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Biogeochemical fluxes of iron from rainwater, rivers and sewage to a Galician Ria (NW Iberian Peninsula). Natural versus anthropogenic contributions

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Abstract The total iron (TFe) concentrations in five rivers to a Galician Ria (averages 1.0–4.5 µM) was within the pristine range, but in rainwater it was higher (17 µM). TFe values of small sewage treatment plants (STP) ranged between 3 and 4 µM, whereas in the largest was 11 µM. Particulate iron in rivers was five times more abundant than dissolved iron, except in the Lagares where it was 20 times higher, but in the STDs the dissolved/particulate coefficients varied from 0.1 to 1.1 and in the rainwater it was lower than 0.4. Equations of water flow versus iron flux were obtained to quantify the iron contribution from the freshwater sources to the Vigo Ria. It receives annually 490 tons of iron (6% in dissolved form) and 90% of this comes from industries focused on metal processes. The contaminated Lagares River accounts for the main input of TFe (327 t a^{-1}), followed by rainwater (78 t a^{-1}), the Oitavén River (28 t a^{-1}) and Vigo STP (33 t a^{-1}). Anthropogenic activities have increased the amount of iron flowing into the Ria by roughly ten times and this could upset the biogeochemical cycle in similar coastal systems.

Keywords Dissolved · Freshwater · Iron · NW Spain · Particulate

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Introduction

Iron is an essential nutrient for the growth and metabolism of aquatic organisms (Falkowski et al. 1998; Morel and Price 2003) and its bioavailability has a profound influence on the productivity, composition and trophic structure of marine planktonic communities (Martin et al. 1991; Sunda 2001). The most important pathway through which iron is transported towards the land–sea margins is the riverine input. It has been mass-balanced in the land–sea boundaries by Martin and Maybeck (1979) in seven of the largest rivers in the world. Recently, the interest in this matter has been reconsidered and extended to small rivers and tributaries (i.e. Neal and Robson 2000; Turner and Williamson 2005).

In the Iberian Peninsula the fluvial iron and its fluxes were mainly quantified in the Tinto River (Ferris et al. 2004). In the northwest corner of this peninsula information about the iron cycle is very scarce (Prego and Cobelo-García 2003). There is only some recent but very limited iron analyses in freshwater systems for particulate (Evans et al. 2003; Cobelo-García et al. 2004) and dissolved iron (DFe) (Prego et al. 2006). This lack of information about the iron levels and fluxes from catchments to a ria system in this geographical region is one of the reasons of this paper. Moreover, in the global iron fluxes to the coast particulate iron (PFe) seem to be two orders of magnitude higher than the dissolved (Poulton and Raiswell 2002). Therefore, it is necessary to provide new information for this question to add it to current studies across Europe and the Iberian Peninsula, in particular.

In addition to the fluvial contribution, the research on iron output on the land–sea boundary must take in account two other sources: sewage inputs and rainwater inflow. In the coastal systems, iron does not usually limit phytoplankton growth (Moore et al. 2002). This may be the reason why its cycle is unknown in the rias and there is no information on rainwater iron content and its flux to the rias. The same may be said for the sewage iron flux and its concentrations are not commonly measured in the residual waters (Karvelas et al. 2003), except for health controls (Chino et al. 1991). Consequently, this work was also undertaken to assess natural and anthropogenic inputs of iron from the land to a marine coastal area of environmental significance, the Vigo Ria. The research has international relevance within the context of biogeochemical iron fluxes and budget from rivers, atmosphere and sewage treatment plants (STP) in the shoreline boundary of a ria coastal system, where, at present, there is a lack of information.

Study site

It is located in the northwest of the Iberian Peninsula, and is the southernmost ria on the Galician Coast (Fig. 1). It is an incised valley where the estuarine zone moves according to climate changes (Evans and Prego 2003).

Direct rainwater on the Ria seawater ranges from 1,400 to 1,700 mm, according to the annual isohyets range (Gómez-Viñas et al. 1996). The fluvial basin of the Ria has an area of 490 km^2 and 1,950 ± 330 mm of annual average runoff (station n.495 of INM meteorological net). It receives the continental supplies of seven water-streams and one river (Fig. 1), the Oitavén-Verdugo (334 km^2), which is the main flow to the Ria with a discharge of 17 m^3 s^{-1}. Moreover, it also receives the output of six sewage pre-treatment plants (STP) from the banks of the Ria (Fig. 1). Vigo's STP treats the residual waters of 300,000 of the 420,000 residents living on this coast and empties 1.9 ± 0.2 m^3 s^{-1} into the Ria. Industrial activities are focused on metals, i.e. a car factory and shipyard,

