ORGANIC MATTER IN RIA SEDIMENTS: RELEVANCE OF TERRESTIAL SOURCES AND TEMPORAL VARIATIONS IN RATES OF ACCUMULATION

Graham Evans[1], Ricardo Prego[2*] and John E. Marshall[1]

[1] School of Oceanography and Earth Sciences, University of Southampton, National Oceanography Centre. European Way, Southampton SO4 3ZH, UK.
[2] Marine Research Institute (CSIC). Eduardo Cabello, 6; E-36208 Vigo, Spain.
* Corresponding author: prego@iim.csic.es

Abstract. The Ria of Vigo, one of the classical rias of SW Europe, is an environment of high production of organic matter naturally induced by the Galician upwelling. The organic matter is partly supplied by small rivers but mainly by sewage plants along the ria shoreline; jointly they contribute 725 $t \cdot y^{-1}$ of POC, of which 72% is of anthropogenic origin. The freshwater flux is equivalent to a supply of 5 $g \cdot m^{-2} \cdot yr^{-1}$ of allochtonous POC to the ria floor. However the rate of accumulation of POC is dominated by the tenfold higher supply of autochthonous material from the net primary production. The present accumulation rate of organic matter (49-58 $g_{POC} \cdot m^{-2} \cdot yr^{-1}$) is lower than the average supply, estimated from the sedimentary record, to the ria since the middle of the nineteen Century (>60 $g_{POC} \cdot m^{-2} \cdot yr^{-1}$). This difference may be due to anthropogenic activity or changes in the upwelling pattern. The composition of the organic matter in the sediment reflects the relative importance of the various sources (terrestrial-marine). While terrestrial woody materials dominate the inner ria, phytoplankton remains dominate the remainder of the ria. Rock-Evaluation analysis indicates the inner ria is the site of deposition of gas-prone material and it is inferred that the outer ria of oil-prone organic matter. The controls on the accumulation of POC in the rias show many differences to those found in estuaries affected by anthropogenic activities e.g. agriculture and increasing human population.

Key words: POM, POC, flux, autochthonous, allochtonous, rock evaluation analyses, NW Spain.

INTRODUCTION AND OBJECTIVES

The shelf zones in general, and particularly the coastal systems, behave as carbon traps (Romankevich, 1984; Wollast, 1991) where part of the organic matter in the overlying waters accumulates in the underlying sediments. In pristine systems, the source of that matter may be dominated by autochthonous material from net primary production (NPP), and allochtonous material supplied by rivers, or both together. Natural eutrophication may sometimes occur due to nutrient loadings and from discharges of industrial plants and sewage treatment works and from other human-influenced ‘diffuse sources’ such as run-off from agricultural catchments that may increase the water eutrophication effects (de Jonge et al., 2002). The enrichment of water by nutrients causes an accelerated growth of algae to provide the causes of eutrophication (de Jonge and Elliott, 2002).

An important fate for both NPP and terrestrial organic matter is burial in the coastal sediments. Thus, it is important to understand the trophic conditions of the coastal system and the sedimentation rate of organic matter. In coastal systems in areas of upwelling, such as the Galician Rias, the impact of allochtonous contributions of organic matter may be different to that of oligotrophic environments where eutrophication may increase productivity as in some shallow seas and coastal lagoons, e.g. the North Sea (Peeters et al., 1993) and the Wadden Sea (de Jonge et al., 1996) sea.

Typical estuarine systems have been extensively investigated. Eutrophication is related to agriculture activities and the increasing human population which has occurred in several of the world estuaries (de Jonge et al., 2002). The ria is another type of coastal system which although classically developed in the Iberian Peninsula, also occurs elsewhere in Brittany in France and

Devon and Cornwall in the British Isles, Korea, parts of the Chinese and the Argentina coasts. Ria is a useful term capable of wide application that should not be locally restricted (Evans and Prego, 2003). The budget of autochthonous and allochthonous organic matter and its fate in the sediments of rias has been poorly studied and is still not completely understood.

The rias of the Galician coast, NW Spain, have attracted considerable attention from scientists since Von Richtofen (1886) introduced the term 'ria' into the geological literature, using Galicia as the type area for this feature. Later, the geomorphological evolution of the area has been studied by workers of various nationalities (see review by Sala, 1984) and the sediments were first comprehensively studied by Dutch workers under the leadership of Pannekoek (Pannekoek, 1966; 1970). Subsequently, contributions were made by the geologists of the 'Instituto Español de Oceanografía' (viz. Rey, 1993), the 'Instituto de Investigaciones Marinas (CSIC)' (Bernárdez et al., 2005; 2006 and the references cited therein), and the University de Vigo (see review in Vilas et al., 2005; Mendez and Vilas, 2005; Garcia et al., 2005). Recently, a series of detailed maps were produced of the bottom sediments of the Vigo and adjacent rias (Vilas et al., 2005). However, the main interest in the Galician Rias has been for oceanographers, because of the fertility and the important commercial fisheries (Díez et al., 2000). The relatively high content of organic matter of the bottom sediments has been noted and discussed by several workers since the early pioneering studies of Margalef (1956), Margalef and Andreu (1958) and Fraga (1960) although little information has been provided on its nature and composition. The existing information was mainly provided by Diz et al. (2002) and Alvarez et al. (2005) who studied the variation in a vertical core of various biomarkers and showed the temporal variation of the types of organic matter which have been supplied to the

Ria of Vigo.

In order to attempt to provide a comprehensive understanding of the behaviour and fate of organic matter in ria systems this study evaluates the importance of the allochthonous contributions of organic carbon and provides an estimate of the relevance of various sources as well as the temporal rate of accumulation of particulate organic matter in the sediment.

Survey area: The Ria of Vigo

The main Ria of Vigo has an area of 156 km^2, is approximately 31 km long and gradually narrows landwards from 6 km near its mouth to 0.6 km near the narrow Rande Strait; beyond which it widens into a wide shallow bay with an area of 18 km^2: the San Simón Bay (Fig.1). Depths vary from 60 m near the entrance of Ria of Vigo to the inner part the San Simón Bay landward of this narrows is less than 5 m over most of its subaqueous part. At the landward head of the ría are broad intertidal sand and mud-flats cut by estuarine channels which form part of a bayhead delta; interestingly, except in a small area partly protected by sea walls, marshes dominated by halophytic plants are absent, although much of the mudflat is colonized by *Zostera sp.*

Several small to medium sized rivers drain an area of 489 km^2 before discharging in to the Ria of Vigo. The main discharge is carried into the landward part of the San Simón Bay by the river Oitavén and the small streams of Ullo, Sidral, Maior and Alvedosa. A few smaller streams such as the Lagares, Postrillón and Fraga enter the middle-outer ría. The Oitavén River is the main tributary contributing around 80% of the total freshwater input to the ria, whose annual average flow is 17 $m^3 \cdot s^{-1}$, ranging from 55 $m^3 \cdot s^{-1}$ in February to 1 $m^3 \cdot s^{-1}$ in August (Río-Barja and

Rodríguez-Léstregas, 1992). Early work by Nombela (1989) showed that in the San Simón Bay, the Alvedosa River (≈2 $m^3 \cdot s^{-1}$), although one of the smallest streams has discharges and loads greater than the other streams. Similarly, the Lagares River (≈4 $m^3 \cdot s^{-1}$), also a relatively small stream, has the highest discharge and sediment load of all the rivers in the outer ria.

