Fluvial contributions of nutrients and dissolved organic matter to the Ria of Ares-Betanzos

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Abstract

This work aims in the study of biogeochemical fluvial fluxes to Ria systems, previously poorly investigated. Nutrients and dissolved organic matter were analyzed in samples from three rivers (Eume, Mandeo and Mendo) flowing to the Ria of Ares-Betanzos (Galicia), covering a whole hydrological year. Ria receives an estimated load of 457, 5.0 and 2140 $t \cdot yr^{-1}$ of inorganic N, P and Si, and 1130 and 71 $t \cdot yr^{-1}$ of organic C and N, respectively. The Mandeo River is the main input path of nutrients to the system, while Mendo River is the biggest contributor of organic matter. Discharge of nutrients from the Eume River is controlled by damming. Relative fluvial contributions, normalized by catchment area, indicate a low anthropogenic influence in the area.

Keywords:

Loads, nutrients, DOC, DON, Eume, Mandeo, Mendo, river, NW Spain.

1. Introduction

Land-ocean interactions occur mainly in the estuarine zones where fluvial contribution of nutrients is a key factor to explain the high coastal primary production. In this way, the LOICZ science plan [Holligan and de Boois, 1993] developed overarching goals, including responses to the variation of terrestrial and oceanic inputs of organic matter and nutrients. In the Galician coastal zone the upwelling events of Eastern North Atlantic Central Water [Fraga, 1981] are considered as the main source of nutrients [Prego et al., 1999]. Therefore, the fluvial flow of inorganic nutrients or dissolved organic matter to the rias is a question treated on a few papers [Vergara and Prego, 1997; Gago et al., 2005; Bernárdez et al., 2013]. The aim of this study is, consequently, the quantification of fluvial contributions to the head of the Ria of Ares-Betanzos to determine its relevance. For this reason, the fluxes of nutrients and dissolved organic matter from the Eume, Mandeo and Mendo Rivers are assessed in one hydrological year period. The continental basin of Ares-Betanzos has a total area of 1196 km^2 supporting an average population density of 43 $inhab \cdot km^{-2}$; climate is temperate and rainy, C_{sb} Köppen type; land uses are diverse: crops (34%), Eucalyptus cultivation (27%), pastures-meadows (14%), scrublands (11%) and forests (9%), urban uses (3%) and mining activities (2%).

2. Material and Method

The aforementioned rivers were monthly sampled from October 2011 to September 2012. Samples were withdrawn close to the river mouth (verified salinity zero). Conductivity and temperature were measured *in situ* (WTW MultiLine F/Set-3). Dissolved Oxygen determined by Winkler titration (702-SM Titrino, Metrohm). Nutrient salts using colorimetric methods of continuous segmented flow analysis modified by Bran-Luebbe for Quaatro analyzer. Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN) by high temperature catalytic oxidation (Shimadzu TOC-V CPH with a TNM-1 unit). All inorganic nutrients, DOC and TDN analysis are accredited by ENAC (UNE-EN ISO/IEC 17025:2005).

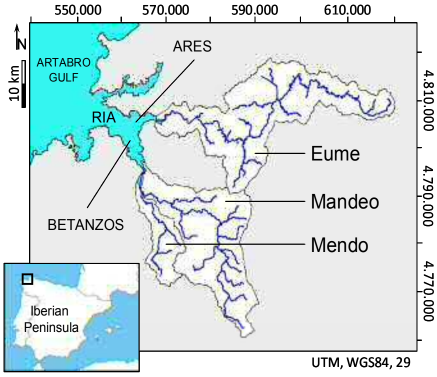

Image 1. Survey

River fluxes were calculated by a ratio estimator method. This procedure is useful for cases where large amount of flow data are available but concentration data are scarce [Quilbé *et al.*, 2006]. Equations 1 to 3, where F_{re} ($mg \cdot s^{-1}$) is the annual average river load; K, a conversion factor; μ_q ($m^3 \cdot s^{-1}$), the mean daily flow in the year; l_m ($g \cdot s^{-1}$), the mean load for the days when the dissolved compound was determined; q_m ($m^3 \cdot s^{-1}$), the mean river discharge for the days when the dissolved compound was determined; n, the number of days with concentration data; q_i ($m^3 \cdot s^{-1}$), the flow determined in each sample; l_i ($g \cdot s^{-1}$), the calculated load for each sample.

Equation 1

$$F_{re} = K \cdot \mu_q \cdot \frac{l_m}{q_m} \cdot \left[\frac{1 + \frac{1}{n} \cdot \frac{S_{lq}}{q_m \cdot l_m}}{1 + \frac{1}{n} \cdot \frac{S_q^2}{q_m^2}} \right]$$

Equation 2

$$S_{lq} = \frac{1}{(n-1)} \cdot \left[\sum_{i=1}^{n} q_i \cdot l_i - n \cdot q_m \cdot l_m \right]$$

Equation 3

$$S_q^2 = \frac{1}{(n-1)} \cdot \left[\sum_{i=1}^{n} q_i^2 - n \cdot q_m^2 \right]$$

3. Results

Conductivity (83-105 $\mu S \cdot cm^{-1}$), temperature (11.9-13.3ºC), dissolved oxygen near saturation (95-98%), low concentration of nitrite (0.2-0.4 µM) and ammonium (1.0-1.7 μM), arises comparable values in the three rivers. Concentrations of nitrate, phosphate and silicate decreased from Mendo (109 μM_N, 0.54 μM_P, 269 μM_{Si}) to Eume (42 μM_N, 0.07 μM_P, 76 μM_{Si}) while dissolved organic compounds, DOC and DON, increased from Eume (102 μM_C, 6.8 μM_N) to Mandeo (176 μM_C, 9.8 μM_N). Eume River showed the minimum concentration for both inorganic and organic compounds.Results are broadly presented in Table 1.