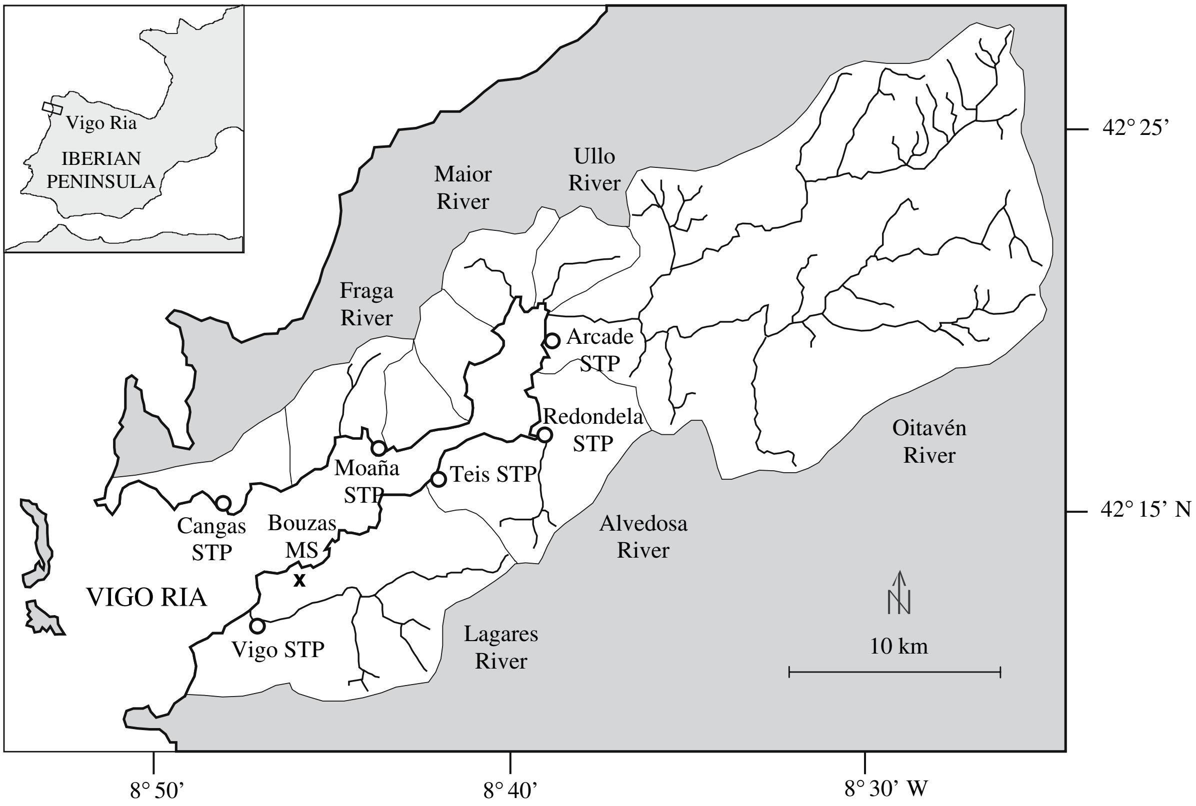

Fig. 1 Basin area of the Vigo Ria displaying the rivers, sewage pre-treatment plants (STP) and meteorological station (MS) sampled

fresh and frozen seafood and harbor goods works (4,000,000 tons per year).

The geology of the area is dominated by igneous and metamorphic rocks dating from the Precambrian-Paleozoic age, which form a series of hills (400–500 m) bordering the Ria and the hinterland. The only younger rocks comprise Miocene-Quaternary continental sediments, which infill a series of N–S graben structures inland, and Quaternary fluvial and coastal sediments (Nombela et al. 1995). The iron concentration in this area oscillates between 10 and 30 mg g^{-1} (Guitian 1992).

Materials and methods

Rainwater samples were collected at the weather station of the Spanish Institute of Meteorology (INM) in the Marine Research Institute (IIM), located in the middle of the southern coast of the Vigo Ria (Fig. 1). Forty-four rainwater samples were gathered from this station during 2004, from 30th December 2003 to 3th January 2005, generally, at intervals of 15 days (twin samples each interval). Polyethylene funnels of 12 cm diameter fitted into 1 L low-density polyethylene (LDPE) bottles were used. Daily rainfall data for Vigo were provided by the INM, which coincided with the precipitation volumes collected in the sampling bottles.

Samples from the rivers and STPs were collected (pH was previously measured in situ with a WTW MultiLine P4 Set) and placed in new 1-L LDPE bottles previously acid-washed and rinsed with Milli-Q water. Sampling fluvial points (salinity <0.2 measured with a WTW MultiLine P4) were situated in the Oitavén River and the water streams of Alvedosa, Lagares, Fraga, Maior and Ullo and sewage points at the Vigo, Teis, Arcade, Redondela, Cangas and Moaña STP (Fig. 1). Each point was sampled monthly during 2004, except for the Oitavén River which was sampled twice a month. The Oitavén River discharge was measured daily at the Sotomaior gauging station. It was calibrated in 2004 by in situ measurements with current-meters as the method 'area-speed' (WMO 1994) and the river flow corrected to all its basin surface according to the rainfall and land used by a hydrological model (Alvarez-Eijo 2000). The decennial flows of the water streams were calculated from the Oitavén discharge and the stream basin surfaces due to the good relationships ($r^2 > 0.9$) obtained by comparing the measurements of their flows (Alvarez-Eijo 2000). STP flows corresponding to the sampling dates and the monthly average discharge during 2004 were provided by the Sewage Plant Companies.