The catchment area of the rivers is dominated by hard PreCambrian and Palaeozoic granites, gneisses, mica-schists and some quartzites. The region surrounding the ria has a warm humid climate. Much of the hinterland is covered by forest and scrub with pasturelands composed of heath with grasses being common (Valdés and Gil-Sánchez, 2001); cultivated land occupies only a small part of the rivers catchments, e.g 12.5% of the Oitavén, and 42.5% in the catchment of the Alvedosa River which is the exception (Pazos et al., 2000). Frequent forest fires occur and these strip the landscape of vegetation. However, the land soon recovers, usually after 1-2 years (Diaz Fierros et al., 1987). Benito et al. (1991) claimed that most of the erosion occurs during the first six months of rain after the fires.

The Ria of Vigo is mesotidal (average tidal range 2.2 m). Its outer and middle zone is mainly oceanic with water salinities >35 decreasing to 31-32 in the Rande Strait and to even lower values <15 around the small river estuaries at the landward head of the San Simón Bay, which is the estuarine ria zone (Evans and Prego, 2003). Generally, the ria has a positive estuarine circulation with water flowing landward along the deeper parts and seawards at the surface separated by a narrow zone of mixing (Otto, 1975; Prego et al., 1990). Water residence times in the ria range from a few days to a month, usually due to fluvial forcing during the wet season and by upwelling events during the dry season (Prego and Fraga, 1992). The circulation of water and nutrients in the Ria of Vigo and adjacent rias as well as their productivity is greatly influenced by the Finisterre marine upwelling which usually occurs from April to October (Blanton et al., 1984) and forces Eastern North Atlantic Central Water (Fraga, 1981) into the interior of the rias (Prego and Bao, 1997). Thus, the primary production in the ria is high and in the middle zone of the Ria of Vigo ranges between 30 to 100 $mgC \cdot m^{-2} \cdot d^{-1}$ in winter, but this increases to 700 to 1200 $mgC \cdot m^{-2} \cdot d^{-1}$ during the rest of the year (Vives and Fraga, 1961).

The importance of anthropogenic activities has increased historically; shipbuilding becomes important at the end of the 19C. However, the biggest increases have been since the 1960s (Howarth et al., 2005), including mussel aquaculture, since when there has been a marked increase in population and industrial activity (Fig.2).

MATERIAL AND METHODS

Water and sediment sampling

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 its entire basin surface according to the rainfall and land used by a hydrological model (Alvarez-Eijo, 2000). The smaller stream flows were calculated from the Oitavén discharge and the stream basin areas due to the good relationships ($r^2>0.9$) obtained by comparing the measurements of their flows (Alvarez-Eijo, 2000). Sewage treatment plants (STPs) flows corresponding to the monthly average discharge during 2004 were provided by the Sewage Plant Companies.

Samples from the rivers and STPs were collected and placed in 1-L glass bottles. Fluvial sampling points (salinity <0.1 measured with a WTW MultiLine P4) were situated on the Oitavén

River, streams of Alvedosa, Lagares, Fraga, Maior and Ullo and the STPs at Vigo, Teis, Arcade, Redondela, Cangas and Moaña (Fig.1). Each point was sampled monthly during 2004, except for the Oitavén River which was sampled twice a month.

Sediment samples were collected from the ria floor using a standard Van-Veen stainless steel grab and a box corer (see Fig.1 for locations). Cores were taken to sample the undisturbed sediment from the box-corers and samples were collected at 1 cm intervals.

Sample pre-treatment and analysis

Freshwater and sewage samples were refrigerated at 4°C and taken to the laboratory on the same day; and, were vacuum filtered, 1 L for the rivers and the small streams and 200 mL for EDARs, through weighed Whatman GF/F filters (0.45 μm filter circles of 2.5 cm diameter) in a filter holder (Pall, Gelman). This was used to operationally define the separation between dissolved and particulate components (Chapman, 1992; Loring and Rantala, 1992). Wet filters containing the suspended particulate matter (SPM) were put into a laminar flow chamber until dry. The filters were then weighed to calculate the SPM concentration, placed in Petri dishes and stored at –20ºC in the freezer until POC analyses. Funnels, bottles, filter holders, tweezers, Petri dishes and other materials were washed with detergent and rinsed with Milli-Q water.

Particulate organic carbon (POC) in the suspended particulate matter was determined combustiometrically analyzing the filters in the EA 1108 CNH analyzer (Carlo Erba Instruments) of the Analytical Service (SAI) of Coruña University (UDC). The analysis of blank filters showed negligible amounts of carbon and acetanilide was used as standard. The concentration of POC (mass/volume) in each sample was calculated multiplying the POC (mass/mass) by SPM (mass/volume) concentration. Finally, the flux of POC was calculated for each source - river, small streams and EDARs - multiplying each water flow by its POC concentration (mass/volume).

Standard grain size techniques were used to determine the sand, silt and clay content of the samples (Folk 1974). Carbonates were previously removed by acidifying the sediment subsamples and the organic carbon was later determined using a standard Perkin-Elmer elemental analyzer apparatus.

Other samples were used for the study of the composition of the organic matter. They were first dried and the large shell fragments removed which otherwise would distort the analyses. They were then weighed and initially treated with concentrated commercial grade HCl to remove carbonates and mobilise any calcium that otherwise interfere with the removal of silicates. This acid treatment was followed by washing until neutral. The silicate removal was achieved with 60% HF acid, initially at low concentration by adding to the sample already in water. After any initial reaction had subsided the acid strength was increased by decanting off the spent acid and recharging with fresh acid. The samples were again decanted and washed until neutral and concentrated HCl added. They were brought to boiling and then rapidly diluted with a large volume of water followed by further sieving at 20 µm. This final acid treatment removed any neoformed fluorides. The resulting kerogen concentrate was checked for quality and then stored in a vial. Samples rich in amorphous organic matter (AOM) were split with one half having the AOM removed using a tunable ultrasonic probe. This preferentially fragments the AOM particles that can then be removed by sieving at 20 µm. Finally, a small part of the kerogen concentrate was mounted on a glass coverslip with Elvacite 2044.

The sediment samples were the examined microscopically and the abundance of the different components determined by point counting as particles to a total count of 400. A relatively simple classification was used into some nine general categories. AOM was not included in the count. The results have been recalculated to remove the effects of data closure inherent in all proportional data the results were also converted to an eight point logarithmic abundance class scale following Kovach and Batten (1994).

The samples used for the Rock-Eval analysis were taken from the top of the box cores and placed in a cold box before being deep frozen and transported immediately to France. They were analyzed by Étienne Brosse of the geochemical laboratories of the 'Institut Francais du Petrole' using standard RockEval procedures (e.g. Tissot and Welte, 1984).

RESULTS

Continental POC contributions to the ria

The annual ranges of POC concentration introduced by the six STPs situated in the littoral of the Ria of Vigo are shown in the Table 1. The annual average varied in the small treatment plants from 1.6 to 3.7 mgPOC·L^{-1} in four of the treatment plants; but there was an increase to 29.1 mgPOC·L^{-1} in the Teis STP where the treatment seems to have been poor. The most important plant, Vigo STP, where sewage from 300,000 inhabitants is processed, has a POC content (5.1 mgPOC·L^{-1}) of the same order as that of the small plants. The impact of these wastewaters into the Ria environment also depends on the discharge, which is lower than 0.1 m^{3}·s^{-1} for Arcade, Redondela, Cangas and Moaña STP; therefore, their annual loads are very low (fifty times lower) in comparison with that from Vigo STP (9.7 gPOC·s^{-1}), to the latters significant flow (1.95 m^{3}·s^{-1}). On the other hand, the load from the Teis STP, is due to its higher concentration of POC since its flow is low (0.07 $m^3 \cdot s^{-1}$), a not insignificant: 2.0 $gPOC \cdot s^{-1}$.

