Álvarez-Vázquez, M.A., Prego, R., Ospina-Alvarez, N., Caetano, M., Bernárdez, P., Doval, M., Filgueiras, A.V., Vale, C., Anthropogenic changes in the fluxes to estuaries: wastewater discharges compared with river loads in small rias, Estuarine, Coastal and Shelf Science (2015), doi: 10.1016/j.ecss.2015.08.022

# Anthropogenic changes in the fluxes to estuaries: wastewater discharges compared with river loads in small rias

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**Abstract.** The modification of chemical inputs into estuaries/rias by wastewater discharges is poorly documented. Concentrations and fluxes of nutrient salts, organic matter and trace metals in rivers and wastewaters to the mesotrophic Rias of Ortigueira (38 $km^2$) and Viveiro (27 $km^2$), located on the western Cantabrian coast (Bay of Biscay), were evaluated to assess changes in the land-sea fluxes. Water was sampled monthly during a year in the Mera (6.0 $m^3 \cdot s^{-1}$) and Landro (9.4 $m^3 \cdot s^{-1}$) rivers flowing into the Rias of Ortigueira and Viveiro, respectively. The urban effluents of Ortigueira (1,800 inhabitants; treated sewage) and the Viveiro (7,100 inhabitants; municipal treated sewage and untreated industrial wastewaters) were also monitored. Concentrations of chemical compounds and their fluxes were quite similar and close to pristine conditions in both rivers. Nitrate (98% of DIN), the limiting nutrient of ria primary production, was controlled by river flow while phosphate by wastewater discharge. Sewage discharges should not disturb the Ria of Ortigueira. Wastewaters fluxes of phosphate, POC, PON, dissolved Cu and particulate Cd, Cu and Zn into the Ria of Viveiro exceeded those of the Landro River, mainly during summer. Also, untreated wastewater effluents from fish food processing in such small fishing ports can be a source of contamination. The Rias of Ortigueira and Vivieiro are a reference point to evaluate fluvial pristine conditions and wastewater discharges on small estuary-ria receptor systems.

**Keywords:** nutrients, organic matter, trace elements, contamination, river, wastewater, estuary, fishing port, Northern Galician Rias, Bay of Biscay.

## 1. Introduction

Rivers represent the main pathway of weathered materials into the ocean through the estuaries. Since the beginning of the 20th century the industrial revolution has resulted in a "drastic release" of nutrients, organic matter and metals into the natural environment (Gaillardet et al., 2003). It is estimated that human influence has more than doubled the annual discharge of materials into the ocean by rivers (Salomons and Förstner, 1984). Smith et al. (2005) demonstrated how human activities altered the global biogeochemical cycles, particularly, the coastal fluxes of C, N and P. Estuarine chemistry has changed during the Anthropocene (Meybeck and Vörösmarty, 2005), in particular urbanized estuaries receiving wastewater discharged. In addition to the natural source of nutrients related to rock weathering and the leaching of organic soils (Viers et al., 2007) anthropogenic inputs from dispersed sources (e.g. fertilizers) or point sources (e.g. wastewater facilities) have altered the land-sea fluxes.

In confined ecosystems, wastewater treatment plants may release higher quantities of nutrients and metals than dispersed or other point sources, altering the natural biogeochemical cycles with pernicious effects in the receiving coastal ecosystems (Carey and Migliaccio, 2009). Whereas nutrients input is a key factor for the functioning of estuarine and coastal ecosystems (de Jonge et al., 2002), excess of nutrients, namely resulting from wastewater effluents, can lead to increase of algal biomass, reduction of dissolved oxygen and ultimately to harmful algal blooms and fish mortality (Carey and Migliaccio, 2009). Metals in estuaries and rias often occur at moderate concentrations (Kennish, 1997; Prego and Cobelo-García, 2003), mainly due to contaminated streams as shown to occur in the Ria of Ferrol (Cobelo-García et al., 2004). Elevated metal concentrations may affect resident and migratory organisms (da Silva Oliveira et al. 2007), as well as reduce the functioning of the ecosystem. The treatment of municipal and industrial wastewater may be a key measure to reduce the metal impact (Santos-Echeandía, 2009). Comparison of metals inputs from natural processes and wastewater have only rarely been made. Paul and Meyer (2001) pointed out that the Archers treatment plant (West Paris, France) increased the Seine River flow by up to 40% in summer periods, and wastewater effluents comprise 69% of the Platte River (Denver, USA) annual flow (Dennehy et al., 1998). Recently, several borderline hypoxic situations (Lanoux et al. 2013) and cases of metal contamination on urban wastewater inputs (Deycard et al. 2014) have been reported from the parts of the fluvial Gironde Estuary. To the best of our knowledge, no comparative data is available for estuaries despite the increase of wastewater treatment plants (WWTPs) in the last decades.

The aim of this study is to assess the relevance of wastewater effluents relative to river loads into an estuary. This comparison was made for nutrients, organic matter and metals in the Rias of Ortigueira and Viveiro, representative of the Northern Galician Rias. Concentrations and fluxes in river inputs and wastewaters effluents were considered.

## 2. Survey area

Northern Galician Rias are located in the southwestern coast of the Bay of Biscay. Rias are funnel-like incised valleys where the lower part of the river has been flooded. Only the inner part can be considered as an estuary from both hydrographic and their resulting sedimentological considerations (Evans and Prego, 2003). Northern Galician Rias include the Rias of Ortigueira and Viveiro (Figure 1), these have surface area respectively 38-27 km2 and are 30-35 m depth at their open mouths which are exposed to the North swell. In the innermost parts they receive the main freshwater input from the Mera River (Ria of Ortigueira) and the Landro River (Ria of Viveiro), which have drainage basins of 127 and 270 $km^2$, respectively. The annual average flow of 6.0 $m^3 \cdot s^{-1}$ of the Mera River and 9.4 $m^3 \cdot s^{-1}$ of the Landro River, during the period of 1975-2013 (data from of 'Augas- de-Galicia' Co.), defines them as small rivers according to the Meybeck et al. (1996) classification.

The climate of northern Galicia is wet and temperate, Cfb Köppen type (i.e. Marine Climate; Hess, 2014), with an annual average temperature of 13.1°C and an average annual precipitation of 1370 mm. Depending on the climate the fluvial regime shows seasonality with higher flows in December-February and lower flows from July to September.

The Mera River flows through a basin composed of metamorphic, mafic and ultramafic rocks while that of the Landro River contains metamorphic and granitic alkaline rocks. The drainage basins are covered by eucalyptus and pine forests and scrublands with only a small proportion of cultivated areas in the floodplains. The soil permeability of the river basins is low (Río-Barja and Rodríguez- Lestegás, 1992). Both rivers have very shallow estuaries containing extensive marshlands and beach barriers in their inner parts.

The population density is low (≈70 inhab·$km^2$) and is mostly concentrated near the river mouths. The town of Ortigueira had 1,800 inhabitants (2008 INE database) and its municipal sewage (≈$3 \cdot 10^5$ $m^3 \cdot yr^{-1}$) is discharged to the inner ria after physico-chemical and biological treatment, including U.V. disinfection in the wastewater treatment plant (WWTP). In 2008 the town of Viveiro had 7,100 inhabitants (2008 INE database) and its wastewater (≈$1.7 \cdot 10^6$ $m^3 \cdot yr^{-1}$) is discharged into the middle ria through a submarine wastewater outlet pipe. This wastewater is composed of different outflows: municipal sewage (biologically treated and disinfected with chlorine in the WWTP of Viveiro) and an untreated discharge from the fishing port of Celeiro, where the main industrial area (fishing, canning and small shipyards) of Viveiro is located.

## 3. Material and Method

### *3.1. Sampling and sample treatment*

The water of the Mera and Landro Rivers and the Ortigueira and Viveiro wastewater effluents were sampled once a month from March 2008 to February 2009 (Fig. 1). In order that sources can be compared, fluvial and wastewater stations were contemporaneously sampled around noon on each monitoring day (2008: March 17, April 21, May19, June 17, July 15, August 18, September 15, October 13, November 17 and December 10; 2009: January 12 and February 18). No detectable intrusion of salt water (salinity <0.1) was found in the river sampling sites, located near their mouths, and minor variation in wastewaters (<0.3 in Ortigueira and 1.3±0.4 in Viveiro). It should be noted that the Viveiro outflow was a mixture of municipal treated sewage from Viveiro Town and the untreated wastewater from Celeiro area (6:1 roughly).

The water samples (rivers and wastewaters) were taken by a plastic container fixed to a telescopic arm. Temperature and salinity were recorded in situ using a WTW MultiLine F/Set-3 apparatus. Using a SevenGo Mettler-Toledo pHmeter pH was also measured. Sample aliquots were separated to analyze dissolved oxygen (50 mL glass flasks, in situ fixed according to the Winkler method; Aminot, 1983); nitrate, nitrite, ammonium and phosphate (50 mL plastic bottles, immediately frozen to -20°C); silicate (10 mL plastic bottles, preserved at 4°C to avoid orthosilicate polymerization that may occur in frozen freshwater samples (Kobayashi, 1966); dissolved organic carbon (DOC) and nitrogen (DON) (50 mL plastic bottles, immediately frozen to -20°C); particulate organic carbon (POC) and nitrogen (PON) (1 L plastic bottles preserved at 4°C until filtration within 4 h through glass microfiber filters -Whatman GF/F-, 25 mm diameter); trace elements (1 L acid clean LDPE bottles, preserved at 4°C until filtration within 4 h). Trace metal ultraclean techniques were used during the sampling procedures to minimize contamination (Howard and Statham, 1993).