Samples were taken to the IIM and refrigerated at 4°C and on the same day, they were vacuum filtered, using Pall hydrophilic polypropylene membranes mounted in a polycarbonate filter holder, inside an ultra-clean laboratory (class 1000) to avoid contamination. The filtration was using 0.45 µm filter circles and this was used to operationally define the separation between dissolved and particulate components (Chapman 1992; Loring and Rantala 1992). Note that this filtration is operationally defined (Neal et al. 1996) and that the 'dissolved phase' can include significant microparticulate material (Grasshoff 1983). Funnels, bottles, plastic filter holders, tweezers, petri dishes and other materials were washed with detergent, rinsed with distilled water, pre-cleaned with 10% (w/w) sub-boiled nitric acid solution for two weeks, rinsed several times with Milli-Q water and dried before use. The filtered water were stored prior to analysis at room temperature in 1-L LDPE acid-washed bottles and acidified to pH 2 by adding 1 µL per mL reagent-grade HNO_3 to prevent adsorption of the metal by the surface of the polyethylene bottles. For filtration pre-weighed filters, acid-washed just before filtration, were used. The first 50 mL of the sample was discarded. Wet filters containing the suspended particulate matter (SPM) were then taken using acid-washed polypropylene tweezers and put into a laminar flow chamber (class 100) until dry. The filters were then weighed (SPM concentration calculated) and placed in cleaned air-tight plastic petri dishes inside zip-lock plastic bags and stored at -20°C in the freezer until digestion. Blanks (one filter each 12 samples) of analysis were treated with the same procedure than the samples.

The analysis of iron, both in SPM and water samples, was carried out by Varian 220 ElectroThermal Atomic Absorption Spectroscopy equipped with Zeeman background correction. 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 EPA guideline 3052. The accuracy of the analytical procedure was checked using the reference materials PACS-2 (marine sediment reference material, NRCC) and SLRS-4 (river water reference material, NRCC), obtaining values of 42.9 ± 1.7 μg g^{-1}, certified 40.9 ± 0.6 μg g^{-1} and 101 ± 4 μg L^{-1}, certified 103 ± 5 μg L^{-1}, respectively. The detection limits of the analytical procedure, defined as three times the standard deviation of the blanks, were 0.17 μg L^{-1}. The precision of the analysis depended on the concentrations of the sample and were, like the relative standard deviation, generally below 10% for all results.

Results

Iron concentration in waters

The highest concentrations of DFe were measured in STP, particularly in Vigo STP showing a mean value of 2.5 μM, followed by Teis (1.8 μM) and Arcade (1.3 μM), Fig. 2. Slightly lower values were obtained for the rivers in the area (pH was 6.81 ± 0.35): the highest concentrations were for the Lagares River (1.1 μM), while the others had concentrations lower than 0.7 μM. In rainwater, the mean iron content was 0.8 μM.

Iron associated with SPM, PFe, was more abundant in the Teis STP, rainwater and in the Lagares River with their mean values being 15, 16 and 29 μM, respectively (Fig. 2). Similar to what occurred with DFe, PFe in the pluvial data was, again, the most variable, ranging from 1 to 61 μM. In contrast, the Arcade and Cangas STPs, and the Oitavén and Maior rivers presented the lowest PFe values, which never surpassed 8.8 μM.

The partition coefficients (K, Table 1) were determined as the quotient between dissolved and PFe, both in μM units. The prevailing phase in all of the rivers flowing into the Vigo Ria is the PFe, which varied between 0.17 and 0.26. It is more pronounced in the Lagares case, where K is 0.05. The opposite occurred with the Oitavén River (K is 0.83) where iron is distributed almost equally between both phases during the whole year, although in July, August and September it is more abundant in DFe (K values of 1.77, 1.98 and 1.60, respectively). In the case of sewage, partition coefficients vary from 0.13 for the Teis to 0.48 for the Moaña STPs. It involves a major presence of iron in SPM, but iron is distributed equally between both phases in Arcade (K of 1.1) and Cangas (1.0) STPs.