While the STP loads were calculated on the basis of monthly data, the river POC contributions could be calculated daily from the flows because there is a significant relationship between the flow and the POC flux, as it is indicated by the equations of Table 2, from a similar calculation procedure that to iron in the Ria of Vigo (Filgueiras and Prego, 2007). Except for the Maior and Ullo streams, the annual load variation is low, ranging from 0.9 $gPOC \cdot s^{-1}$ (Fraga stream) to 3.5 $gPOC \cdot s^{-1}$ (Oitavén River), Table 2.

As a whole, the Ria of Vigo receives annually 721 $t \cdot yr^{-1}$ (20 $g \cdot s^{-1}$) of allochtonous POC, according to the fluxes shown in Fig.3. There are two main sources of allochtonous POC. One is natural (one third of total) and is introduced by the rivers that are dominated by the contribution of unpolluted River Oitavén, which carries 16% of the allochtonous POC inputs. The other is anthropogenic (two thirds of total) from the treatment plants, of which 55% of the allochtonous POC to the ria is supplied by the Vigo STP.

Organic matter in ria sediments

The organic matter of the bottom sediments varies from high values in the axial parts of the main ria and the outer parts of the San Simón Bay with lower values along the flanks and in the inner parts of the Bay. The organic carbon shows little or no consistent pattern with depth in the topmost 30 cm of sediment studied in the box cores from the San Simón Bay. The values are within the same range as the surface samples (i.e. 2.0-5.0%) except for a few isolated values of 6.0-7.0% (Fig.4a). On the other hand, the nitrogen content of the surface sediments of the San Simón Bay are rather variable and are usually are between 0.4-0.5 percent (Fig.4b). As with the organic carbon, the same range of values occur at depth, at least as far down as 30 cm without any discernable variation. Carbon- nitrogen ratios vary from 3.0-13.3 with the highest values occurring near the Rande Strait.

Examination of the organic fraction of selected samples of the bottom sediments of the Ria (see Fig.1 for locations) show that there are marked differences between those of the outer Ria and those of the San Simón Bay (Table 3). This is in the form of the abundance of terrestrial phytoclast, both light wood, plant tissue and the much less abundant dark wood. The latter is effectively confined to the Bay. Plant tissue declines steeply away from the margins of the Bay and the source of terrestrial input. Other components, which show marked changes, are dinoflagellate cysts that progressively increase away from the sources of terrestrial input and conversely the cuticles that show an inverse decline within the Bay.

Significantly, the presence of the thickets of *Zostera sp*. in the northern part of the Bay (samples 1 and 8; Fig.1) appear to have no effect on the proportions of cuticle and tissue and are presumably not contributing to the mineral acid resistant palynological residue. As regards the outer part of the Ria system there is evidence for an increasing marine influence within the palynofacies. Primarily, this takes the form of an abundance of dinoflagellate cysts. The outer Ria also shows the concentration of more mobile palynomorphs primarily bisaccate pollen which reach a maxima before declining seawards. An interesting group is the foraminiferal test linings which show a progressive increase throughout the system. In estuaries, the work of Farr (1989) has shown that they are generally well mixed systems with little segregation of marine and terrestrial components. Here, it appears that the test linings, which normally originate from benthic foraminifera that live within the sediment, have the potential to provide an *in situ* signal. The presence of AOM (Amorphous Organic Matter) only in the outer Ria indicates that there the effect of increased productivity/enhanced preservation has been to preserve part of the otherwise unfossilised component of the phytoplankton. The logarithmic abundance class scale also shows these trends. This transformation removes the closure from the data and provides a method for revealing broad trends within the system. This emphasises the restriction of the light and dark wood phytoclast groups to the Bay together with a minor peak in spores. The increase in dinoflagellate cysts from the Bay to outer the Ria is also shown (Fig.5). Again, this transformed data shows the marked progressive increase in foraminiferal test linings seaward.

These variations in the various components are shown clearly by the logarithmic class scale. Such a transformation removes the closure from the data and reveals the broad trends. It emphasises the restriction of the light and dark wood phytoclasts to the San Simón Bay and also the minor peak of spores. The increase in dinoflagellate cysts as well as the progressive increase in foraminiferal test linings from the San Simón Bay, towards the seaward mouth of the rias is clearly shown.

The Rock-Eval evaluation parameters show that the sediments are characterized by immature organic matter as would be expected in recently deposited sediments (Table 4). The S_2 values indicate that they have a relatively good potential as a source of hydrocarbons. The HI (Hydrogen Index, S2 normalised by TOC) suggests that the organic matter appears to be of kerogen type III and is dominantly of continental rather than marine origin.

DISCUSSION

Quantitative significance of Allochthonous POC contributions

The Ria of Vigo, in common with other Galician rias, receives particulate organic matter from several sources. The allochthonous supply is dominated by material carried into the rias by the rivers from the heavily vegetated hinterland. Also, an important source, which has increased in importance since the growth of the local population and industries, is the sewage and industrial waste from the urban centres which surround the Ria (Evans et al., 2000). The inputs from fluvial and sewage sources is currently estimated to be 725 $t \cdot y^{-1}$ of POC of which 67% is derived from treatment plants and 5% from the polluted Lagares River. Until now, the continental inputs of POC to the Ria of Vigo were evaluated as being due to a supply by the pristine Oitavén River (Gago et al., 2005). These authors calculated its contribution to be 97 $t \cdot y^{-1}$. In the present study the POC flux from the Oitavén has been calculated to have a similar value, i.e. 112 $t \cdot y^{-1}$. However, other freshwater inputs to the ria must also be taken into account (Fig.3). When the loads of all the inflowing streams are considered, the fluvial discharges of POC is estimated to be 241 $t \cdot y^{-1}$ and in addition, there is 484 $t \cdot y^{-1}$ of POC from the sewage treatment plants. Consequently, the total continental contribution of POC to the ria is approximately 7.5 times higher than previous evaluations and 72% of this total POC is of anthropogenic origin. Interestingly, as a whole, the POC flux corresponds to an average concentration of 0.78 $mg \cdot L^{-1}$ of POC, which is lower than the average for unpolluted rivers proposed by Meybeck (1982).

The importance of these allochthonous contributions of POC to the ria as an organic reservoir can be only defined when their autochthonous POC fluxes are known. The latter are a result of the processes of photosynthesis, remineralization, and sedimentation inside the Ria of

Vigo and were quantified using a reservoir budget (Prego 1993a,b) summarized in Figure 6. The Ria of Vigo is, as are the other Galician Rias, the site of deposition of sediments relatively rich in organic matter. It is an area of high productivity due to euthrophic events of upwelling and extensive photosynthesis in the photic layer of the water column. It has been estimated the mean photosynthesis rate in the Ria of Vigo is 350 $mgC\cdot m^{-2}\cdot d^{-1}$. This is in agreement with those measured previously by Vives and Fraga (1961) and Fraga (1976) in the Ria of Vigo and Varela et al. (2005) in other rias.

Because the rias are zones of relative high primary production compared with nearby oceanic regions (Finenko, 1978), they exhibit elevated processes of remineralisation and sedimentation of the organic matter. Consequently, although some of the POC supplied to the ria is lost to the open sea (19%) due to the estuarine circulation and some to mineralization (41%) a considerable amount is trapped in the bottom sediments (34% or 41% if the mussel removal is included; i.e. 144 $mgC\cdot m^{-2}\cdot d^{-1}$). The Ria behaves like a carbon trap and presents similar average rate of POC on the continental margin suggested by Romankevich, (1984) during the Late Quaternary or in coastal zones estimated by Wollast (1991). The composition of the POC accumulating in the sediment reflects the importance of the various sources. Today, the contemporary supply of POC to the floor of the ria is dominated by autochthonous material (44-53 $g_{POC}\cdot m^{-2}\cdot yr^{-1}$) whilst allochtonous material contributes (5 $g_{POC}\cdot m^{-2}\cdot yr^{-1}$). These rates are based on one year measurements and of course they may vary; however, at the moment, the extent of this variation is unknown although the year of measurement may be considered meteorologically as a standard year.