Dissolved and particulate fractions for trace elements analyses were separated by filtration through polycarbonate membranes (0.45 µm), previously acidwashed (Suprapure HCl 1%) dried and pre-weighed, fitted in Nalgene plastic filter holders and housed inside a laminar flow cabinet (ISO 5 class). Filtrates were transferred to acid-cleaned LDPE bottles, acidified to pH 2 (Suprapure HCl 1%) and packed in zip-lock plastic bags until analysis. Membranes retaining suspended particulate matter (SPM) were dried at laboratory temperature inside a clean cabinet, weighted to calculate the amount of particulate matter and stored at -20°C until a microwave digestion was made for metal analysis. Polycarbonate filters were completely digested in a Milestone MLS 1200 Mega microwave oven following EPA 3052 guidelines for siliceous-type matrices (US-EPA, 1996). Digestion was carried out with HF (3 mL 48%) and $HNO_3$ (9 mL 65%) in closed PTFE pressure vessels. The content of the bombs was transferred into 25 mL volumetric flasks filled with ultrapure Milli-Q water.

### *3.2. Water analysis*

Dissolved Oxygen was analyzed the following day of sampling by the Winkler method (Aminot, 1983) using a 702-MS Tritino (Methrohm). Oxygen saturation was calculated based on concentration, salinity and temperature data of each sample (error range of ±0.2).

Nutrient salts were analyzed in an Integral Futura autoanalyzer system (Alliance Instruments) with separate lines for nitrate, nitrite, ammonium, phosphate and silicate according to standard colorimetric methods (Hansen and Koroleff, 1999). The accuracy of the analytical procedure was assessed by the nutrient analysis of certified reference material MOOS-1 (NCR Canada) and obtained good agreement with the certified values. The precision as relative standard deviation was less than 5%.

Total dissolved nitrogen (TDN) and DOC were determined by a Shimadzu TOC-V CPH analyzer with a TNM-1 unit by high temperature catalytic oxidation and non-dispersive infrared and chemiluminiscence detection respectively following the procedure described by Alvarez-Salgado and Miller (1998). The precision was ±0.8 $\mu molC \cdot L^{-1}$ and ±0.3 $\mu molN \cdot L^{-1}$ respectively. The accuracies were tested (obtained: 44.2±1.7 µM of DOC and 31.8±1.9 of TDN, n=92) with the reference materials (45±1 µM of DOC and 32.8±0.8 of TDN) provided by Prof. D. Hansell (Univ. of Miami). DON was calculated by subtracting from the TDN the concentration of dissolved inorganic nitrogen (DIN). DIN was calculated as the sum of nitrate, nitrite and ammonium.

Particulate organic carbon (POC) and particulate organic nitrogen (PON) were analyzed using a FlashEA 11-12 Termoquest CNH analyzer. Filter blanks showed POC and PON contents lower than 0.01%. In the case of POC, carbonate was not removed from the filters, as the contribution of carbonate to total carbon was below the detection limit of the equipment used.

Dissolved metals (Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, V and Zn) were determined by a quadrupole ICP-MS (Thermo-Elemental X-series) equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. The chemical digests of particulate metals were analyzed by GFAAS using a Varian SpectrAA 220 equipped with Zeeman background correction (Cd, Co, Cr, Cu, Fe, Ni, Pb, V and Zn) and by

FAAS (Al) using a Varian SpectrAA 220 FS with a nitrous oxide-acetylene flame. In both phases, dissolved and particulate, procedural blanks accounted for less than 2% of elemental concentration in the samples. Procedure precision and accuracy were determined by the analysis of certified reference materials (CRM) SLRS-4 for dissolved metals and PACS-2 for particulate metals, both from the National Research Council of Canada (NRCC). Results were in good agreement of CRMs (Table 1).

### *3.3. Ratio and load calculations*

Concentrations of nutrient salts (nitrate, nitrite, ammonium, phosphate and dissolved silicate), organic matter (DOC, DON, POC and PON) and dissolved and particulate metals (Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, V and Zn) were used to calculate and compare their fluxes from the wastewater of Ortigueira and Viveiro and the Mera and Landro Rivers. Daily flow data from both rivers were supplied by 'Augas-de-Galicia' Company (gauging stations 438 and 443 for the Landro and Mera Rivers, respectively). Flow discharge data from wastewater facilities (Ortigueira and Viveiro) were provided by 'Augas-de-Galicia' Co. Based on the assumption that river flows do not vary during the sampling day, the fluxes were calculated. Loading rate or flux is defined as 'the instantaneous rate at which the load is passing a point of reference on a river' (Richards, 1998). So, flux was calculated for each monitoring date multiplying the river or wastewater flow by the concentration of the chemical constituent in its respective river or wastewater source. In the case of POC, PON and particulate metals, particulate concentration was calculated by multiplying the concentration of suspended particles by the element content in SPM; then, their particulate fluxes were calculated by multiplying particulate concentration by the river or wastewater flow.

The particle-water distribution coefficient ($K_{dp}$) was calculated by dividing particulate matter (i.e. filter-retained) concentration (nM) by dissolved concentration (nM) of the same metal. This dimensionless coefficient $K_{dp}$ provided information about the phase in which metal is most abundant in the wastewater.

The Concentration Ratio (CR) and the Flux Ratio (FR) were used for comparisons between wastewater and river discharges of dissolved and particulate metals into each ria. The concentration Ratio was calculated for each monitoring by dividing the constituent concentration in wastewater by its concentration in river water, i.e. Ortigueira and Viveiro wastewater versus Mera and Landro water, respectively. Likewise, Flux Ratio of a constituent is its quotient between wastewater and river fluxes.

## 4. Results

### *4.1. Hydrological conditions and key variables*

In the sampling period of one year, from March 2008 to February 2009, the small Mera and Landro Rivers drained into the rias with average water flow of 8.2 $m^3 \cdot s^{-1}$ and 13.5 $m^3 \cdot s^{-1}$, respectively. Taking into account the days of sampling only, the fluvial flows ranged from 0.7 to 17.2 $m^3 \cdot s^{-1}$ in the Mera River and from 2.0 to 25.3 $m^3 \cdot s^{-1}$ in the Landro River. Daily flows exceed the aforementioned ranges nine times (Figure 2), which four of them were higher than 60 $m^3 \cdot s^{-1}$ (2008: Landro with 86 $m^3 \cdot s^{-1}$ on April 9 and 86 $m^3 \cdot s^{-1}$ on November 1 and Mera with 64 $m^3 \cdot s^{-1}$ on December 10; January 23- 29, 2009: Mera with 109 $m^3 \cdot s^{-1}$ and Landro with 138 $m^3 \cdot s^{-1}$ The river flow varied similarly in both systems (Figure 2): their levels rose in April, November and December 2008 and February 2009 and were low and relatively constant in the summer (July-October). During the aforementioned period the Ortigueira WWTP discharged an average of $9\cdot10^{-3}$ $m^3\cdot s^{-1}$ of treated sewage while the Viveiro wastewater outflow was higher, $54\cdot10^{-3}$ $m^3\cdot s^{-1}$ (Fig. 2). Both wastewater flows were independent of rainfall.

The water temperature ranges in the Mera (8.4-17.4°C) and in the Landro (7.7-18.8°C) Rivers and the wastewater outflows of the Ortigueira (12.9-21.6°C) and Viveiro (10.9-24.1°C) showed a seasonal temperate pattern. Dissolved Oxygen (DO) in river water was close to the saturation over the studied period ranging between 93% and 100%, with annual averages of 97±2% and 96±2% in the Mera and Landro, respectively. In wastewater effluents DO saturation varied between 55% and 79% (average of 70±10%) in the Ortigueira sewage and from 3% to 79% (average of 38±29%) in the Viveiro wastewater. The low oxygen saturation occurred in the summer. In both, rivers and wastewaters, pH remained close to neutrality in the studied period: 6.8±0.2 and 7.3±0.4 in the wastewater effluent of Ortigueira and Viveiro, respectively; 7.3±0.5 and 7.1±0.4 in the Mera and Landro Rivers, respectively.

The suspended particulate matter (SPM) concentration ranged within one order of magnitude in both rivers: 0.2-5.8 $mg\cdot L^{-1}$ (average of 2.1±1.5 $mg\cdot L^{-1}$) in the Mera River and 0.3-8.2 $mg\cdot L^{-1}$ (2.9±2.2 $mg\cdot L^{-1}$) in the Landro River. Two periods of increased levels were identified: spring and autumn. Variations of the river flow coincide with maxima of precipitation. The SPM content in the Ortigueira WWTP discharge varied irregularly from 0.8 to 8.8 $mg\cdot L^{-1}$, with a similar pattern to the Mera River water. Otherwise, levels in the Viveiro wastewater discharge ranged from 56 to 417 $mg\cdot L^{-1}$ and were up to two orders of magnitude higher than those measured in the Landro River water. In the Viveiro wastewater, SPM concentration increased in the June-October period (from 341 to 417 $mg\cdot L^{-1}$) reaching SPM maximum in October 2008.

### *4.2. Inorganic Nitrogen Phosphorous and Silicon*

The ranges and average concentrations of nutrient salts and dissolved inorganic nitrogen (DIN, defined as the sum of nitrate, nitrite and ammonium) are shown in Table 2. From the inorganic forms of dissolved nitrogen, the most abundant was nitrate in river waters (98±1% of DIN) and ammonium in wastewater (88±10% of DIN). The fluvial concentrations of nitrate were in the Mera 53±13 μM and 48±15 μM in the Landro; wastewater discharges of Ortigueira (51±42 μM) and Viveiro (111±89 μM) were of the same order of magnitude, although were variable and elevated in the Viveiro wastewater. The main difference between river and wastewaters was the ammonium enrichment in the wastewater. Ammonium concentrations were 1600 times higher in the Ortigueira WWTP sewage effluent (870±450 μM) than in the Mera River water (0.63±0.39 μM), and 690 times higher in the Viveiro wastewater discharge (550±370 μM) than in the Landro River water (0.89±0.56 μM). Fluvial contributions of DIN to the rias (Table 2) were in the range of 6-1220 $mmol\cdot s^{-1}$ with the lower fluxes during the dry season. Average values of loading rates were comparable being in the Mera River 313 $mmol\cdot s^{-1}$ and 418 $mmol\cdot s^{-1}$ in the Landro River. Wastewater DIN fluxes varied between 1.2 and 14.8 $mmol\cdot s^{-1}$ in Ortigueira and between 11 and 81 $mmol\cdot s^{-1}$ in Viveiro and did not show a seasonal trend. In both wastewater loads the ammonium was the main flux (>85%). As a whole, DIN loading rates from wastewater in both rias were close to one third of the respective river loads.