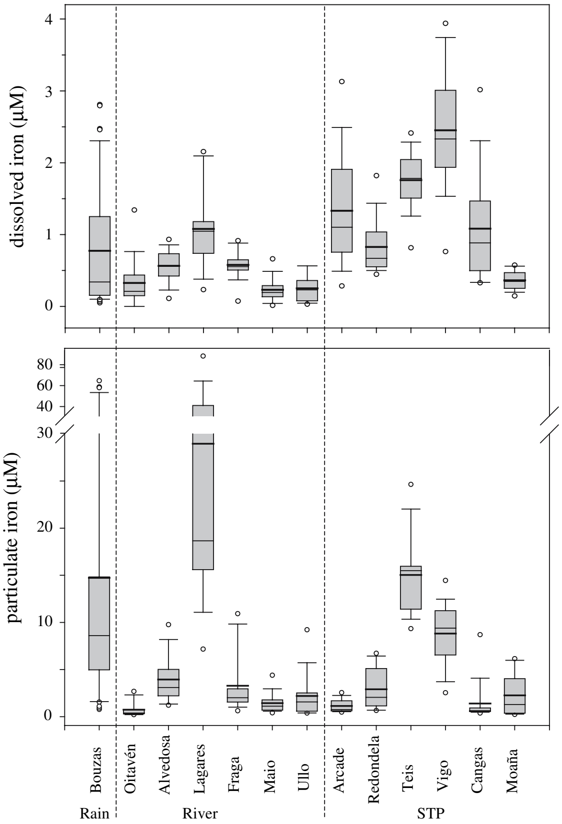

Fig. 2 *Box-and-whisker plots* of the iron levels in its water sources to the Vigo Ria. The length of the *box* represents the interquartile range, which contains 50% of the values, and the *thin horizontal line inside the box* indicates the median whereas *heavy horizontal line* represent mean. The whiskers are lines that extend from the *box* to the highest and lowest values excluding outliers and extremes. 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

Freshwater iron fluxes

The contributions of iron flowing towards the Ria can be evaluated from the relations between the flux of iron versus the water flow of the rivers, STP and rain. The results are shown for the three principal contributions in Fig. 3 and for all the iron sources under consideration in Table 1 on the basis of exponential equations (Thomas and Meybeck 1992). Most of the mathematical expressions obtained presented high correlation coefficients and levels of significance. They allowed us to calculate the iron flux -dissolved, particulate or total- simply by knowing the water flow.

Table 1 Iron contribution to the Vigo Ria from the different freshwater sources according to the equation $F = a{\cdot}Q^b$

	Source	aaf*	Dissolved iron			Particulate iron			$[Fe]_d/[Fe]_p$
		$m^3\ s^{-1}$	*a*	*b*	*r* (*p*)	*a*	*b*	*r* (*p*)	*K*
River	Oitavén	16.33	21.9	0.82	0.82 (<0.001)	17.2	1.24	0.95 (<0.001)	0.83 ± 0.63
	Alvedosa	1.63	29.2	1.11	0.93 (<0.001)	186	1.05	0.91 (<0.001)	0.17 ± 0.08
	Lagares	3.68	51.1	1.04	0.92 (<0.001)	1314	1.35	0.90 (<0.001)	0.05 ± 0.03
	Fraga	0.40	36.5	1.13	0.93 (<0.001)	344	1.48	0.94 (<0.001)	0.26 ± 0.13
	Maior	0.40	5.06	0.67	0.71 (<0.01)	130	1.33	0.94 (<0.001)	0.18 ± 0.09
	Ullo	0.74	9.25	0.95	0.81 (<0.01)	64.2	0.84	0.69 (<0.02)	0.17 ± 0.10
Rain	Bouzas	8.12**	0.018	1.25	0.72 (<0.001)	0.95	0.09	0.14	0.15 ± 0.26
STP	Arcade	0.017	11.3	0.59	0.43	23.5	0.80	0.54 (<0.1)	1.13 ± 0.74
	Redondela	0.073	85.7	1.27	0.72 (<0.01)	1098	1.84	0.62 (<0.05)	0.39 ± 0.19
	Teis	0.072	93.7	0.97	0.87 (<0.001)	233	0.53	0.57 (<0.05)	0.13 ± 0.05
	Vigo	1.960	57.4	2.10	0.73 (<0.01)	140	2.60	0.78 (<0.01)	0.31 ± 0.11
	Cangas	0.061	39.4	0.93	0.41	54.5	1.14	0.74 (<0.01)	1.02 ± 0.63
	Moaña	0.087	8.24	0.66	0.40	5.18	−0.09	0.02	0.48 ± 0.41

F is the iron flux in mg s^{-1}, *Q* the water flow in $m^3\ s^{-1}$, *a* and *b* the constants of equation; *r* is the regression coefficient and *p* the level of significance; *K* is the ratio of the dissolved to particulate iron concentration in water

* aaf is the annual average flow in 2004

** to the 156 km^2 of Ria surface during 2004

The quantification of the annual iron contribution from each source could be based in the annual average flow and the annual average concentration of iron but it suppose a rough estimation because the iron flux is not a lineal in relation to the flow. Consequently, the information on the daily flow during 2004 for the Oitavén and the decennial data for other rivers, in addition to the equations given in Table 1, have enabled us to quantify the annual iron contributions to the Ria. Similar to the STPs and their monthly average flows, iron outputs can be estimated. This estimation was carried out on rainwater by considering the sampling periods, rainfall, iron content and the Ria surface and assuming that the rain is homogeneous throughout its marine basin. In Fig. 4 the contributions to the Ria from the different iron sources considered are summarized on a map.