The POC fluxes show that the natural eutrophication during the upwelling events (Prego et al., 1999; Prego, 2002) controls the POC budget in the ria. Moreover, when the causes (nutrients) and the results (POC increase) of eutrophication are considered (de Jonge and Elliott, 2002) in rias the allochtonous POC, which is mainly anthropogenic, cannot increase the water eutrophication effects because the allochtonous sources of POC are very low in comparison with the autochthonous. When the pattern of flux of POC to rias is compared with that of the typical world estuaries affected by agriculture and increasing human population, e.g. the Humber (Boyes and Elliott, 2006), they are different in many ways (de Jonge et al., 2002).

Deposition and nature of POM in the bottom sediments

The bottom sediments of the San Simón Bay contain similar carbon contents with the greatest values (>5.0%) in the fine grained sediments which extend into the Bay from the Rande Strait (Nombela et al 1995; Belunze-Segarra et al 1997). Analysis of the inner ria sediments by rock-evaluation techniques has confirmed that the POC accumulation in the inner parts of the San Simón Bay is of dominantly terrestrial sources and has a good hydrocarbon potential. There is considerable gas produced in the ria sediments. This was first reported by Acosta (1981) in the sediments of Muros Ria. Later studies of the sediments of San Simón by Nombela et al (1995) and later by Alvarez-Iglesias (2006) showed an abundance of small gas cavities in the sediments of the outer part of the bay around the mussel rafts (Nombela et al., 1995). Detailed geophysical studies by Rey (1993) and subsequent work by Garcia Gil et al. (1999) have revealed what appears to be abundant evidence of gas in the contemporary sediments of the Ria of Vigo. Unfortunately, no rock-evaluation studies were able to be made of the outer ria sediments. However, from the palynological analysis, it would seem likely that these sediments would be richer in type I kerogen and more oil-prone than the gas-prone sediments of San Simón Bay. The geometry of the sediment-fill of the Ria of Vigo and its grain size composition would make it a potential future stratigraphic hydrocarbon trap i.e. an elongate mud-dominated organic rich sediment body infilling an incised valley, which is what a ria really is (Evans and Prego, 2003). This mud body passes landwards up-dip into a substantial sand body composed of clean washed porous medium-fine sands of the ria-head delta which is capped by a sheet of intertidal and marsh mud.

Consequently, the autochthonous-allochthonous organic material is not homogeneously distributed in the ria sediments. Although the allochthonous contributions to the ria are small, its inner part, i.e. San Simón Bay, is an estuarine domain where the continental influence is important, as indicated by the sediment record. This part of the ria is more prone to change (see Evans and Prego, 2003) and as shown by Varela et al. (2008) in the neighbouring Ria of Pontevedra. This pattern is different from that observed in eutrophic estuaries, e.g. the Humber (Boyes and Elliott, 2006).

There is some data on the rate of sedimentation in the Ria of Vigo. However, this proved to be difficult in San Simón Bay due to the disturbance of bottom sediment by biological reworking, waves and probable anthropogenic activity, possibly due to the dragging of nets, became clear in the earlier studies by the University of Vigo and Imperial College (Evans et al., 1994; Nombela et al. 1995). Attempts to obtain ^{14}C dates from good shell material taken from some cores by Vilas, Evans and Nombela in the early 1990s, gave disparate results with no clear relationship between age and depth beneath the sediment surface. Similarly, Howarth et al.

(2005) failed to obtain any unambiguous rates of sedimentation in the sub- aqueous parts of the San Simón Bay using ^{210}Pb dating. Nevertheless, the latter were able to determine the rate of sedimentation on a few small marshes on the landward parts of the San Simón Bay to be 5.6 mm·yr^{-1}) based on ^{210}Pb, with the accumulation rate of sediment of 0.3 g·cm^{-1}·yr^{-1} (confirmed by Cs dating which gave a rate of sedimentation of 5.0 mm·yr^{-1}. Also Quintana et al. (2006) measured a rate of sedimentation of the uppermost sediment of the intertidal flats of the San Simón Bay of 5.6 mm·yr^{-1}. Later Alvarez-Iglesias et al (2007) using ^{137}Cs and ^{210}Pb dating measured a rate of sedimentation of 3-6 mm·yr^{-1} on the intertidal flats of San Simón Bay. Also Pérez-Alvarez (2007), in a further study, determined a rate of sedimentation of 5-6 mm·yr^{-1} on the upper parts of the intertidal flats near the mouth of the Oitavén River. Alvarez-Iglesias et al. (2006) suggested that the rate of sedimentation in the sub-aqueous part of San Simón Bay would be slightly lower than this figure i.e. approximately 3.8 mm·yr^{-1}.

Furthermore, preliminary examination of the pollen in a core, collected in 1988 by Evans, Vilas and Nombela from the middle of the San Simón Bay just west of Isla de San Simón, by Ms Ge Yuy (personal communication to G. Evans) showed the first appearance of *Eucalyptus sp*. pollen at approx 50 cm indicating a rate of deposition of 3.7 mm·yr^{-1} since 1856, (this is the date suggested for the introduction of Eucalyptus species by Desprat et al. (2003)). Later, a very detailed palynological study of a core from the deeper water of the middle of the Ria of Vigo by Desprat et al. (2003) showed the first appearance of *Eucalyptus sp* pollen at a depth which indicates a similar rate of sedimentation of 3.9 mm·yr^{-1} since 1856.

The core studied by Ms Ge Yuy from the middle of the San Simón Bay had an average sediment density of 1.06; so, if a value of between 4-5 % of POC (see Nombela et al 1995) is taken as typical of the muddy sediment of the Bay, this indicates a rate of accumulation of organic carbon of 160-200 g·m^{-2}·yr^{-1} in the inner part of the ria (17.4 km^2 of surface area) since the middle of the 19th Century. On the other hand, in the core studied by Despart et al. (2003) from the main Ria of Vigo, if it is assumed that the average sediment density is 1.06 (no values were given by these authors) and the organic carbon content of the upper sediment is taken to be between 3-4 % (Diz et al. 2002), the rate of accumulation of organic carbon since the middle of the 19th Century has been approximately 120-160 g·m^{-2}·yr^{-1} in the middle part of the ria (39.0 km^2 of surface area). Moreover, two cores from the outer ria boundaries (Caetano et al., 2009; Martins et al., 2011) have provided some additional data on rates of sedimentation using ^{14}C dating which are rate disparate of 0.76 and 0.04 cm·yr^{-1}. The average of these gives a rate of sedimentation of 0.39 cm·yr^{-1}; using the aforementioned weight of dried sediment per cm^3 and an average POC content of 3.4±0.3%; this indicates a rate of accumulation of organic carbon of 135-160 g·m^{-2}·yr^{-1} in the outer part of the ria (99.8 km^2 of surface area). Area-averaging the sediment rates from the three parts of the ria gives a rate of accumulation of POC of 130-165 g·m^{-2}·yr^{-1}, which is greater than the present rate of production. However, if the lowest value of 0.04 cm·yr^{-1} is considered using the same sediment density and POC content, the rate of accumulation of POC is only 15-20 g·m^{-2}·yr^{-1} in the outer part of the ria. Then, area averaging the sediment rates for the three parts of the ria gives a rate of accumulation of POC of 60-75 g·m^{-2}·yr^{-1} which is close to that of the present rate of production of 50-60 g·m^{-2}·yr^{-1}.