Fluvial phosphate concentrations were very low with annual averages of 0.12±0.08 μM in the Mera River and 0.14±0.11 μM in the Landro River (Table 2). In spring phosphate was depleted in both river waters. Phosphate concentrations in the Ortigueira WWTP effluent (2.9-8.1 μM; annual average of 4.4±1.4 μM) were 25 times lower and less scattered than that of the Viveiro discharge (18-380 μM; 129±107 μM). In the Ria of Ortigueira sewage phosphate enrichments were 40 times the Mera River concentration. In the Ria of Viveiro the concentration of this nutrient in wastewaters from Viveiro was 990 times higher than those found in the Landro River. However, phosphate discharges (Table 2) from the Ortigueira WWTP to its Ria (0.02-0.09 mmol·$s^{-1}$) meant that is formed only one third of the Mera River load (0.01-1.91 mmol·$s^{-1}$). The phosphate input from Viveiro wastewater (1-18 mmol·$s^{-1}$) into the Ria of Viveiro was around 10 times greater than of the Landro River load (0.3-10.6 mmol·$s^{-1}$) and 200 times greater than of the Ortigueira wastewater flux.

Dissolved silicate concentrations were similar in magnitude for rivers and wastewaters (annual average of 166±34 μM in the Mera River, 134±23 μM in the Landro River, 265±51 μM in Ortigueira sewage and 203±47 μM in Viveiro wastewater, Table 2) although slightly higher in the wastewaters. However, the wastewater flows were low and dissolved silicate fluxes in the wastewater to the two rias (2.3±0.5 and 10.8±2.0 mmol·$s^{-1}$ from Ortigueira and Viveiro wastewater, respectively) represented less than 2% of the fluvial loads (Table 2).

### *4.3. Organic Carbon and Nitrogen*

Annual average concentrations of dissolved organic carbon (DOC) were 600±180 μM and 7100±6070 μM in Ortigueira and Viveiro wastewater, respectively (Table 2). In the Ortigueira WWTP effluent levels were five times higher than those in the Mera River (112±34 μM). In the Viveiro wastewater, DOC concentration was up to 32 times the values measured in the Landro River (217±97 μM). In spite of that the DOC contribution to the rias was mainly from the rivers. The DOC loading rate from Ortigueira WWTP effluent (3.3-7.8 mmol·$s^{-1}$) accounted for less than a 2% of the Mera River load (23-1270 mmol·$s^{-1}$) to the Ria of Ortigueira (Table 2). However, the DOC discharge into the Ria of Viveiro from Viveiro wastewater (91-950 mmol·$s^{-1}$) was around 15% of the Landro River Load (340- 6660 mmol·$s^{-1}$).

Particulate organic carbon (POC) concentrations were equivalent to approximately 15-20% of DOC in the two studied rivers (Table 2). In the Ortigueira WWTP effluent the POC/DOC relationship was similar to that in the rivers while that in the Viveiro wastewater POC was increased up to 110% of DOC. The Viveiro wastewater was highly enriched in POC (annual average of 7800±4700 μM, Table 2), 250 times the Landro River concentration (32±22 μM), and POC discharges to the Ria of Viveiro (Table 2) were similar (73-830 mmol·$s^{-1}$) to the Landro River load (29-1940 mmol·$s^{-1}$), except for during summer (≈10 times higher the wastewater flux than fluvial). The same concentration pattern was found in the Mera River (22±17 μM) and Ortigueira WWTP sewage (128±69 μM) although this was slightly enriched in POC (6 times). Contrary to what was observed in the Ria of Viveiro, the fluvial input of POC discharged from the Mera River (23±17 mmol·$s^{-1}$, Table 2) was higher when compared with the Ortigueira WWTP sewage load (1.2±0.6 mmol·$s^{-1}$).

The organic nitrogen (TON) in the river waters was mainly present in the dissolved form (DON). Particulate organic nitrogen (PON) accounted for less than a 5% of TON (Table 2). Both rivers had similar DON concentrations during 2008 (Mera: 53±10 μM and Landro: 47±8 μM) while PON was variable. The

Landro River had higher concentrations and greater ranges of PON (1-8 μM; average 2.4±1.9 μM) than the Mera River (0.4-3.6 μM; 1.5±1.0 μM). In the Ortigueira WWTP effluent, DON concentration (440±440 μM) was eight times the values found in the Mera River water (53±10 μM). PON concentration (8.5±5.6 μM ) was six times the Mera River average. Ortigueira WWTP dissolved and particulate nitrogen loads (ranging from 0.4 to 10.8 and from 0.01 to 0.19 mmol·$s^{-1}$, respectively) were less than 5% of the Mera River input (9-830 and 0.36-3.57 mmol·$s^{-1}$, respectively; Table 2). The Viveiro wastewater effluent was highly enriched in organic nitrogen: average wastewater DON concentrations (2760±2260 μM) were 56 times higher than the Landro River water (47±8 μM), while PON concentration (730±420 μM) were, on average, 317 times higher with respect to the river (2.4±1.9 μM). Loading rates of DON to the Ria of Viveiro from wastewater (141±107 mmol·$s^{-1}$, Table 2) were only 10% those of the Landro River input (450±410 mmol·$s^{-1}$), although from July to October these fluxes were at least as important as the fluvial ones (up to 3 times higher). The discharge of PON from the Viveiro wastewater (6-83 mmol·$s^{-1}$) was similar to the river load (3-192 mmol·$s^{-1}$), *i.e.* 12 times greater than that of the river during summer.

### *4.4. Dissolved trace metals*

The waters of the Landro and Mera Rivers had similar ranges of dissolved metal concentrations (Table 3). The exception was Al and Co that showed higher concentrations in the Landro River. Chromium remained below the detection limit (0.42 nM).

Trace metal concentrations in the two wastewater effluents were quite different (Table 3). In the Ria of Ortigueira water, the treated effluent had similar or slightly higher concentrations of dissolved metals than in the Mera River. The concentration Ratio (CR) of metals between wastewater and river water were higher than two for Pb (CR=4.3), V (5.1) and Zn (5.3) and closer to unity for Cd and Cu. However, sewage loading rates of metals flowing into the Ria of Ortigueira only accounted for 1-5% to Al, Co, Ni, Pb, V and Zn and less than 1% for the remaining metals of the Mera River fluxes (Table 3). For example, the range of the Mera River loads were <0.3-24.7 μmol·$s^{-1}$ of Co and 192-4260 μmol·$s^{-1}$ of Fe, while the treated sewage only contributed <0.001-0.068 μmol·$s^{-1}$ of Co and 2.4-10.5 μmol·$s^{-1}$ of Fe, i.e. two orders of magnitude lower, to the ria.

The Viveiro wastewater effluent, municipal+industrial, was highly enriched in dissolved metals (Table 3). Compared to the Landro River, dissolved Cd (CR=17), V (18), Pb (26), Zn (33) and Cu (142) were enriched in the wastewater effluent. Dissolved trace metal contributions from wastewater to the Ria of Viveiro were, in general, lower than those from the fluvial input (Table 3). For example, 2-242 μmol·$s^{-1}$ of Co and 2400-16700 μmol·$s^{-1}$ of Fe were discharged by the Landro River to the ria; in comparison, their fluxes in the wastewater were 0.07-0.46 μmol·$s^{-1}$ of Co and 52-286 μmol·$s^{-1}$ of Fe. Wastewater loads did not exceed one tenth of river discharges for Al, Co, Fe, and Ni and two-thirds for Cd, Pb, Cr, V and Zn. The amount of Cu in wastewater flux (4.3±2.1 μmol·$s^{-1}$) of Viveiro was two hundred times higher than in the load (0.021±0.028 μmol·$s^{-1}$) of the Ortigueira WWTP.

### *4.5. Particulate trace metals*

Fluvial particulate trace metal concentrations, calculated multiplying SPM concentration in water by SPM metal content, showed similar ranges for both the Mera and Landro Rivers (Table 4). Higher concentrations of Cr, Cu, Ni and V were observed in the Mera River (up to 9 nM of Cu, 9 nM of Ni, 12 nM of V and 16 nM of Zn) while the Landro River showed an increased level of Pb (1.4 nM of Pb). The variation of all particulate trace metals parallels the time evolution of SPM concentration in both rivers. In wastewaters there was only a statistically significant correlation particulate metal-SPM for Cu, Pb and V in the Ortigueira WWTP and for Cr, Ni, Pb and Zn in the Viveiro.

Particulate trace metal concentrations in the wastewater showed a greater variation than did river waters (Table 4). Surprisingly, the treated wastewater of Ortigueira contained only a low fraction of particulate trace metals, which accounted for only up to 3% the Mera River load. Otherwise, in the Ria of Viveiro particulate trace metal concentrations were enriched in the wastewater with respect to the Landro River. The increased metal concentration ratio was between 10 and 30 to Fe, Al, V and from 31 to 60 to Cr, Ni, Pb, Cd and CR higher than 100 to Cu and Zn. In the Ria of Viveiro, particulate trace metal loading rates of wastewater were lower than in the fluvial with fluxes ratios <0.5 for Al, Co, Cr, Fe, Ni and V (Table 4). Wastewater effluent was higher than in the fluvial for Zn (average of 63 $\mu mol\cdot s^{-1}$ vs. 20 $\mu mol\cdot s^{-1}$) and seasonally for Cu in summer (FR≈7.5) and Cd in autumn-winter (FR≈3.5).