Discussion

Natural sources of iron in the freshwater flowing into the Ria

The dissolved and PFe content measured in the rivers under study, except for the Lagares River, may be considered naturally occurring. These values fall within the range of the World Rivers average (Table 2) and they are also characteristic of unpolluted rivers (Meybeck 1988), having similar total iron (TFe) levels to quasi-pristine rivers (Martin and Windom 1991). The partition coefficients (*K*, Table 1) indicated a predominance of the particulate phase. Neal et al. (1996) observed that iron in rivers constitutes an element that is especially associated with silicate and oxide phases.

According to a seasonal observations of these fluvial sources, the highest DFe concentrations in the Oitavén River (Fig. 5) took place at the end of summer (August, September and October), which may be related to the organic matter mineralization and the wash of the basin with the first autumnal rains. Afterwards, DFe decreased by dilution during the rainy season, a process previously observed in the freshwater runoff (Poikäne et al. 2005). Thus, there is a clear PFe pattern in the Oitavén River, with a peak in April that may be interpreted as being the result of the spring phytoplankton bloom (Jickells et al. 1991) and another one in October, probably owing to the mudslides from the heavy rains at the beginning of the rainy season (Neal and Robson 2000; Poikäne et al. 2005). The other tributaries of the Ria presented similar behaviour patterns.

Seasonal variation can also be studied by means of QC representations, i.e. river flow versus iron concen-

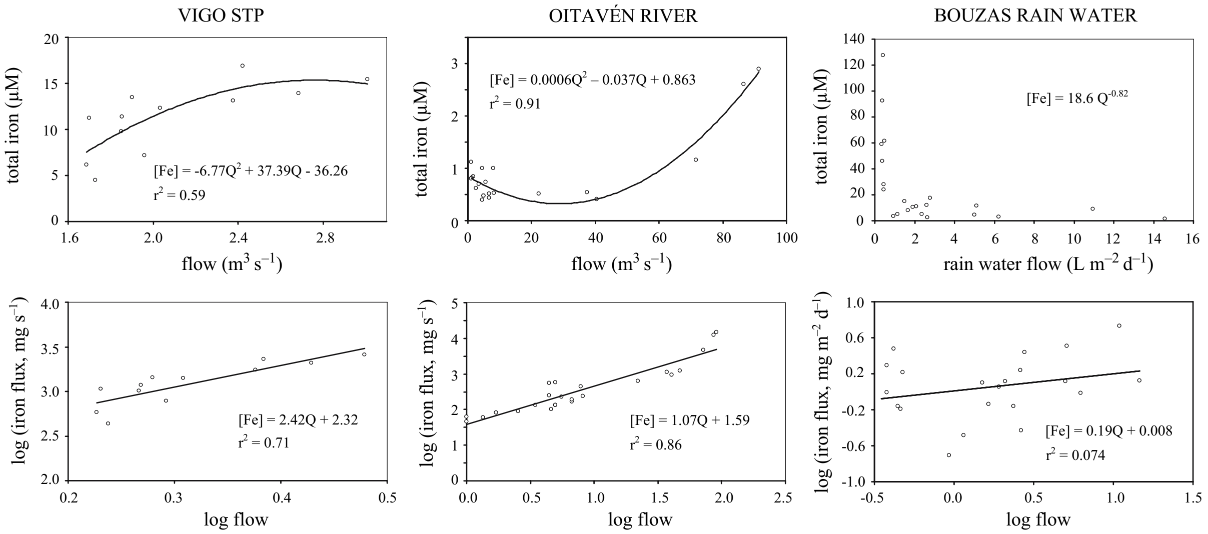

Fig. 3 Concentration of total iron versus water flow for three types of sources (Vigo STP, Oitavén River and Bouzas MS), and logarithm relation of the total iron flux versus water flow at the same sources

tration (Fig. 3), because in temperate climates, the variation in rainy/dry seasons usually follows a sequence similar to the seasonal one for rainfalls and fluvial flows. As is the case of rivers, in the Oitavén there is a good relationship between both parameters, Q and C, for iron and, consequently, the iron flux increases with flow (Neal et al. 1997). The natural contribution of TFe from rivers (save Lagares) to the Vigo Ria can be estimated at 47.6 t a^{-1}, which 18% of which corresponds to DFe (Fig. 4). The TFe flux, ranging from 80 to 210 kg km^{-2} a^{-1}, is in the order of those described for agricultural-urban rivers (Webb et al. 2000; Neal and Davies 2003).