The contemporary supply of POC to the ria bottom is dominated by the autochthonous organic carbon, which is more than ten times higher than the allochtonous supply from rivers and sewage loads. Although there is an important inflow of sewage, which has increased the supply of allochtonous POC, 16% of which is from the Oitavén River and 72% of which is of anthropogenic origin; on the other hand, there has been a marked reduction of the area covered by woodland in the river catchments feeding the ria. Also, there has been a further reduction in the supply of sediment and associated POC by the Oitavén River, the main sediment supplier to the ria, due to the construction of a dam which was completed in 1977.

There is a disparity between the rate of POC deposition today (49-58 $g_{POC}\cdot m^{-2}\cdot yr^{-1}$) and the estimated average rate of accumulation since the middle of the 19th Century: >60 $g_{POC}\cdot m^{-2}\cdot yr^{-1}$. Considering the large increase in human activities in the area bordering the Ria of Vigo since the beginning of the 20th Century and particularly since 1960s with its concomitant discharge of human and industrial wastes, the apparent reduction in the rate of accumulation of POC in the sediments is rather surprising.

There are only a few dates to determine the latter, but they all yield rates which are the same order of magnitude. There are several factors which might explain the apparent reduction in the rate of POC accumulating on the floor of the ria. The process of the photosynthesis and also the degree of preservation of POC in sediments may have been affected by the marked increase of metals and other toxic substances which have been increasingly discharged into the Ria of Vigo with human waste and from industrial complexes around the ria as well as from air borne material from a bridge and intensive road networks (Howarth et al., 2005). Also, the reduction of discharge of the Oitavén River due to the dam construction would have reduced the supply of POC to the ria. In addition, this reduction in flow may have weakened the estuarine circulation and made the ria a less efficient trap. However, due to the importance of autochtonous contribution to the sediment, the apparent reduction in POC accumulation is unlike to have resulted only from anthropogenic induced changes, but could possibly have occurred due to mainly environmental changes. Different scenarios for the production of phytoplankton in the rias under various climate circumstances have been proposed by Varela et al. (2008). They showed that if the NE wind regime in summer is reduced (i.e. favourable conditions for upwelling are reduced) a decrease in the phytoplankton production and biomass should occur; similarly, a decrease in production would also occur if the runoff becomes lower during spring. The opposite occurs when the runoff intensifies during spring or the NE winds increase during the summer (although strong upwelling events could prevent phytoplankton accumulation inside ria due to the increase of the ria outflow). Hence it may be hypothesized that upwelling fluctuations controlled by climate changes, as stated in the Varela et al. (2008) paper, are a possible reason to the temporal differences observed in the sedimentation rates of POC. Again, this is another difference between rias and eutrophic estuaries.

Acknowledgements. The writers would like to record their gratitude to members of the former Department of 'Recursos Naturales y Medio Ambiente (Univ. of Vigo)' for helping in collecting the samples with the support of CICYT projects NAT 89-1075 and AMB 93-0300; to METRIA project participants and, particularly, to Dr. Santos-Echeandía and Mr. Otxotorena, for their help with the sampling; to Dr. Z. Ali and Mr. M.A. Ahmad of the former Department of Geology (Imperial College of London) for the carbon and nitrogen analyses; to Dr Ettienn Drosse (Institut Français du Pétrole) for the rock-evaluation values; to Mr. Portela for the gauging station measurements in the Oitavén River and to Dr. Alvarez Eijo (USC) for the gauging station calibration and river flow quantification; to Ms. Rodríguez-Riveiros for her technical assistance; and to the sewage plant companies 'Pridesa', 'Aqualia', 'Espina y Delfín' and 'Fergó Galicia' for their kindness in cooperating in the sampling and providing sewage flow and population equivalent data. This work is a contribution to the Spanish LOICZ program and was partially supported by CICYT under the project 'Biogeochemical budget and 3D transport model of trace metals in a Galician Ria' (reference REN2003-04106-C03).

References

Acosta, J., 1981. Apantallamientos acústicos en la Ría de Muros y Noya y en el Margen Continental de Cadiz. Boletín IEO 7, 127-149.

Álvarez, M.C., Flores, J.A., Sierro, F.J., Diz, P., Francés, G., Pelejero, C., Grimalt, J., 2005. Millennial surface water dynamics in the Ría de Vigo during the last 3000 years as revealed by coccoliths and molecular biomarkers. Palaeogeography, Palaeoclimatology, Palaeoecology 218, 1- 13.

Alvarez-Eijo, M.A., 2000. Análisis regional de frecuencia aplicado a las precipitaciones máximas y mínimas. Ph.D. Thesis, Univ. Santiago de Compostela, Spain, unpublished.

Alvarez-Iglesias, P., 2006. El registro sedimentario reciente de la Ensenada de San Simón (Ría de Vigo, Noroeste de España): interacción entre procesos naturales y actividades antropogénicas. Ph.D. Thesis, Univ. Vigo , Spain, unpublished, 356 pp.

Alvarez-Iglesias, P., Quintana, B., Rubio, B., Arlucea, M., 2007. Sedimentation rates and trace metal input history in intertidal sediments from San Simón Bay (Ría de Vigo, NW Spain) derived from 210Pb and 137Cs chronology. Journal of Environmental Radioactivity 98, 229-250.

Álvarez-Iglesias, P., Rubio, B., Pérez-Arlucea, M., 2006. Reliability of subtidal sediments as "geochemical recorders" of pollution input: San Simón Bay (Ría de Vigo, NW Spain). Estuarine, Coastal and Shelf Science 70, 507-521.

Belzunce-Segarra, M.J., Bacon, J.R., Prego, R., Wilson, M.J., 1997. Chemical forms of heavy metals in surface sediments of the San Simon inlet, Ria de Vigo, Galicia. Journal and Environmental Science and Health A32, 1271-1292.

Benito, E.,Soto, B.,Diaz-Fierros, F., 1991. Soil Erosion Studies in north-western Spain. In: Sala, M., Rubio, J.L., Garcia-Ruiz, G.M. (Eds.), Soil Erosion in Spain. Geoterma, Madrid, pp. 47-55.

Bernardez, P., Prego, R., Francés, G., Gonzalez-Alvarez, R., 2005. Opal content in the Ría de Vigo and Galician continental shelf: biogenic silica in the muddy fraction as an accurate paleoproductivity proxy. Continental Shelf Research 25, 1249.

Bernardez, P., Frances, G., Prego, R., 2006. Benthic-pelagic coupling and postdepositional processes as revealed by the distribution of opal in sediments: The case of the Ria de Vigo (NW Iberian Peninsula). Estuarine, Coastal and Shelf Science 68, 271.

Blanton, J.O., Atkinson, L.P., Femández de Castillejo, F., Lavin Montero, A., 1984. Coasta1 upwelling off the Rias Bajas. Galicia, Northwest Spain. 1: Hydrographic estudies. Rapports et Process Verbaux C.I.E.M. 183, 79-90.

Boyes, S., Elliott, M., 2006. Organic matter and nutrient inputs to the Humber Estuary, England. Marine Pollution Bulletin 53, 136–143.

Caetano, M., Prego, R. Vale, C., dePablo, H., Marmolejo-Rodríguez, J., 2009. Record of diagenesis of Rare Earth Elements and other metals in a transitional sedimentary environment. Marine Chemistry 116, 36-46.