## 5. Discussion

### *5.1. Eutrophication: the role of wastewater efluents*

The Rias of Ortigueira and Viveiro are paradigmatic due to the absence of upwelling events inside ria (Ospina-Álvarez et al. 2014a). For this reason, as usually occurs in estuaries (Aston, 1980), the continental supply of nutrients is a key factor controlling primary production in these rias. In this way, the nitrate concentration, which is the largest DIN fraction (98%), in the Mera and Landro Rivers were within the concentration range of less anthropogenically affected rivers along the Cantabrian coast (Prego and Vergara, 1998). Phosphate concentrations in these two rivers were within the range for natural waters (0.1-0.8 μM; Meybeck et al., 1996). Based on the freshwater concentrations of inorganic nitrogen and phosphorous in the Mera and Landro Rivers (Table 2), both rivers can be classified as oligotrophic (Smith, 2009). Moreover, dissolved silicate fit the overall range for pristine rivers in medium sized watershed (Meybeck, 2003), too.

In comparison with the fluvial nutrients, the wastewater discharge of DIN, unlike rivers, was mainly due to ammonium, resulting from the anaerobic mineralization of organic matter during WWTP treatment and untreated waste possibly from the industry of Celeiro harbor. However, the wastewater concentration of DIN in both rias was 25% of average concentration in urban sewage (Aktar, 2009). Dissolved silicate release was controlled by the water volumes and presented similar concentrations in both waste and river waters. Thus, fluvial fluxes control the nitrate, DIN as well (Table 2), and dissolved silicate inputs to the Rias of Ortigueira and Viveiro (Table 2). Phosphate consumption showed a big difference between the two wastewater effluents. The phosphate loading rates from the Ortigueira WWTP were not significant with regard to the Mera River discharge (Figure 3); in contrast, a high phosphate concentration was observed in the Viveiro wastewater (129±107 μM versus 0.12±0.08 μM of Mera water), which was much higher than wastewaters from urban sources (Aktar, 2009). Phosphate concentrations in the Viveiro wastewater were in the order of magnitude of the untreated wastewater (130-400 µM-P; Carey and Migliaccio, 2009). Thus, the loading rates from Viveiro wastewater were high with a flux ratio of 12 in relation to those of the Landro River. Despite this FR, it is necessary to note that the wastewater loads may decrease during the night (Ort and Gujer, 2006; Plósz et al., 2010), but that of the river did not, and the daily wastewater load should be lower than the daytime flux. In spite of this, the phosphate discharges to the Ria of Viveiro can be considered, at least, of the same order of magnitude as that of river load. The same pattern was observed in Plymouth Sound (UK) where wastewater delivery of phosphate accounted for 93% of the total input to the estuary (Nedwell et al., 2002).

The nutrient availability is crucial after the spring bloom when nutrients are close to depletion in the Rias of Ortigueira and Viveiro (Ospina-Alvarez et al., 2010; Prego et al, 2012) and fluvial nutrients contribution decreases with the river flows (Prego and Vergara, 1998). The relevance of wastewater phosphate shows a remarkable pattern in the ria of Viveiro but also the loading rate varied during the year. The maximum phosphate flux (Figure 3) in July-October (FR≈30) may promote ria eutrophication. Ammonium showed a similar pattern to that of phosphate (Fig. 3), but the continental DIN contribution to these rias, the limiting nutrient to ria primary production (Ospina- Alvarez et al., 2010; Prego et al, 2012), was controlled by fluvial nitrate. So, with the exception of phosphate in Viveiro, nutrients from fluvial origin remained as the dominant input to both rias.

Therefore, in these rias the typical eutrophication effects, e.q. an accelerated algae growth, usual in many world estuaries (de Jonge et al., 2002), was not observed (Ospina-Alvarez et al., 2014a) as yet.

The low availability of nutrients from continental sources to the Rias of Ortigueira and Viveiro is the other key, together with the absence of upwelling events, which explains why they have been classified as of the oligo-mesotrophic ria-type (Ospina-Álvarez et al. 2014a). Contrary to these non- upwelling rias, in the upwelling rias large regular injections of inorganic nutrients occurs during upwelling episodes (Prego, 2002). Scaling the nutrient salts to carbon units, these upwelling rias may be considered as net autotrophic (Dale and Prego, 2005; Evans et al., 2011). The Rias of Ortigueira and Viveiro showed a trend towards net heterotrophy in marine systems (Smith et al., 1991). In this way, total organic carbon supply to the Mera and Landro Rivers comes mainly in the dissolved form (Table 2) and the value of the contributions of organic carbon in these rivers is below that provided by rivers in the temperate zone (Meybeck, 1982).

The loading rates of dissolved organic carbon and nitrogen from wastewater to both rias were lower than 10% of fluvial and <20% to POC and PON in the Ria of Ortigueira. The exception was the particulate organic matter in the Ria of Viveiro. The concentration of total nitrogen (DIN+TON) in the effluent of Vivero was within the typical range for untreated wastewater with low input of industrial wastewater (2.1-7.1 mM of N; Henze and Comeau, 2008). The POC and PON may affect the ria only during summer, as was the aforementioned case of phosphate, when POC and PON fluxes surpassed the fluvial loading rates (Figure 4) and floods are very unusual events to decrease the wastewater/river ratio of POC (FR≈10) and PON (FR≈11). In spite of this, the supply of organic matter from wastewater to the Ria of Viveiro would not promote eutrophication, as is the case for typical estuaries of the world affected by agriculture and increasing human population (e.g. the Humber; Boyes and Elliott, 2006).

### *5.2. Metal contamination: relevance of untreated wastewater*

The concentrations of total trace metals (dissolved + particulate) in the Mera and Landro Rivers for Al, Cd, Cr, Cu, Ni, Pb and Zn were within the background range for natural river waters (Salomons and Förstner, 1984; Gaillardet et al., 2003). In addition, concentrations of total Co, Cu and Zn, defined as key trace elements by Goldman (2010), did not exceed the ranges provided by this author for natural surface waters. Particulate Al and Fe concentrations were higher than in the dissolved phase, as expected in rivers (Salomons and Föstner, 1984). Thus, the composition of the dissolved fraction of trace metals in the Mera and Landro Rivers reflects a natural source related to the aluminosilicates produced by the weathering of soils and base rocks (White, 2003) in their catchment basins (Carral et al., 1995; Bernárdez et al., 2012). The contents of trace metals in the SPM provides evidence of their natural origin. They were not higher than those for river suspended sediments (Salomons and Förstner, 1984) and showed similar contents to those of Galician soils (Macías-Vázquez and Calvo-Anta, 2008). Moreover, dissolved trace metal concentrations did not exceed those measured in pristine world rivers (Hart and Hines, 1995). For these reasons the trace metals in the Mera and Landro Rivers did not show any evidences of contamination.

Concentrations of metals in the pristine Mera and Landro Rivers presented a suitable reference to assess the human influence in the wastewater from Ortigueira and Viveiro. Average concentrations of metals in the sewage effluent from the Ortigueira WWTP were in the same order of magnitude as those measured in the Mera River (except for dissolved V and Zn with CR≈5). The wastewater effluent of Viveiro showed high metal enrichments in comparison with those of the Landro River freshwater. The total concentration of Al and Zn were within, or above, the typical ranges in urban wastewater with low contribution of industrial wastewater (Henze and Comeau, 2008). The remainder of the concentrations of metals were below the typical ranges in urban wastewater. In the Ortigueira WWTP metals should be removed during the wastewater treatment (Brown et al., 1973; Karvelas et al., 2003). However, primary treatment removes only metals present in an insoluble form. During secondary treatment, dissolved metals may be removed by association with the sinking biomass in the sludge (Lester, 1983). However, coagulation-flocculation cannot treat the metal wastewater completely (Fu and Wang, 2011). This partial removal of metals, as observed in other estuaries (Deycard et al., 2014), may explain the low presence of metals in the Ortigueira WWTP outflow in comparison with the Viveiro wastewater. The distribution coefficient between dissolved and particulate metals of Al, Cr, Cu and Fe, with $K_{dp}$ ranging from 0.2 to 0.7, in the wastewater of Ortigueira and $K_{dp}$ from 0.1 to 0.5 Al, Cr, Cu, Fe and Pb in the wastewater of Viveiro showed as the particle-reactive elements all have relatively low dissolved concentrations. Similarly, Cd and Pb with $K_{dp}$≈5, Ni and Zn ($K_{dp}$≈50) and V ($K_{dp}$>100) in the wastewater of Ortigueira and Cd, Co and Ni with $K_{dp}$ =1.5-2.5, Zn (k≈1) and V ($K_{dp}$≈20) in the wastewater of Viveiro are not likely to undergo particle-water interactions and this increase in the dissolved phase may be due to metal-colloid associations (Shafer et al., 2004).

The loading rates of dissolved and particulate trace metals from the Mera and Landro Rivers (Table 3 and 4), were similar to or even below those the lowest among all rivers draining into the North Sea from the UK (Neal & Davies, 2003). In the Ria of Ortigueira the average flux ratio of metals between wastewater and river water were between 0.1 and 0.01 to dissolved Al, Co, Ni, Pb, V and Zn and particulate Al and Cr; the remaining metals showed FR lower than 0.01. In the Ria of Viveiro the average of FR was between 0.4 and 0.1 to dissolved Cd, Cr, Pb and Zn and particulate Al, Cr, Fe, Ni, and V; FR between 0.1 and 0.01 to dissolved Al, Co, Fe and Ni, and to particulate Co. The FR of these metals may decrease if the flood events are considered. Fluvial flows during samplings reached to 17.2 $m^3 \cdot s^{-1}$ and 25.3 $m^3 \cdot s^{-1}$ in the Mera and Landro Rivers, respectively. River flows exceeded the aforementioned ranges at various times during the study period, all of which were during the wet season, i.e. from November to February (Fig. 2), except one from April 9-10. Hence, metal dumping in wastewater to the Ria of Ortigueira is very low compared to the fluvial flux and do not contaminate the ria environment. The same is true of the aforementioned metals discharged through the wastewater to the Ria of Viveiro. Their loading rates are lower compared with those of contaminated rivers with untreated wastewaters flowing to the Ria of Ferrol (Cobelo-García et al., 2004) or the dissolved metal outputs from other sources in the Ria of Vigo, as the benthic fluxes, except for Zn which was similar, (Santos-Echeandía et al., 2009) and land-sea exchanges in the wide Ria of Vigo (Prego et al., 2006; 2010). At a local scale, the wastewater fluxes of Co, Cr and Ni in the Ria of Ortigueira were around 1% of diffuse fluxes in intertidal flats (Ospina-Alvarez et al., 2014b) and in the rainfall (Prego et al., 2014).

