, nutrientes, clorofila, fitoplancton, zooplancton y abundancia de ciliados se midieron en secciones ubicadas en las rías de Viveiro, Barqueiro y Ortigueira y sus plataformas adyacentes. El transporte de Ekman se calculó a través de datos procedentes del satélite QuikSCAT, la intensidad del afloramiento fue calculada mediante el índice de afloramiento (UI) a partir del promedio diario de los vientos geostróficos; y los mapas de temperatura superficial del mar (SST) proporcionados por el satélite de la NASA GHRSST. El transporte de Ekman y el comportamiento de la SST presentaron dos patrones diferentes: (i) dirección hacia el mar y condiciones favorables de afloramiento del 13 al 22 de julio, (ii) dirección hacia la costa, y condiciones favorables de contra-surgencia del 23 de julio al 19 de agosto.

Durante el afloramiento, el diagrama TS mostró una intrusión de Agua Central del Atlántico Noreste (ENACW) que afectó la plataforma continental, pero no las rías. Las concentraciones de sales nutrientes aumentaron con la profundidad, alcanzando sus valores máximos cerca de la boca de la ría de Ortigueira. Durante la contra-surgencia, las aguas costeras aumentaron de temperatura (18.5 a 19.8°C) y se retuvieron dentro de las rías, los nutrientes se agotaron, excepto en el interior ria, debido a los aportes fluviales. En la zona interior de la ria de Barqueiro, se observó el máximo de clorofila-*a*. Una baja abundancia de fitoplancton existió en ambas rias, aunque se detectó una marea roja de *Lingulodinium polyedrum*. Entre mayo a septiembre de 1990 a 2008, en la plataforma norte de Galicia el promedio surgencia / contra-surgencia) fue de 1.9±0.8 / 2.1±1.0 eventos por año, considerando al menos una semana con condiciones de viento favorables y promedios de UI mayores a ± 500 $m^3 \cdot s^{-1} \cdot km^{-1}$.

2. A winter upwelling event in the Northern Galician Rias: frequency and oceanographic implications.

Alvarez, I.; Ospina-Alvarez, N.; Pazos, Y.; deCastro, M.; Bernardez, P.; Campos, M.J.; Gomez-Gesteira, J.L.; Alvarez-Ossorio, M.T.; Varela, M.; Gómez-Gesteira, M.; Prego, R.

Estuarine, Coastal and Shelf Science (2009) 82: 573–582.

DOI: 10.1016/j.ecss.2009.02.023

Impact Factor 2009: 1.970

Abstract

A winter upwelling event was observed in the northern Galician rias (NW Iberian Peninsula) on 20th February 2008. This upwelling episode can not be considered an isolated event. In fact, results from the analysis of Ekman transport data from 1967 to 2007 revealed that the number of days per month under upwelling favourable conditions in winter (January-March) is not negligible (8-10 days) showing that upwelling events along the northern Galician coast are also possible during this period. In addition, the probability of finding winter upwelling favourable conditions with duration of at least 1 day was ~ 35%, decreasing to ~12% when events of at least 5 days were considered. Salinity and temperature distribution revealed that the upwelled water inside the rias corresponds to shelf bottom water which is not associated with Eastern North Atlantic

Central Water (ENACW) or water transported by the Iberian Poleward Current (IPC). Nutrient salts concentrations were the half of typical ENACW in the continental border and did not varied significantly with regard to a previous cruise carried out in January. Plankton showed the existence of spring conditions and also corroborated the intrusion of shelf water inside the rias.

Resumen

Un evento de afloramiento invernal fue observado en las rías del norte de Galicia (NW Península Ibérica) el 20 de febrero de 2008. Este evento no puede ser considerado como un hecho aislado. El análisis del transporte Ekman desde 1967 a 2007, revela que el número de días por mes bajo condiciones favorables de afloramiento en invierno (enero-marzo) no es despreciable (8-10 días), mostrando que los eventos de afloramiento a lo largo del norte de la costa gallega también son posibles durante este período. Adicionalmente, la probabilidad de encontrar condiciones favorables de afloramiento en invierno con una duración de al menos 1 día fue ~35%, disminuyendo a ~12% cuando se consideraron eventos de al menos 5 días de duración. La distribución de la salinidad y la temperatura reveló que el agua aflorada en el interior de las rías correspondió a agua de la plataforma inferior, asociada con Agua Central del Atlántico Noreste (ENACW) o con agua transportada por la Corriente Ibérica dirigida hacia el polo (IPC). Las concentraciones de sales nutrientes fueron la mitad los valores típicos de ENACW en la plataforma continental y no variaron significativamente con respecto del muestreo previo llevado a cabo en enero. El plancton mostró condiciones de primavera y corroboró la intrusión del agua de plataforma en el interior de la ría.