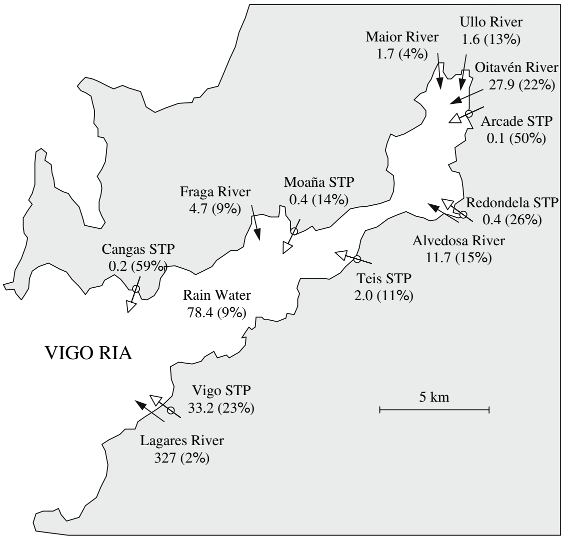

Fig. 4 Total iron fluxes (tons per year) from the considered freshwater sources to the Vigo Ria during 2004. Between *brackets* is the flow percentage of dissolved iron

Low anthropogenic enriched sources of iron in the freshwater flowing into the Ria

Total iron contents in rainwater were higher than those reported in the Atlantic Ocean area (Table 2) and they were similar in range to those found in populated and industrial coastal areas (Manoj et al. 2000), which would suggest that part of rainwater iron in the Vigo Ria may be of anthropogenic origin. The rainwater had a *K* coefficient of 0.15, indicating that iron is predominantly associated with particulate matter, as has already been reported (Halstead et al. 2000). However, in keeping with the observations of Neal et al. (2004), it may be the influence of atmospheric particles being removed by rain and the dry deposition of matter which accumulates on the rainfall collector. The concentration of dissolved and PFe in the rain was dry/wet season dependent (Fig. 5). In the months having the greatest rainfall in 2004 (October and November, Fig. 5), the iron particulate levels decreased (*K* was 0.92) suggesting a lower particle content in the atmosphere associated with lengthy rainy periods. High PFe maximums have been seen to occur in periods of drought, as reported previously by Kanellopoulou (2001) and Neal et al. (2004). So, high

Table 2 Iron concentrations average (range between brackets) in the freshwater of different locations

	Location	(g kg^{-1})	Particulate iron (µM)	Dissolved iron (µM)	Total iron (µM)	Reference
Rain	Atlantic Ocean				(0.03–1.14)	Helmers and Schrems 1995
	Bermuda Atlantic Station		(0.08–0.12)	(0.11–0.23)	(0.23–0.31)	Willey et al. 2004
	Wilmington Coast (USA)		0.16 ± 0.05	0.06 ± 0.02	0.21 ± 0.05	Kieber et al. 2001
	Plynlimon (U.K.)			0.17 (0.00–2.45)		Neal et al. 1997
	Frilsham Meadow (U.K.)			0.24 (0.05–1.77)		Neal et al. 2004
	Warren Farm (U.K.)			0.44 (0.03–8.95)		
	Black Wood, Hampshire (U.K.)			0.32 (0.00–1.74)		Neal et al. 1994
	Vigo Ria (Spain)		16.0 (0.9–61.3)	0.77 (0.05–2.81)	16.8 (1.6–61.5)	This study
River	World average	48.0		0.72		Martin and Meybeck 1979
	US EPA guideline				17.9	EPA 1986
	Beaulieu (U.K.)			9.47 ± 0.07		Turner and Williamson 2005
	Carnon (U.K.)			168 (0–877)		Neal et al. 2005a
	Odiel River (Spain)				420 (1–4704)	Olías et al. 2004
	Tinto River (Spain)	<1.0		(2330–5780)		Ferris et al. 2004
	St Lawrence mouth (Canada)	53.1 ± 7.3		0.36 ± 0.16		Rondeau et al. 2005
	Humber basin(U.K.)			(0.11–20.0)		Neal et al. 1996
	Afon Hafren (U.K.)			1.53 (0.41–5.30)		Neal et al. 1997
	Upper Afon Hore (U.K.)			1.50 (0.55–5.18)		
	LOIS river programme (U.K)			15.0		Robson and Neal 1997
	LOIS river programme (U.K.)		(0.00–228)	(0.00–19.0)		Neal and Robson 2000
	Pang (U.K.)			0.37 (0.07–3.53)		Neal et al. 2004
	Lambourg (U.K.)			0.18 (0.07–0.55)		
	Dun (U.K.)			0.41 ± 0.30 (0.10–0.96)		Neal et al. 2005b
	Oitavén (main river)	61.9 (8–185)	0.65 (0.2–2.7)	0.34 (0.02–1.34)	1.0 (0.4–2.9)	This study
	Lagares (contaminated)	44.5 (7–71.)	29.0 (7.2–88.0)	1.08 (0.59–2.15)	30.0 (8–89)	
	Other water streams	28.4–55.4 (8–100)	1.4–4.0 (0.4–10.9)	0.21–0.58 (0.02–0.93)	1.67–4.51 (0.4–11.8)	
STP	TSE Southwest England			0.81 ± 0.02		Turner and Williamson 2005
	Montreal (Canada)	47.3 ± 46.0		5.70 ± 5.20		Gobeil et al. 2005
	Thessaloniki (Greece)				6.80 ± 0.84	Karvelas et al. 2003
	Rural Kennet/Dun (U.K.)			0.63 ± 0.44 (0.05–1.71)		Neal et al. 2005b
	Vigo Ria (big plant: Vigo)		8.8 (2.5–14.5)	2.45 (0.76–3.90)	11.3 (4.5–16.9)	This study
	Vigo Ria (small plants*)		1.2–2.9 (0.2–8.7)	0.36–1.33 (0.15–3.10)	2.63–4.20 (0.4–23.0)	