The loading rates of dissolved Cd, Cu and Zn and particulate Cu from wastewater to the Ria of Viveiro showed a different pattern during summer in relation to the other metals. From July to October, when flood events were not observed until now, the wastewater fluxes of these metals exceeded the fluvial (exemplified by Cu in Figure 5). Their FRs ranged from 3 to 18 and, although wastewater loads may decrease during the night (Ort and Gujer, 2006; Plósz et al., 2010), the discharge of these potentially toxic elements (Thornton et al., 2001) in the wastewater effluent from Viveiro may be a contamination source during summer to that ria, while the wastewater contribution of Cd, Cu and Zn is irrelevant compared with the fluvial contribution in the Ria of Ortigueira (Fig. 5).

## 6. Conclusions

The Rias of Ortigueira and Vivieiro may depict the common features of small temperate mesotrophic estuarine systems (<40 $km^2$ of surface area) where streams/small rivers (<10 $m^3 \cdot s^{-1}$ of annual average flow) run into the sea, eleven rias in the Galician coast and eight in the Cantabrian coast are of this type. Rivers are quite similar and pristine in both western Cantabrian rias. Therefore, the Mera and Landro Rivers provide a suitable reference for contamination studies. Dissolved and particulate metal loads from the Ortigueira WWTP sewage were less than 5% of the Mera River load and the uncontaminated fluvial contributions of nutrients, organic matter and trace metals were the main continental sources, even during the dry season. Wastewater fluxes of nutrient salts, organic matter and trace metals were higher in the Ria of Viveiro than in the Ria of Ortigueira. Moreover, wastewater discharges of phosphate, POC, PON, DON, dissolved Cu and particulate Cd, Cu, Pb and Zn into the Ria of Viveiro exceeded the fluvial (the Landro River). In spite of urban sewage treatment, untreated wastewater effluents from the canning industry and fish food processing in small fishing ports can be a source of contamination, mainly during summer, to estuaries and rias. Thus, the pristine conditions must be preserved through wastewater treatment even for small coastal systems with less than 70 $inhab \cdot km^2$.

The Rias of Ortigueira and Vivieiro are useful as a reference point to evaluate fluvial pristine patterns and wastewater discharges on small estuary-ria receptor systems.


## Aknowledgements

We sincerely thank the staff of INTERESANTE and MEFIO projects for their kind cooperation during the sampling, 'Delegación Territorial en Lugo of Consellería de Medio Rural e do Mar' for laboratory facilities in the Celeiro harbor and 'Augas de Galicia' for river and wastewater flow data. The authors also thank the meticulous review and valuable comments of two anonymous reviewers and the kind English language review by Prof. Graham Evans (National Oceanography Centre, Southampton, UK). Dr. Ospina-Alvarez gratefully acknowledges support from AXA Research Fund (Paris, France). This study was supported by the Spanish programs of CICYT (INTERESANTE project, ref. CTM2007-62546- C03/MAR) and (MEFIO (ref. CTM2011-28792-C02).

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Table 1. Accuracy control (n=6) of the analytical procedures for dissolved and particulate metal determinations (average ± SD). River water certified reference material (SLRS-4) and marine sediment (PACS-2) from the National Research Council of Canada.

| | Dissolved (SLRS-4) in $\mu g \cdot L^{-1}$ | | Particulate (PACS-2) in $\mu g \cdot g^{-1}$ | |
|---|---|---|---|---|
| | Certified | Obtained | Certified | Obtained |
| Al | 54 ± 4 | 65 ± 11 | 66.1 ± 5.3 | 62.5 ± 2.1 |
| Cd | 0.012 ± 0.002 | 0.015 ± 0.002 | 2.11 ± 0.15 | 2.06 ± 0.05 |
| Co | 0.033 ± 0.006 | 0.029 ± 0.003 | 11.5 ± 0.3 | 11.4 ± 0.1 |
| Cr | 0.33 ± 0.02 | 0.29 ± 0.03 | 90.7 ± 4.6 | 89.5 ± 0.6 |
| Cu | 1.81 ± 0.08 | 1.72 ± 0.13 | 310 ± 12 | 310 ± 9 |
| Fe | 102 ± 5 | 101 ± 2 | 40.9 ± 0.6 | 39.9 ± 1.0 |
| Ni | 0.67 ± 0.08 | 0.63 ± 0.05 | 39.5 ± 2.3 | 40.5 ± 1.3 |
| Pb | 0.086 ± 0.007 | 0.079 ± 0.005 | 183 ± 8 | 190 ± 3 |
| V | 0.32 ± 0.03 | 0.34 ± 0.01 | 133 ± 5 | 135 ± 4 |
| Zn | 0.93 ± 0.10 | 0.80 ± 0.10 | 364 ± 23 | 372 ± 10 |

Table 2. Range and average (± SD) concentrations (μM) and loading rates ($mmol \cdot s^{-1}$) of nutrient salts, dissolved and particulate organic carbon and nitrogen running into the two studied rias during one year of monthly sampling.

| | nitrate | nitrite | ammonium | DIN* | phosphate | silicate | DOC | POC | DON | PON |
|---|---|---|---|---|---|---|---|---|---|---|
| Ria of Ortigueira: the Mera River | | | | | | | | | | |
| Concentration range | 36 - 80 | 0.07 - 0.33 | 0.09 - 1.23 | 37 - 80 | 0.02 - 0.30 | 111 - 204 | 56 - 164 | 8 - 67 | 38 - 68 | 0.4 - 3.6 |
| Mean ± SD | 53 ± 13 | 0.19 ± 0.08 | 0.63 ± 0.39 | 54 ± 13 | 0.12 ± 0.08 | 166 ± 34 | 112 ± 34 | 23 ± 17 | 53 ± 10 | 1.5 ± 1.0 |
| Flux range | 6 - 1210 | 0.03 - 2.35 | 0.14 - 5.57 | 6 - 1220 | 0.01 - 1.91 | 35 - 3030 | 23 - 1270 | 8 - 67 | 9 - 830 | 0.36 - 3.57 |
| Mean ± SD | 310 ± 370 | 0.73 ± 0.64 | 1.67 ± 1.72 | 313 ± 369 | 0.54 ± 0.61 | 780 ± 870 | 490 ± 440 | 23 ± 17 | 214 ± 238 | 1.52 ± 1.02 |
| Ortigueira wastewater | | | | | | | | | | |
| Concentration range | 4 - 146 | 0.2 - 7.3 | 142 - 1640 | 193 - 1650 | 2.9 - 8.1 | 150 - 333 | 355 - 840 | 20 - 236 | 44 - 1800 | 0.9 - 20.4 |
| Mean ± SD | 51 ± 42 | 3.1 ± 2.2 | 870 ± 450 | 930 ± 430 | 4.4 ± 1.4 | 265 ± 51 | 600 ± 180 | 128 ± 69 | 440 ± 440 | 8.5 ± 5.6 |
| Flux range | 0.04 - 1.59 | 0.002 - 0.068 | 0.8 - 14.2 | 1.1 - 14.8 | 0.02 - 0.09 | 1.6 - 3.2 | 3.3 - 7.8 | 0.2 - 2.2 | 0.4 - 10.8 | 0.01 - 0.19 |
| Mean ± SD | 0.50 ± 0.48 | 0.030 ± 0.023 | 7.9 ± 3.7 | 8.5 ± 3.7 | 0.04 ± 0.02 | 2.3 ± 0.4 | 5.3 ± 1.4 | 1.2 ± 0.6 | 3.4 ± 3.9 | 0.07 ± 0.05 |
| Ria of Viveiro: the Landro River | | | | | | | | | | |
| Concentration range | 35 - 78 | 0.07 - 0.35 | 0.20 - 1.86 | 35 - 78 | 0.02 - 0.34 | 97 - 169 | 105 - 425 | 14 - 77 | 36 - 61 | 0.9 - 7.6 |
| Mean ± SD | 48 ± 15 | 0.17 ± 0.08 | 0.89 ± 0.56 | 49 ± 16 | 0.14 ± 0.11 | 134 ± 23 | 217 ± 97 | 32 ± 22 | 47 ± 8 | 2.4 ± 1.9 |
| Flux range | 78 - 1000 | 0.4 - 2.7 | 1.1 - 28.3 | 81 - 1030 | 0.3 - 10.6 | 350 - 2650 | 340 - 6660 | 29 - 1940 | 100 - 1370 | 3 - 192 |
| Mean ± SD | 450 ± 330 | 1.3 ± 0.7 | 7.0 ± 7.7 | 460 ± 340 | 1.8 ± 2.9 | 1240 ± 770 | 2360 ± 2390 | 460 ± 660 | 450 ± 410 | 34 ± 56 |
| Viveiro wastewater | | | | | | | | | | |
| Concentration range | 28 - 319 | 1 - 48 | 188 - 1430 | 293 - 1530 | 18 - 380 | 109 - 262 | 1310 - 19700 | 1370 - 15200 | 404 - 7270 | 120 - 1810 |
| Mean ± SD | 111 ± 89 | 24 ± 16 | 550 ± 370 | 750 ± 430 | 129 ± 107 | 203 ± 47 | 7100 ± 6070 | 7800 ± 4700 | 2760 ± 2260 | 730 ± 420 |
| Flux range | 1.3 - 18.8 | 0.06 - 2.5 | 9.0 - 75.9 | 11 - 81 | 1 - 18 | 7.2 - 13.4 | 91 - 950 | 73 - 830 | 21 - 349 | 6 - 83 |
| Mean ± SD | 6.4 ± 5.5 | 1.3 ± 0.8 | 30 ± 21 | 35 ± 24 | 6.7 ± 5.1 | 10.8 ± 2.0 | 360 ± 280 | 410 ± 270 | 141 ± 107 | 39 ± 21 |