3. Poleward intrusion in the northern Galician shelf.

Alvarez, I.; Ospina-Alvarez, N.; deCastro, M.; Varela, M.; Gómez-Gesteira, M.; Prego, R.

Estuarine, Coastal and Shelf Science (2010) 87: 545-552.

DOI: 10.1016/j.ecss.2010.02.009

Impact Factor 2010: 1.887

Abstract

The evolution of a warm water mass related to the Iberian Poleward Current (IPC) was characterized along the northern Galician shelf in November 2008 by means of Sea Surface Temperature and wind data. It was observed that under upwelling favorable conditions water temperature decreased along the northern coast and a temperature break appeared between Cape Vilano and Cape Ortegal showing a relaxation of the poleward intrusion. The effect of the IPC was also analyzed inside the Northern Galician Rias taking into account the hydrographical and biogeochemical properties measured on November 18. Water driven by the IPC was observed close to the mouth of the rias, around Cape Estaca de Bares, causing a nutrient salts decrease. Inside the rias a slight biological activity was found near surface resulting from fluvial contributions.

Resumen

La evolución de una masa de agua cálida a lo largo de la plataforma norte de Galicia, relacionada con la Corriente Ibérica dirigida hacia el polo (IPC), fue caracterizada durante noviembre de 2008 mediante imágenes de temperatura superficial del mar (SST) y datos de viento. Se observó que bajo bajo condiciones favorables de afloramiento la temperatura del agua disminuyó a lo largo de la costa norte, con un rompimiento entre Cabo Vilano y el Cabo Ortegal que indica una relajación de la intrusión de la IPC. El efecto de la IPC también se analizó en el interior de las rías del norte de Galicia, teniendo en cuenta las características hidrográficas y biogeoquímicas medidas el 18 de noviembre. La masa de agua dirigida por la IPC se observó cerca de la boca de las rías, alrededor del Cabo Estaca de Bares, causando un descenso de sales nutrientes. Adicionalmente, dentro de las rías se encontró una ligera actividad biológica cerca de la superficie asociada a la influencia fluvial.

4. Hydrochemical characterisation and land inputs by pristine temperate rivers (SW Europe).

Bernárdez, P.; Ospina-Alvarez, N.; Caetano, M; Prego, R.

Submitted to Biogeochemistry in Abril, 2012.

Impact Factor 2010: 2.674

Abstract

A summary of the water characteristics of the rivers Sor, Mera and Landro that drain into the Northern Galician Rias (NW Iberian Peninsula) is presented. The analysis was based on fortnightly monitoring during year 2008, for major and minor chemical elements in the dissolved and particulate phase (Al, As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, U, Zn), nutrients (nitrate, nitrite, ammonium, phosphate, silicate), suspended particulate matter, chlorophyll-a, and tracers of water quality chemistry (DIN, PON, DOC, POC, C/N ratio). The data cover rivers not urban, agriculturally or industrially impacted. Continental inputs of dissolved and particulate material via rivers into the Northern Galician Rias were evaluated and annual fluxes of the chemical elements to the rias were calculated. In spite of the high variability in water flow, this study provides a good estimate of the overall amounts of nutrients and metals in the dissolved and particulate phases discharged to pristine ria systems.