Chapman, D., 1992. The use of particulate matter. In: Chapman, D. (Ed.), Water quality assessments. University Press, Cambridge, pp. 121–170.

de Jonge, V.N., Elliott, M., 2002. Causes, historical development, effects and future challenges of a common environmental problem: eutrophication. Hydrobiologia 475/476, 1–19.

de Jonge, V. N., Bakker, J.F., van Stralen, M.R., 1996. Possible change in the contribution of the river Rhine and the North Sea to the eutrophic status of the western Dutch Wadden Sea. Netherland Journal of Aquatic Ecology 30, 27-39.

de Jonge, V.N., Elliott, M., Orive, E., 2002. Causes, historical development, effects and future challenges of a common environmental problem: eutrophication. Hydrobiologia 475/476, 1–19.

Desprat, S., Sanchez-Goñi, M.F., Loutre, M.F., 2003. Revealing climatic variability of the last three millennia in northwestern Iberia using pollen influx data. Earth and Planetary Science Letters 213, 63-78.

Diaz-Fierros, F., Benito, E., Pérez, M., 1987. Evaluation of the USLE for the prediction of erosion in burntforest areas in Galicia (NW Spain). Catena 14, 189-149.

Diez I., Secilla, A., Santolaria, A., Gorostiaga, J.M., 2000. The North Coast of Spain. In: C.R.C. Shepard, (Ed.), Seas at the Millenium – an environmental evaluation. Pergamon, Amsterdam, vol.1, 135-150.

Diz, P., Francés, G., Pelejero, C., Grimalt, J.O., Vilas, F., 2002. The last 3000 years in the Ría de Vigo (NW Iberian margin): climatic and hydrographic signals. The Holocene 12, 445-458.

Evans, G., Erten, H., Yu, G., Nombela, M.A., Vilas, F., 1994. Sedimentary processes in the Ría de Vigo. Abs: Marine Studies Group Geological Society of London 11/12 Oct., p. 6.

Evans, G., Howarth, R.J., Nombela, M.A., 2000. Metals in the sediments of Ensenada de San Simón (Inner Ría de Vigo), Galicia, NW Spain. Applied Geochemistry 15, 973-996.

Evans, G., Prego, R., 2003. Rias, estuaries and incised valleys: is a ria an estuary? Marine Geology 196, 171.

Farr, K.M., 1989. Palynomorph and palynodebris distributions in modern British and Irish estuarine sediments. In: Batten, D.J., and Keen, M.C. (Eds.), North West European Micropalaeontology and Palynology, Ellis Horwood Ltd, Chichester, pp. 265-285.

Finenko, Z.Z., 1978. Production in plant populations. In: Kinne, O. (Ed.), Marine Ecology, IV. Dynamics, Wiley, Chichester, pp. 13-87.

Filgueiras, A.V., Prego, R., 2007. Biogeochemical fluxes of iron from rainwater, rivers and sewage to a Galician Ria (NW Iberian Peninsula). Natural versus anthropogenic contributions. Biogeochemistry 86 , 319-329.

Folk, R.L., 1974. Petrology of Sedimentary Rocks. Hemphill Publishing, Austin, Texas, 182 pp.

Fraga, F., 1960. Variation estacional de la materia organica suspendidav y disuelta en la ria de Vigo. Influencia de la luz y la temperatura. Investigación Pesquera 17, 127-140.

Fraga F., 1976. Fotosintesis en la Ria de Vigo. Investigación Pesquera 40, 151- 167.

Fraga, F., 1981. Upwellingofthe Galician coast, Northwest Spain. In: Richards, F. A. (Ed.), Coastal upweling American Geophysical Union, Washington, pp. 176-182.

Fraga, F., Prego, R., 1989. Condicciones hidrograficas previas a la purga de mar. In: Fraga, F., Figueiras, F. G. (Eds.), Cuadernos del Area de Ciencias Mariñas Vol. 4: La purga de mar como fenómeno natural. Las mareas rojas. Ediciones do Castro, La Coruña, pp. 21-24.

Gago, J., Álvarez-Salgado, X.A, Nieto-Cid, M., Brea, S., Piedracoba, S. 2005. Continental inputs of C, N, P and Si species to the Ría de Vigo (NW Spain). Estuarine, Coastal and Shelf Science 65, 74-82.

Garcia-Garcia, A., Garcia-Gila,S., Vilas,F., 2005. Quaternary evolution of the Ría de Vigo, Spain. Marine Geology 220, 153-179.

García-Gil, S., Vilas, F., Muñoz, A., Acosta, J., Uchupi, E., 1999. Quaternary sedimentation and thermal diapirism in the Ría de Pontevedra (Galician), Northwest Spain. Journal of Coastal Research 15,1083-1090.

Howarth, R.J., Evans, G., Croudace, I.W., Cundy, A.B., 2005. Sources and timing of anthropogenic pollution in the Ensenada de San Simón (inner Ría de Vigo), Galicia, NW Spain: an application of mixture modelling and nonlinear optimization to recent sedimentation. Science of the Total Environment 340, 149-176.

Kovach, W.l., Batten, D.J., 1994. Association of palynomorphs and palynodebris with depositional environments: quantitative approaches. In: Traverse, A. (Ed.), Sedimentation of Organic Particles, CUP, Cambridge, pp. 391-407.

Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Science Reviews 32, 235–283.

Margalef, R., 1956. Paleoecología postglacial de la Ria de Vigo. Investigación Pesquera 5, 89-112.

Margalef, R., Andreu, B., 1958. Componente vertical de los movimientos del agua en la Ria de Vigo y su posible relacion con la entrada de la sardina. Investigación Pesquera 11, 105-126.

Martins, V., Araújo, M.F., Silva, E.F., Dias, J.M.A., Calisto, R., Jouanneau, J.-M., Weber, O., Rocha, F., 2011. Upwelling dominated oceanographic periods in the Ria de Vigo during the late Holocene. Journal of Coastal Research SI64, 1998-2001.

Mendez, G., Vilas, F., 2005. Geological antecedents of the Rías Baixas (Galicia, NW Iberian peninsula). Journal of Marine Systems 54, 195-2007.

Meybeck M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. American Journal of Science 282, 401-450.

Nombela, M.A., 1989. Oceanografía y sedimentología de la Ría de Vigo. Ph.D Thesis, Univ. Complutense de Madrid, Spain, unpublished, 292 pp.

Nombela, M.A., Vilas, F., Evans, G., 1995. Sedimentation in the mesotidal Rías Bajas of Galicia (north-western Spain): ensenada de San Simón, inner Ría de Vigo. Special Publications International Association of Sedimentologist 24, 133-149.

Otto, L., 1975. Oceanography of Ria de Arosa (NW Spain). Konink Meteor International Medelingen en Verlan 96, 210 pp.

Pannekoek, A.J., 1966. The ria problem: the role of antecedence, deep weathering, and Pleistocene slope-wash, Tijdschrift van het Koninklijk Nederlandsch Aardrijkakunsif Genootschap 83, 289-297.

Pannekoek, A.J., 1970. Additional geomorphological data on the ría area of western Galicia (Spain). Leidse Geologische Mededeling 37, 185-194.

Pazos, O., Nombela, M.A., Vilas, F., 2000. Continental contribution of suspended sediment to an estuary: Ría de Vigo. Scientia Marina 64, 295-302.

Peeters, J.C.H., Haas, H.A., Peperzak, L., de Vries, I., 1993. Nutrients and light as factors controlling phytoplankton biomass on the Dutch Continental Shelf (North Sea) in 1988–1990. Report DGW-93.004, Rijkswaterstaat Tidal Waters division, Middelburg.