*Dissolved inorganic nitrogen (nitrate + nitrite + ammonium)

Table 3. Range and average (± SD) values of concentrations (nM) and loading rates (μmol·s$^{-1}$) of dissolved metals running into the two studied rias during one year of monthly sampling.

| | Al | Cd | Co | Cr | Cu | Fe | Ni | Pb | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Ria of Ortigueira: Mera River | | | | | | | | | | |
| Concentration range | 340 - 1780 | <0.03 - 0.28 | <0.15 - 4.8 | <0.4 | <0.4 - 8.9 | 250 - 1130 | 6 - 35 | <0.05 - 0.65 | 5 - 17 | 15 - 42 |
| Mean ± SD | 790 ± 480 | 0.12 ± 0.10 | 1.7 ± 1.4 | <0.4 | 4.2 ± 3.3 | 530 ± 310 | 16 ± 8 | 0.29 ± 0.24 | 12 ± 4 | 26 ± 8 |
| Flux range | 79 - 13000 | <0.005 - 3.8 | <0.29 - 24.7 | <7 | <0.4 - 71 | 192 - 4260 | 1.9 - 258 | <0.01 - 11.2 | 3 - 250 | 4 - 420 |
| Mean ±SD | 4340 ± 4680 | 0.92 ± 1.37 | 5.9 ± 7.6 | 2.2 ± 2.3 | 18 ± 22 | 1780 ± 1350 | 79 ± 82 | 2.3 ± 3.6 | 57 ± 75 | 141 ± 148 |
| Ortigueira wastewater | | | | | | | | | | |
| Concentration range | <320 - 4990 | 0.08 - 0.29 | 0.2 - 6.3 | <0.4 - 2.9 | <0.4 - 8.4 | 221 - 1610 | 15 - 33 | 0.3 - 1.9 | 15 - 130 | 59 - 216 |
| Mean ± SD | 1660 ± 1850 | 0.15 ± 0.08 | 3.5 ± 1.9 | 0.9 ± 0.9 | 2.4 ± 2.4 | 790 ± 440 | 26 ± 5 | 0.70 ± 0.59 | 61 ± 42 | 143 ± 51 |
| Flux range | <3 - 49 | 0.0005 - 0.0035 | <0.001 - 0.068 | <0.002 - 0.029 | <0.004 - 0.082 | 2.4 - 10.5 | 0.14 - 0.32 | 0.002 - 0.018 | 0.13 - 1.20 | 0.6 - 2.3 |
| Mean ±SD | 13 ± 15 | 0.0014 ± 0.0009 | 0.031 ± 0.019 | 0.009 ± 0.009 | 0.021 ± 0.028 | 6.5 ± 2.6 | 0.23 ± 0.05 | 0.006 ± 0.006 | 0.56 ± 0.42 | 1.3 ± 0.6 |
| Ria of Viveiro: the Landro River | | | | | | | | | | |
| Concentration range | 320 - 5140 | <0.03 - 0.46 | 1.0 - 10.7 | <0.4 | <0.4 - 2.2 | 350 - 1550 | 10 - 42 | <0.05 - 0.63 | 3 - 18 | 14 - 53 |
| Mean ± SD | 1960 ± 1300 | 0.14 ± 0.15 | 3.4 ± 3.3 | <0.4 | 0.83 ± 0.64 | 850 ± 380 | 21 ± 10 | 0.20 ± 0.20 | 8.3 ± 5.0 | 29 ± 10 |
| Flux range | 2800 - 116000 | <0.06 - 11.7 | 2 - 242 | <10 | <1 - 43 | 2400 - 16700 | 19 - 1050 | <0.1 - 15.9 | 13 - 250 | 50 - 1330 |
| Mean ±SD | 20200 ± 3330 | 2.1 ± 3.3 | 55 ± 89 | 4.2±3.3 | 9.4 ± 14.1 | 7150 ± 5520 | 275 ± 330 | 2.9 ± 4.6 | 66 ± 63 | 320 ± 360 |
| Viveiro wastewater | | | | | | | | | | |
| Concentration range | 340 - 3040 | 0.3 - 7.8 | 1.1 - 6.9 | 4.5 - 16.6 | 33 - 166 | 1020 - 5010 | 22 - 62 | 1.2 - 9.8 | 76 - 278 | 222 - 1560 |
| Mean ± SD | 1560 ± 920 | 2.7 ± 2.4 | 4.3 ± 2.0 | 10.8 ± 3.4 | 81 ± 42 | 2180 ± 1140 | 33 ± 11 | 4.4 ± 3.0 | 145 ± 67 | 820 ± 490 |
| Flux range | 18 - 152 | 0.02 - 0.40 | 0.07 - 0.46 | 0.26 - 0.76 | 2.1 - 8.8 | 52 - 286 | 1.2 - 3.0 | 0.06 - 0.52 | 3.8 - 15.3 | 16 - 77 |
| Mean ±SD | 83 ± 46 | 0.15 ± 0.13 | 0.23 ± 0.12 | 0.57 ± 0.15 | 4.3 ± 2.1 | 118 ± 63 | 1.8 ± 0.6 | 0.24 ± 0.17 | 7.8 ± 3.8 | 43 ± 23 |

Table 4. Range and average (± SD) values of concentrations (nM) and loading rates (µmol·$s^{-1}$) of particulate metals running into the two studied rias during one year of monthly sampling.

| | Al | Cd | Co | Cr | Cu | Fe | Ni | Pb | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Ria of Ortigueira: the Mera River | | | | | | | | | | |
| Range | 540 - 7630 | <0.002 - 0.034 | 0.2 - 2.7 | <0.1 - 11.7 | 0.9 - 8.5 | 1120 - 4620 | 1.1 - 9.4 | <0.02 - 0.77 | 1.4 - 12.5 | 2 - 16 |
| Mean ± SD | 3160 ± 2300 | 0.020 ± 0.012 | 1.5 ± 0.8 | 5.1 ± 3.5 | 3.0 ± 2.3 | 2160 ± 970 | 3.9 ± 2.6 | 0.31 ± 0.24 | 4.3 ± 3.7 | 6.3 ± 3.9 |
| Flux range | 92 - 81400 | <0.001 - 0.45 | 0.04 - 35.3 | 0.4 - 119 | 1 - 49 | 247 - 49800 | 0.2 - 103 | 0.01 - 13 | 2 - 137 | 0.4 - 148 |
| Mean ±SD | 21000 ± 26800 | 0.09 ± 0.13 | 9.4 ± 10.7 | 30 ± 42 | 15 ± 16 | 12200 ± 14200 | 23 ± 31 | 2.6 ± 4.1 | 29 ± 42 | 41 ± 51 |
| Ortigueira wastewater | | | | | | | | | | |
| Range | 1780 - 12600 | <0.004 - 0.033 | <0.02 | <0.2 - 23.9 | 0.3 - 8.2 | 266 - 2830 | <0.15 - 0.81 | <0.04 - 0.87 | <0.1 | 1 - 32 |
| Mean ± SD | 7250 ± 3920 | 0.085 ± 0.093 | <0.02 | 7.8 ± 7.8 | 3.3 ± 2.4 | 1450 ± 980 | 0.31 ± 0.21 | 0.23 ± 0.27 | <0.1 | 14 ± 12 |
| Flux range | 15 - 142 | $<0.6\cdot10^{-5}$ - $20\cdot10^{-5}$ | $<0.3\cdot10^{-4}$ - $4.1\cdot10^{-4}$ | <0.0004 - 0.26 | 0.002 - 0.089 | 2.5 - 26.1 | <0.001 - 0.005 | <0.0001 - 0.0080 | $<1\cdot10^{-4}$ - $16\cdot10^{-4}$ | <0.01 - 0.35 |
| Mean ±SD | 66 ± 42 | $6.8\cdot10^{-5} \pm 6.1\cdot10^{-5}$ | $2.3\cdot10^{-4} \pm 1.1\cdot10^{-4}$ | 0.08 ± 0.09 | 0.030 ± 0.026 | 12.4 ± 8.0 | 0.003 ± 0.002 | 0.0018 ± 0.0023 | $9.6\cdot10^{-4} \pm 4.4\cdot10^{-4}$ | 0.09 ± 0.12 |
| Ria of Viveiro: the Landro River | | | | | | | | | | |
| Range | 480 - 7640 | <0.001 - 0.054 | <0.004 - 2.6 | <0.08 - 13.7 | <0.1 - 3.2 | 840 - 4540 | <0.04 - 6.95 | <0.01 - 1.42 | <0.01 - 1.42 | 1.4 - 5.7 |
| Mean ± SD | 3550 ± 2420 | 0.02 ± 0.02 | 0.9 ± 0.8 | 2.8 ± 3.8 | 1.1 ± 0.8 | 2200 ± 1230 | 1.7 ± 1.9 | 0.4 ± 0.4 | 1.1 ± 1.5 | 3.9 ± 1.5 |
| Flux range | 1090 - 172000 | <0.001 - 0.83 | <0.01 - 58 | <0.6 - 311 | <1 - 72 | 2790 - 102400 | <0.6 - 157 | <0.03 - 32 | <0.03 - 105 | 3.1 - 51.2 |
| Mean ±SD | 40400 ± 50800 | 0.17 ± 0.26 | 12.5 ± 17.1 | 36 ± 87 | 13.6 ± 19.7 | 24030 ± 28800 | 23 ± 44 | 6.4 ± 9.9 | 13 ± 31 | 19.7 ± 15.7 |
| Viveiro wastewater | | | | | | | | | | |
| Range | 14000 - 85900 | 0.4 - 3.7 | 1.8 - 10.5 | 11 - 162 | 65 - 402 | 2810 - 28500 | 3 - 87 | 4 - 67 | 1 - 63 | 169 - 3210 |
| Mean ± SD | 48300 ± 26600 | 1.5 ± 0.9 | 4.5 ± 3.1 | 70 ± 47 | 192 ± 96 | 14500 ± 9200 | 38 ± 28 | 29 ± 20 | 27 ± 23 | 1220 ± 940 |
| Flux range | 744 - 4660 | 0.019 - 0.183 | <0.2 - 0.62 | 0.7 - 11.4 | 3.4 - 28.2 | 146 - 1620 | 0.18 - 6.07 | 0.20 - 4.69 | 0.08 - 3.32 | 9 - 154 |
| Mean ±SD | 2590 ± 1510 | 0.084 ± 0.046 | 0.20 ± 0.19 | 4.0 ± 3.2 | 10.7 ± 6.9 | 770 ± 500 | 2.1 ± 1.7 | 1.6 ± 1.3 | 1.5 ± 1.2 | 63 ± 46 |