Resumen

Un resumen de las características del agua de los ríos Sor, Mera y Landro, ríos prístinos que desembocan en las rías del norte de Galicia (NW Península Ibérica), es presentada es este estudio. El análisis se basó en un seguimiento quincenal durante el año 2008, para elementos mayores y menores, en su fase disuelta y particulada (Al, As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, U, Zn), sales nutrientes (nitratos, nitritos, amonio, fosfato, silicato), materia particulada en suspensión, clorofila-*a*, y marcadores de calidad del agua (DIN, PON, DOC, POC, relación C/N). Los aportes continentales de material disuelto y particulado fluvial hacia las rías del norte de Galicia fueron evaluados, y se cuantificaron sus contribuciones anuales. Este capítulo proporciona una estimación pionera de la cantidad total de nutrientes y elementos traza en la fase disuelta y particulada descargada a sistemas de ría prístinos.

5. Exchange of nutrients across the sediment-water interface in intertidal ria systems (SW Europe)

Ospina-Alvarez, N.; Caetano, M.; Vale, C.; Santos-Echeandía, J.;Bernárdez, P.; Prego, R.

Submitted to Journal of Sea Research in September, 2011.

Impact Factor 2010: 2.444

Abstract

Concentrations of nitrate, nitrite, ammonium, phosphate and silicate were determined in river water, tidal water that floods the intertidal sediment (flooding water) and pore water of those sediments in the Northern Galician Rias of Ortigueira and Viveiro (NW Iberian Peninsula). The field surveys were done in the productive seasons of spring and summer 2008. Short-sediment cores and tidal flooding water were sampled at the intertidal area during the first 20 minutes that the tide inundates the sampling site. Nutrient fluxes of rivers (Lourido and Landro) flowing into the rias were in the order of H_4SiO_4 > NO_3^- > NH_4^+. Nutrients inputs from those rivers were low relative to the total discharge to the coastal area. Striking changes of nutrient levels in flooding and pore waters of intertidal sediments were observed in the short periods of tidal inundation. Nutrient fluxes driven by molecular diffusion and tidal induced transport across the sediment-water interface were quantified and compared to the nutrient river contribution. Diffusive fluxes ranged from 9.3 to 13.7 nmol·cm^{-2}·d^{-1} for nitrate+nitrite, -1.32 to 30.1 nmol·cm^{-2}·d^{-1} for ammonium, -0.01 to 0.49 nmol·cm^{-2}·d^{-1} for phosphate, and -13.2 to 0.2 nmol·cm^{-2}·d^{-1} for silicate. Tidal induced transport always exceeded diffusive fluxes, with differences reaching up to four orders of magnitude for the silicate. The overall results of this study emphasize the relevance of tide in promoting the sediment-water interchange of nutrients in intertidal sub-ecosystems.

Resumen

Las concentraciones de nitrato, nitrito, amonio, fosfato y silicato se determinaron en agua fluvial, agua de inundación mareal y agua intersticial de los sedimentos intermareales, en las rías de Ortigueira y Viveiro (NW de la Península Ibérica). Los estudios de campo se realizaron en la primavera y verano de 2008. Los testigos de sedimentos y el agua de inundación mareal se muestrearon en la zona intermareal, donde los sedimentos quedan expuestos al aire, tomando varias muestras durante los primeros 20 minutos de inundación mareal. Los flujos de nutrientes de los ríos (Lourido y Landro) que desembocan en las rías, disminuyeron en el siguiente orden: H_4SiO_4 > NO_3^- > NH_4^+. El aporte de nutrientes de los ríos fue relativamente bajo en relación a la descarga total de la zona costera. Se observaron cambios significativos en los niveles de nutrientes en el agua de inundación mareal y agua intersticial de los sedimentos intermareales durante los cortos períodos de inundación. Los flujos de bentónicos de nutrientes debidos a la difusión molecular y al transporte inducido por la marea fueron cuantificados y comparados con el aporte de nutrientes de los ríos. Los flujos difusivos variaron desde 9.3 a 13.7 nmol·cm^{-2}·d^{-1} para nitrato+nitrito, -1.32 a 30.1 nmol·cm^{-2}·d^{-1} para amonio, -0.01 a 0.49 nmol·cm^{-2}·d^{-1} para fosfato y -13.2 a 0.2 nmol·cm^{-2}·d^{-1} para silicato. El transporte inducido por la marea siempre superó a los flujos difusivos, alcanzando una diferencia de hasta cuatro órdenes de magnitud en el caso del silicato. Los resultados de éste estudio enfatizan la importancia de la marea en el intercambio sedimento-agua en sub-ecosistemas mareales.