Pérez-Arlucea, M., Álvarez-Iglesias, P., Rubio, B. 2007. Holocene Evolution of Estuarine and Tidal-flat Sediments in San Simón Bay, Galicia, NW Spain. Journal of Coastal Research SI50, 163-167.

Prego, R., Fraga, F., Rios, A. F., 1990. Water interchange between the Ria of Vigo and the continental shelf. Scientia Marina 54, 95-100.

Prego, R., Fraga, F. 1992. A simple model to calculate the residual flows in a Spanish ria. Hydrographic consequences in the ria of Vigo. Estuarine, Coastal and Shelf Science 34, 603-615.

Prego, R., 1993a. Biogeochemical pathways of phosphate in a Galician ria (north-western Iberian Peninsula). Estuarine, Coastal and Shelf Science 37, 437.

Prego, R. 1993b. Eutrofización de las aguas costeras gallegas. In Penas, X. (Ed.) A contaminación mariña do litoral galego. Edicios do Castro, Sada, pp. 25-48.

Prego, R., Bao, R., 1997. Upwelling influence on the Galicia coast: silicate in shelf water and underlying surface sediments. Continental Shelf Research 17, 307.

Prego, R., Barciela, C., Varela, M., 1999. Nutrient dynamics in the Galician coastal area (Northwestern Iberian Peninsula): do the Rias Bajas receive more nutrient salts than the rias Bajas?. Continental Shelf Research 19, 317-334.

Prego, R., 2002. Nitrogen Fluxes and Budget Seasonality in the Ria Vigo (NW Iberian Peninsula). Hydrobiologia 475/476, 161-171.

Quintana, B., Alvarez-Iglesias, P., Santamaria,R., Rubio,B., Perez-Arlucea, M., 2006. Low level gamma spectrometry for pollution assessment in San Simón Bay (Vigo, NW Spain). Journal of Physics, Conference Series 41, 400-407.

Rey, J., 1993. Relación morfosedimentaria entre la plataforma continental de Galicia y las Rías Bajas y su evolución durante el Cuaternario. Publicaciones especiales del IEO 17, 232 pp.

Río Barja, F.J., Rodríguez Lestegás, F., 1992. Os ríos galegos. Consello da Cultura Galega. Santiago, 333 pp.

Romankeviche, A., 1984. Geochemistry of Organic Matter in the Ocean. Springer-Verlag, Berlin, pp. 153-158.

Sala, M., 1984. Iberian Massif: Galician Massif. In: Embleton, G. (Ed.). Geomorphology of Europe. The Macmillan Press, London, pp. 294-299.

Stenuit, R. 1969 Tesoros y Galeones Hundidos. Editorial Juventud, Barcelona, 224 pp.

Tissot, B. P., Welte, D.H., 1984. Petroleum Formation and Occurrence. Springer-Verlag (2da Edition), Berlin, 699 pp.

Varela, M., Prego, R., Pazos, Y., Moroño, A., 2005. Influence of upwelling and river runoff interaction of phytoplankton assemblages in a Middle Galician Ria ans comparison with northern and southern rias (NW Iberian Peninsula). Estuarine, Coastal and Shelf Science 64, 721-737.

Varela M, Prego R, Pazos Y., 2008. Spatial and temporal variability of phytoplankton biomass, primary production and community structure in the Pontevedra Ria (NW Iberian Peninsula): oceanographic periods and possible response to environmental changes. Marine Biology 154, 483-499.

Valdes, C.M., Gil Sanchez, L., 2001. La transformación histórica del paisaje forestal en Galicia. Ministerio de Medio Ambiente, Madrid, 159 pp.

Vilas, F., Bernabeu, A., Méndez, G., 2005. Sediment distribution pattern in the Rias Baixas (NW Spain): Main facies and hydrodynamic dependence. Journal of Marine Systems 54, 261-276.

Vives, F., Fraga, F., 1961. Producción básica en la ría de Vigo (NW de España). Investigación Pesquera 19, 129-137.

Von Richthofen, F., 1886. Führer für Forschungsreisende, Oppenheim, Berlin.

WMO 1994. Guide to hydrological practices. Data acquisition and processing, analysis, forecasting and other applications. World Meteorological Organization, Geneva, No. 168.

Wollast, R.,1991. The coastal organic carbon cycle: Fluxes, sources and sinks. In: ed. R. F. C. Mantoura, R.F.C et al. (Eds.), Ocean Margin Processes in Global Change. Wiley & Sons, London, pp. 365-382.

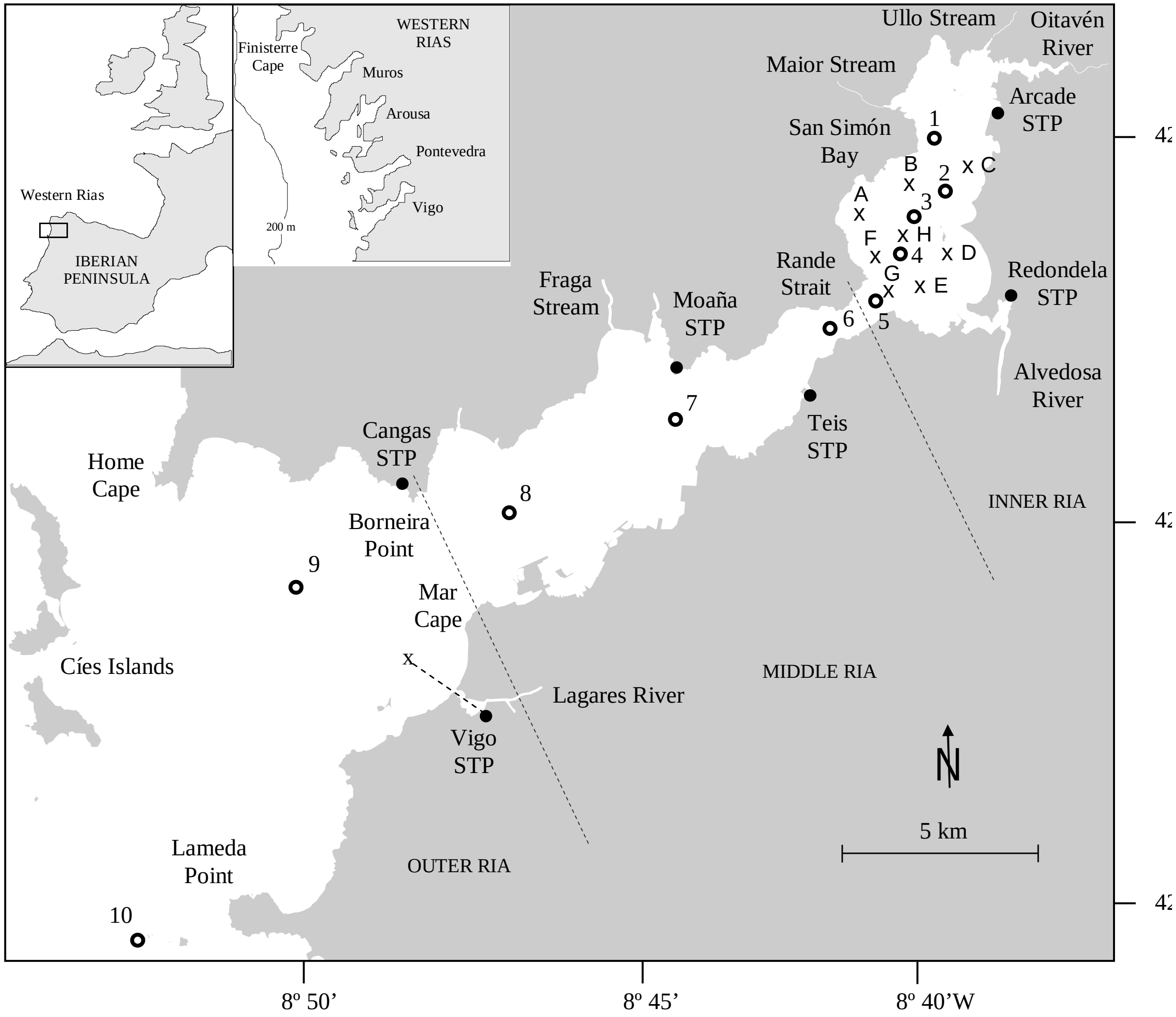

Figure 1. Ria of Vigo with their three main zones and geographical names. Rivers, sewage treatment plants (STP), submarine emissary of Vigo STP, surface sediment (st.1-10), box corer (st. A-H) used for carbon, nitrogen and rock-eval (st.B and D to H) are also shown.