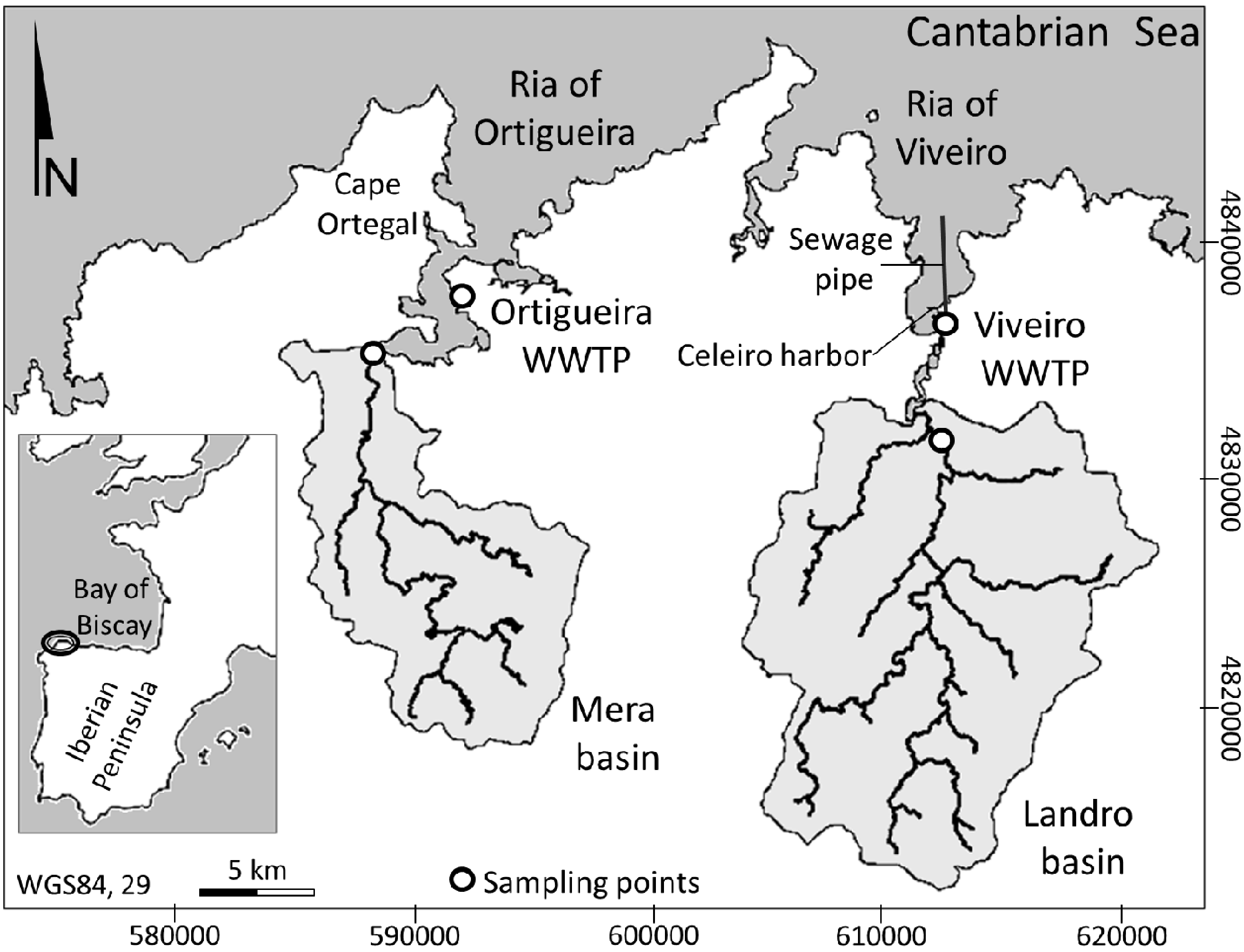


Figure 1. Geographic setting of the fluvial basins and wastewater treatment plants (WWTPs) of the Western Cantabrian coast (Bay of Biscay) from Sitga (http://mapas.xunta.es/portada) and Sigpac (http://sigpac.mapa.es/fega/visor/). The Mera River and the Ortigueira WWTP flowing into the Ria of Ortigueira; the Landro River and the Viviero WWTP (together with an untreated flux from the Celeiro) flowing into the Ria of Viveiro.

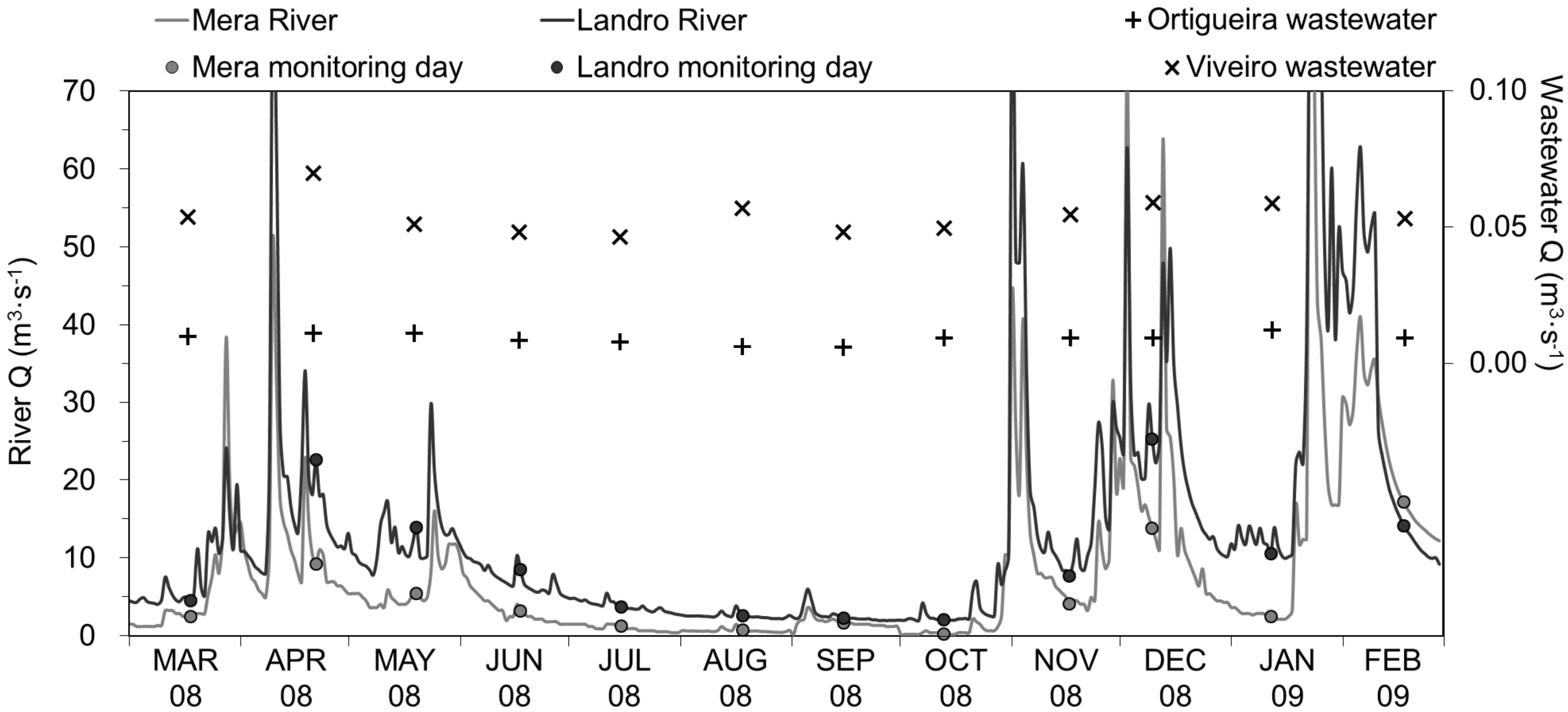


Figure 2. Continental discharges to the Ria of Ortigueira and the Ria of Viveiro from March 2008 to February 2009. Daily flow from the Mera and Landro Rivers showing dates of the sampling dates and wastewater dumping from Ortigueira and Viveiro (data supplied by 'Augas-de-Galicia' Company).