Table 1: Average parameters (±STD) and load estimation (annual average flow).

Hydrological year	River			
Oct.11 – Sept.12	Eume	Mandeo	Mendo	Unit
Flow	(13.2) 9.30	(15.5) 6.83	(2.1) 1.05	$m^3 \cdot s^{-1}$
Conductivity	86 ± 27	83 ± 15	105 ± 31	$\mu S \cdot cm^{-1}$
Temperature	11.9 ± 2.0	13.1 ± 3.9	13.2 ± 4.0	°C
Oxygen saturation	98 ± 2	97 ± 3	95 ± 3	%
Nitrate	42 ± 5	95 ± 18	109 ± 14	μM
Nitrite	0.2 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	μM
Ammonium	1.7 ± 0.8	1.0 ± 0.5	1.3 ± 0.4	μM
Phosphate	0.07 ± 0.05	0.23 ± 0.15	0.54 ± 0.12	μM
Silicate	76 ± 18	136 ± 26	269 ± 30	μM
DOC	102 ± 28	176 ± 75	124 ± 37	μM
DON	6.8 ± 2.8	9.8 ± 3.9	7.6 ± 1.4	μM
Basin surface	470	457	90	km^2
		Loads		
Nitrate	380	404	541	$kgN \cdot km^{-2} \cdot yr^{-1}$
Nitrite	1.7	2.4	2.2	$kgN \cdot km^{-2} \cdot yr^{-1}$
Ammonium	20.6	10.3	8.3	$kgN \cdot km^{-2} \cdot yr^{-1}$
Phosphate	1.1	5.1	6.4	$kgP \cdot km^{-2} \cdot yr^{-1}$
Silicate	1310	1590	2480	$kgSi \cdot km^{-2} \cdot yr^{-1}$
DOC	750	1940	704	$kgC \cdot km^{-2} \cdot yr^{-1}$
DON	60	116	38	$kgN \cdot km^{-2} \cdot yr^{-1}$

The combined basin of Eume, Mandeo and Mendo take up 85% of continental Ares-Betanzos watershed. Estimated loads from this watershed resulted 457 $t \cdot yr^{-1}$ of inorganic N, 5.0 of $t \cdot yr^{-1}$ of inorganic P and 2140 $t \cdot yr^{-1}$ of Si and 1130 and 71 $t \cdot yr^{-1}$ of organic C and N, respectively. The higher load of nutrient salts, DOC and DON to the Ria come from the Mandeo river. The area-normalized fluxes (Table 2) highlight Mandeo river as the main land source of nutrient salts and Mendo river of DOM.

4. Discussion

The concentrations of nutrients, DOC and DON in the Eume and Mandeo rivers are in the order of those measured in the unpolluted Galician rivers [Bernárdez et al., 2013]. Mendo river is an exception, it nearly doubled the average level of nitrate, phosphate and silicate of the other two rivers. The nitrogen compounds are primarily influenced by biological processes, anthropogenic inputs and rainfall [Meybeck and Helmer, 1989]. Concentrations determined in this study correspond to poor anthropogenic inputs (e.g. nitrogen fertilisers). Phosphate concentrations were low in comparison with other rivers of Galicia [Vergara and Prego, 1997] indicating a little agricultural and urban influence within their watersheds. Phosphorous appears to be the limiting nutrient in the rivers flowing into the Ares-Betanzos Ria as in many world fluvial systems [Correl, 1999].

Biological processes might control phosphates concentration and, in consequence, DIN and primary production. Dissolved organic matter is highly dependent on the biological processes acting in the fluvial environment as well as the sources of organic matter to these rivers [Spitzy & Leenheer, 1991]. The three rivers exhibit a DOC concentration typical for rivers draining mid-latitude areas [Neal and Robson, 2000] and similar to unpolluted Galician rivers [Bernárdez et al., 2013]. Hessen [1999] suggested that, for most pristine temperate watersheds, nitrogen loads are in the range 80-200 $kgN \cdot km^{-2} \cdot y^{-1}$ while watersheds moderately influenced by human activity are within 500-2000 $kgN \cdot km^{-2} \cdot y^{-1}$. Loads, normalized by the catchment area, to the Ares-Betanzos Ria indicate a low anthropogenic influence. Hydropower station of Eume provides more than 90% of the river flow and there was a phosphate depletion together with a nitrate and silicate decrease. In consequence, the upstream dam may cause an indirect anthropic control on fluvial nutrients by retaining nutrients in its sediments as organic matter.

Net primary production (NPP) in Galician Rias is between 280 and 1250 $gC \cdot m^{-2} \cdot y^{-1}$ [Ospina-Alvarez et al., 2014], corresponding, as state by the Redfield C:N molar ratio of 106:16 and 72 km^2 of Ares-Betanzos surface, to 3550-15850 $tN \cdot y^{-1}$. Therefore, taking into account that fluvial loads of inorganic N were 457 $t \cdot yr^{-1}$ (dry year conditions), fluvial contributions should only support between 3% and 13% of NPP in the Ria of Ares-Betanzos.

5. Conclusions

The three rivers can be set as low human impacted areas, being the Mandeo River specially loaded by nutrients and the Mendo by DOM. Biogeochemical loads in Eume River are hardly influenced by an upstream dam. Fluvial loads could be responsibly of a 3-13% of the NPP in the Ares-Betanzos Ria.

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