*Save Teis

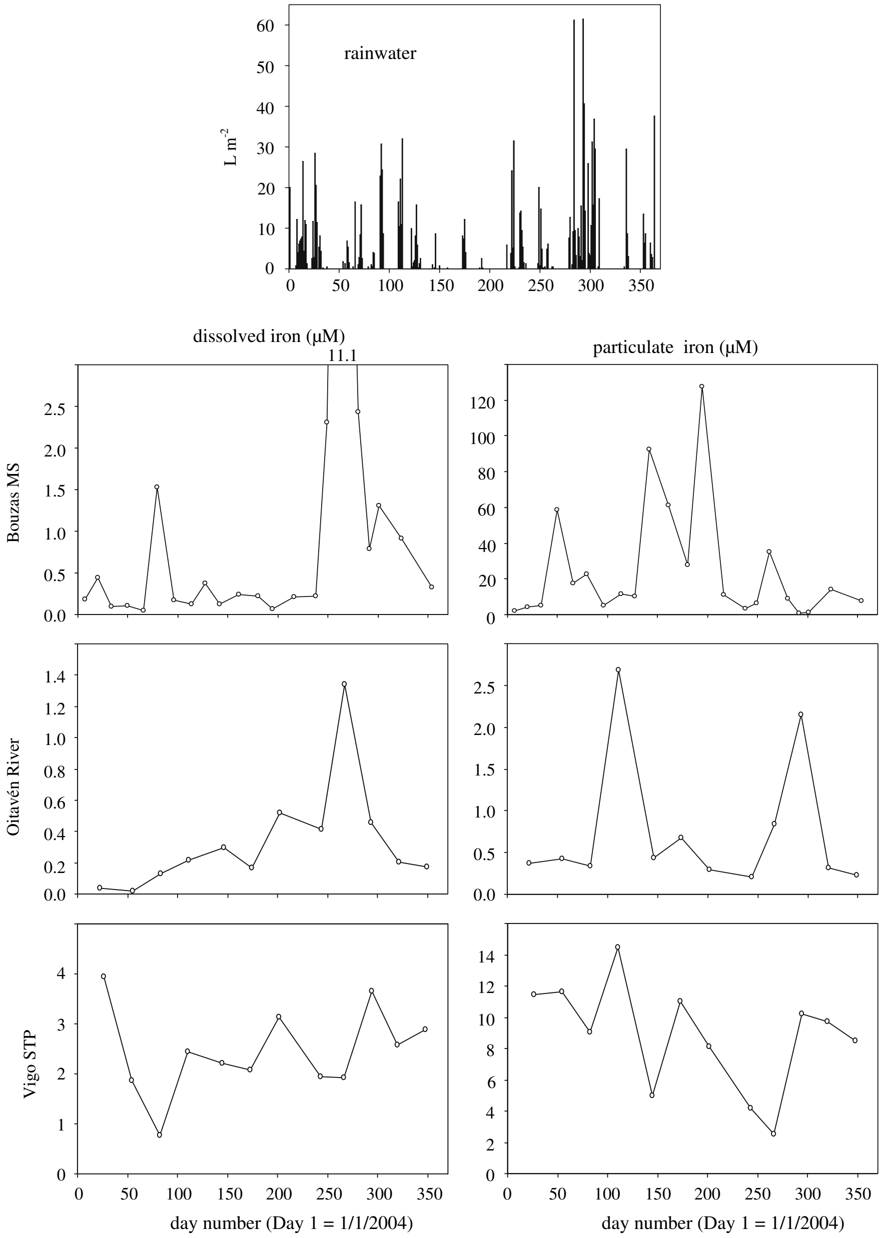

Fig. 5 Annual time-series of dissolved and particulate concentrations of iron from three types of sources to the Vigo Ria: river water (Oitavén), sewage (Vigo STP) and rainwater (Bouzas MS)

concentrations of iron in the Vigo area were measured during rainfalls after dry periods, similar to other systems (Al-Khashman 2005), whereas top DFe concentrations occurred with the first intense rains of autumn.