6. Phytoplankton assemblages and Oceanographic Periods in the western boundary of Cantabrian Sea.

Ospina-Alvarez, N.; Varela, M.; Doval, M.D.; Prego, R.

Submitted to Estuarine, Coastal and Shelf Science in June, 2011.

Impact Factor 2010: 1.887

Abstract

Physico-chemical parameters, phytoplankton assemblages, chlorophyll, and primary production were studied in the Ria of Barqueiro (43°45.509'N-07°39.493'W, Western Cantabrian Sea) from January/08 to January/09. Throughout the year nutrients values, Chl-*a*, primary production and phytoplankton abundance were clearly lower compared to those reported for the Western and Middle Galician Rias. Annual primary production for the Ria of Barqueiro was 280 gC·m^{-2}·y^{-1}. Mean chlorophyll was low in all periods ranged from 0.52 µg·L^{-1} in autumn to 1.07 µg·L^{-1} in spring.

The oceanographic periods defined were: Spring, Summer stratification, Autumn and Winter, unlike to the Atlantic rias of Galicia, where the influence of upwelling is much more relevant. The diatoms and dinoflagellates accounted for the 85% of the phytoplankton species identified. Diatoms dominated phytoplankton assemblages especially during spring and autumn blooms. In summer, in absence of upwelling, a mixing of diatoms and dinoflagelllates co-dominated phytoplankton community with a lower contribution of diatoms as compared with the rest of Galician Rias. Micro and nano-flagellates, increased their relative contribution to biomass during summer. Nitrogen was identified as the main limiting factor for phytoplankton growth throughout all periods and especially during autumn. The natural/anthropogenic eutrophication reported for other Galician Rias was not observed in the Ria of Barqueiro, which can be cataloged as a pristine area, according to the good quality status of its waters. The area of study can be considered as the Northern boundary of Eastern North Atlantic Upwelling System (ENAUS), where the upwelling of North Atlantic Waters is negligible, resulting in a plankton cycle typical of temperate zones.

Resumen

Diferentes parámetros físico-químicos, composición del fitoplancton, clorofila y producción primaria, se estudiaron durante enero de 2008 a enero de 2009 en la ría de Barqueiro (43°45.509'N-07°39.493'W, Mar Cantábrico). Durante todo el año los valores de nutrientes, clorofila, producción primaria y la abundancia de fitoplancton fueron claramente inferiores comparados con los valores reportados para las Rías Medias y Bajas de Galicia. La producción primaria anual de la ría de Barqueiro fue de 280 gC·m^{-2}·año^{-1}. El valor medio de clorofila fue bajo en todos los períodos oscilando entre 0.35 µg·L^{-1} en otoño a 1.47 µg·L^{-1} en primavera. Los periodos oceanográficos definidos fueron: Primavera, Estratificación de Verano, Otoño e Invierno, en contraste con las rías Atlánticas de Galicia, donde la influencia del afloramiento es mucho más relevante. Las diatomeas y dinoflagelados representaron el 85% de las especies de fitoplancton identificadas. Las diatomeas dominaron el fitoplancton, especialmente durante el bloom de primavera y otoño. En verano, en ausencia afloramiento, una mezcla de diatomeas y dinoflagelllates co-dominaron la comunidad fitoplanctónica, con una menor contribución de las diatomeas en comparación con el resto de las rías gallegas. Los micro y nano-

flagelados aumentaron su contribución a la biomasa durante el verano. El nitrógeno fue identificado como el principal factor limitante para el crecimiento de fitoplancton a lo largo de todos los periodos, especialmente durante el otoño. La eutrofización natural/ antropogénica reportada en otras rías gallegas no se observó en la ría de Barqueiro, que puede ser catalogado como un área prístina de acuerdo con el buen estado de la calidad de sus aguas. El área de estudio puede ser considerado como el límite norte del ENAUS, donde el afloramiento de las aguas del Atlántico Norte es insignificante, lo que resulta en un ciclo de plancton típico de una zona templada.