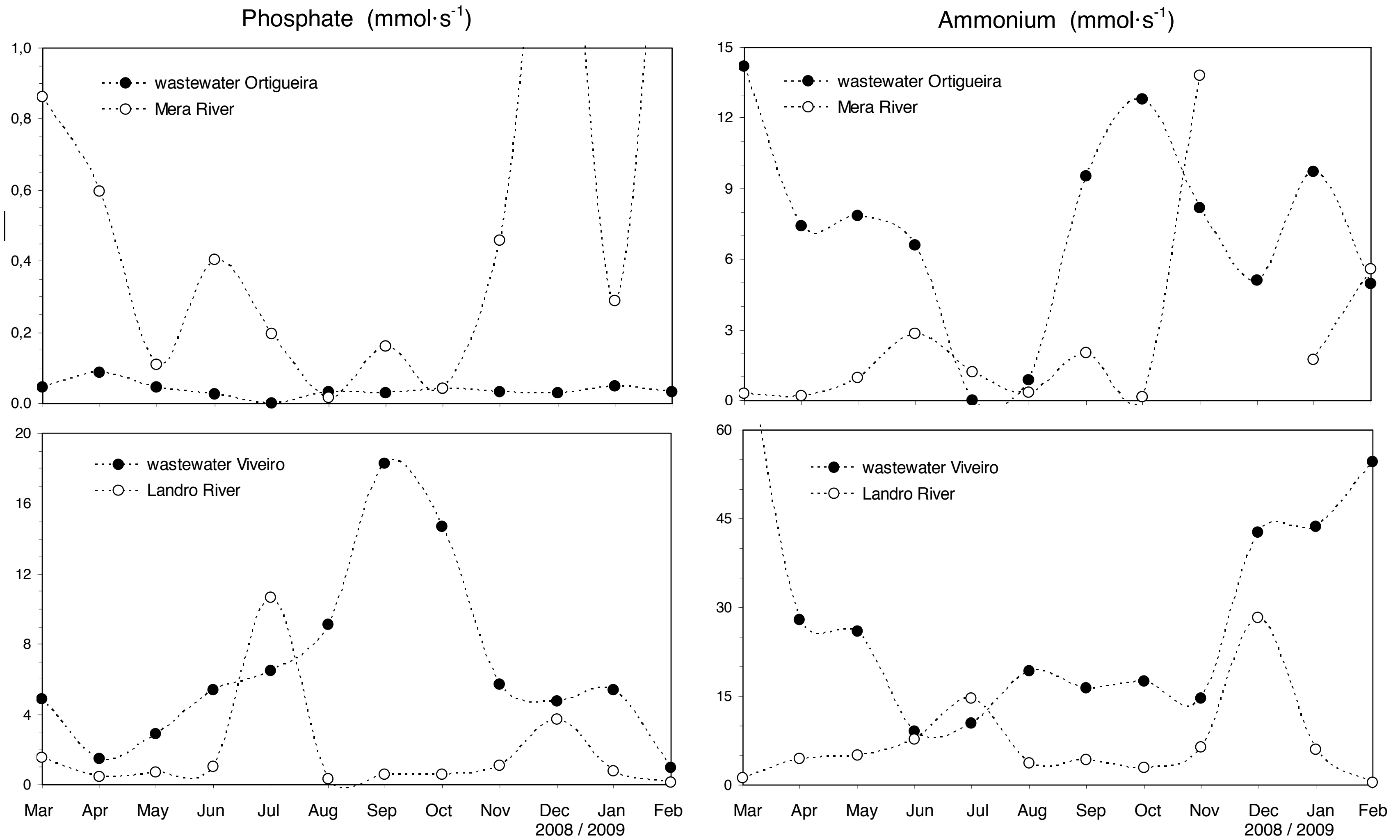


Figure 3. Comparison of loading rates of phosphate and ammonium from rivers and wastewaters in the Rias of Ortigueira and Viveiro.

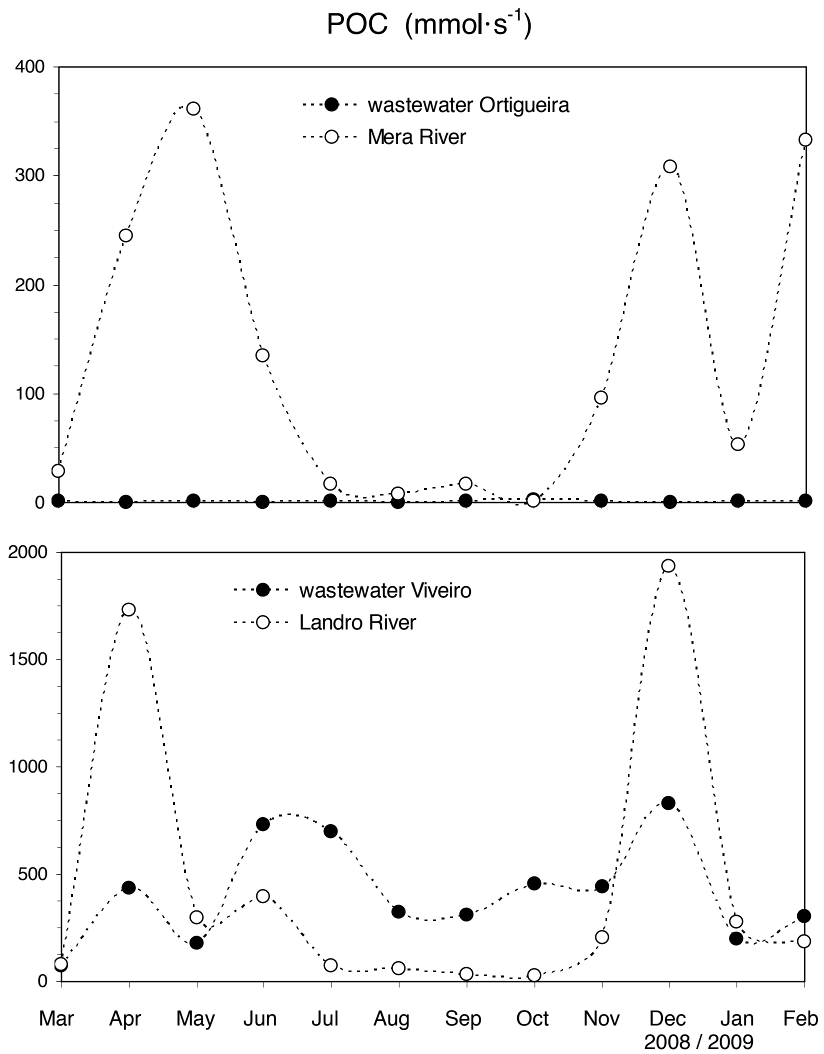


Figure 4. Comparison of loading rates of particulate organic carbon (POC) from rivers and wastewaters in the Rias of Ortigueira and Viveiro.

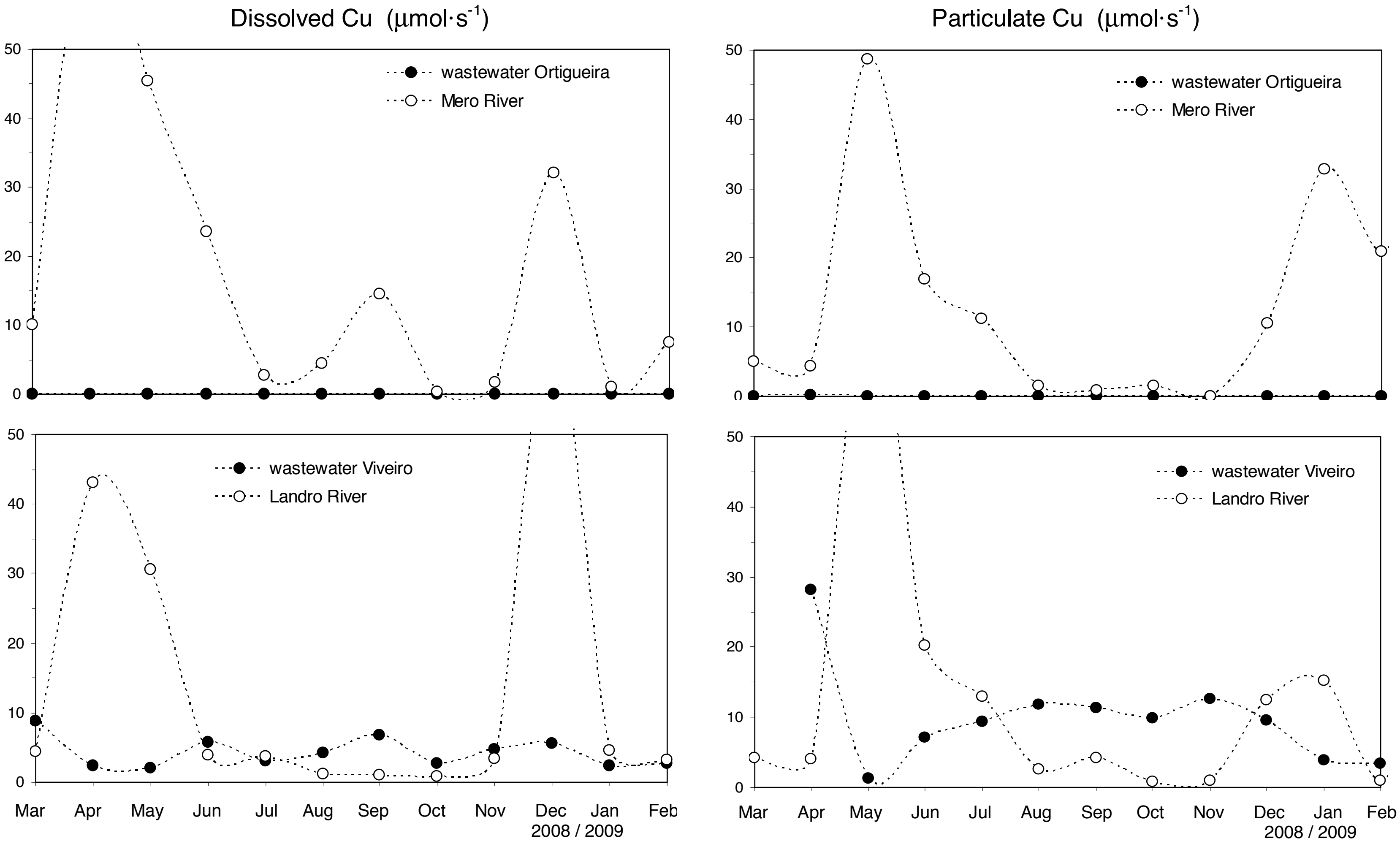


Figure 5. Comparison of loading rates of dissolved and particulate Cu from rivers and wastewaters in the Rias of Ortigueira and Viveiro.