In rainwater, QC equations varied as an exponential negative (Fig. 3), i.e. iron concentration increased with a decreasing volume of rainfall and vice versa, similar to what Neal et al. (1997) observed in another temperate zone (mid Wales). Therefore, the QF relation showed, in general, that iron flux increased with the rain precipitation volume for DFe, but it was not possible to predict the iron flux to the PFe because a good QF correspondence was not obtained. The annual iron contribution in the rainwater to the Vigo area was 457 kg km^{-2} a^{-1} of PFe and 45 kg km^{-2} a^{-1}

of DFe, higher than the contribution measured to some British rural areas (Neal et al. 2004). It represents a flux of 77.3 t a^{-1} to the Vigo Ria surface.

High anthropogenic enriched sources of iron in the freshwater flowing into the Ria

The Lagares River water as well as the sewage of the STPs are subject to anthropogenic influence. The Lagares River represents the most extreme Ria river case with concentrations ten times higher in PFe and two times higher in DFe than the rivers in the Ria area (Table 2). Hence, in the Lagares, the levels of TFe were twice as high as those recommended by the EPA (1986) for freshwater. This increase could be due to the local lithology or to industrial activity (Robson and Neal 1997; Yuce et al. 2006). The latter reason is the most probable, as this situation occurs in other contaminated rivers (Rondeau et al. 2005; Poikäne et al. 2005), since an important part of industrial wastewaters from Vigo spill into the Lagares River. It presented high DFe values in January and February. This behaviour has also been observed in contaminated rivers where DFe increased during the first months of the winter (Olías et al. 2004; Morillo et al. 2005).

On the other hand, STP may also be an important source of metals in the environment. However, iron is not considered to be a toxic element, and is sometimes even used as a reagent in the treatment plants themselves. When TFe was measured (Chino et al. 1991; Karvelas et al. 2003), the concentrations were found to be of the same order as those measured in the plants of Arcade, Redondela, Cangas and Moaña, but lower than in the Teis and Vigo STP, in particular (Table 2). This may be attributed to the type of treatment used on the residual waters or to an insufficient capacity to treat the volume of residues rather than to changes in the pH (STPs were 6.92 ± 0.29). Generally, STPs involve a major presence of iron in SPM, similar to what occurred in other treatment plants (Karvelas et al. 2003; Gobeil et al. 2005). High DFe values were found in the STPs during the summer and at the beginning of the autumn, but they were also high in the Vigo STD during January (Fig. 5). When the STP flow increased, the concentration tended to be constant and the iron flux of STPs increased with the sewage spilled volume. The TFe flux can be estimated at 36.2 t a^{-1} (Fig. 4), ranging between 0.015 and 0.227 g day^{-1} per population equivalent of TFe; of these 0.004–0.051 g day^{-1} corresponds to DFe, which is similar to the value measured by Neal et al. (2005) using the same type of filters. The TFe flux of STPs was around ten times lower than in the Lagares River. Moreover, this River has discharged 3,565 kg km^{-2} a^{-1}, i.e. 20 times higher than the other tributaries to the Vigo Ria. Therefore it can be considered heavily iron-enriched and is the main iron contributor of iron to the Ria (327 t a^{-1}, Fig. 4).

Conclusion

The biogeochemical cycle of iron in oceanic environments is once again being given special attention, since it has been discovered that this element is a limiting nutrient for primary production. Meanwhile, in coastal areas where nitrogen and not iron is the limiting element of the productivity, this metal flux has received little or no attention (for example, the Galician Rias). The iron contribution in its different fluxes has now been quantified in one of these systems: 490 tons of iron is being spilled annually into the Vigo Ria with a dissolved-particulate relationship of 1:15. In this coastal system the natural fluvial contributions are not the most important iron pathway to the land–sea transport. It was estimated to be only 10% of the TFe. The freshwater iron arriving to the oceans from the coastal zone may play an ever more important role if its flux is increasing, as is happening in the Vigo Ria where 36 t a^{-1} from the STP and 327 t a^{-1} from the contaminated Lagares River are discharged. Thus, in a temperate coastal system such as the Vigo Ria, anthropogenic activities have increased the input of iron to the Ria approximately tenfold. Therefore, the sole quantification of the main wide river iron flux to a ria or an estuary, as is common in the case of the biogeochemical cycle of nutrient salts, may be not enough to make an appropriate estimation of the iron freshwater contributions.

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