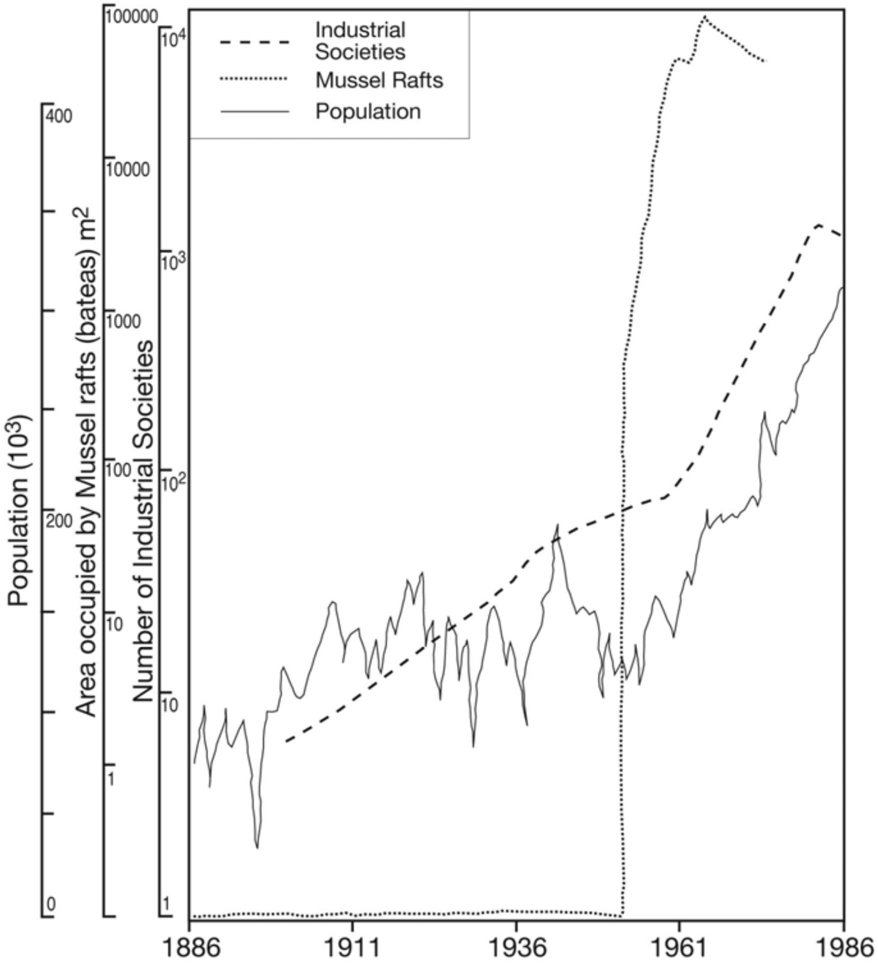

Figure 2. Human activity in the Vigo Ria area.

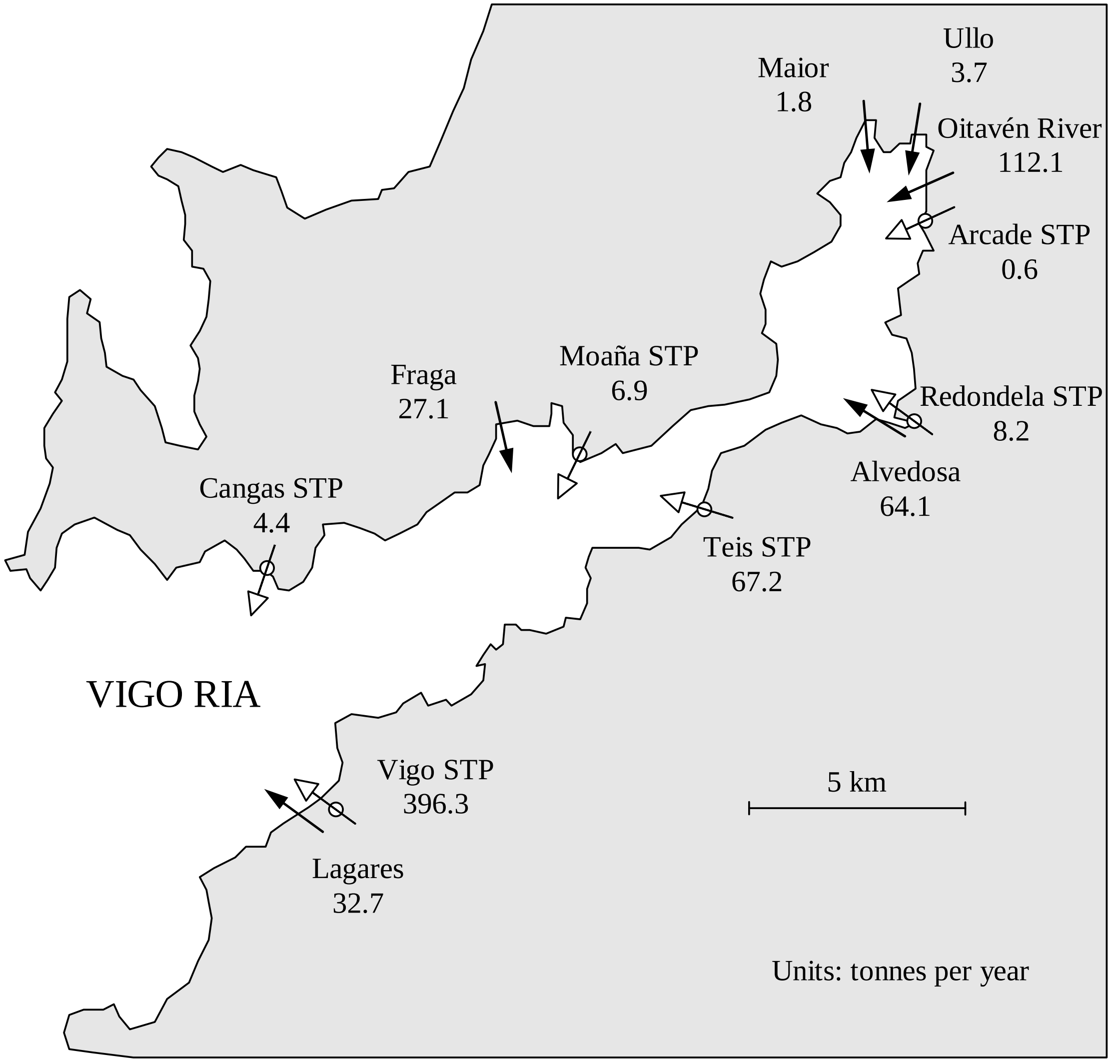

Figure 3. Allochtonous POC contributions to the Ria of Vigo. Black arrows correspond to river load and empty arrows to sewage discharges.

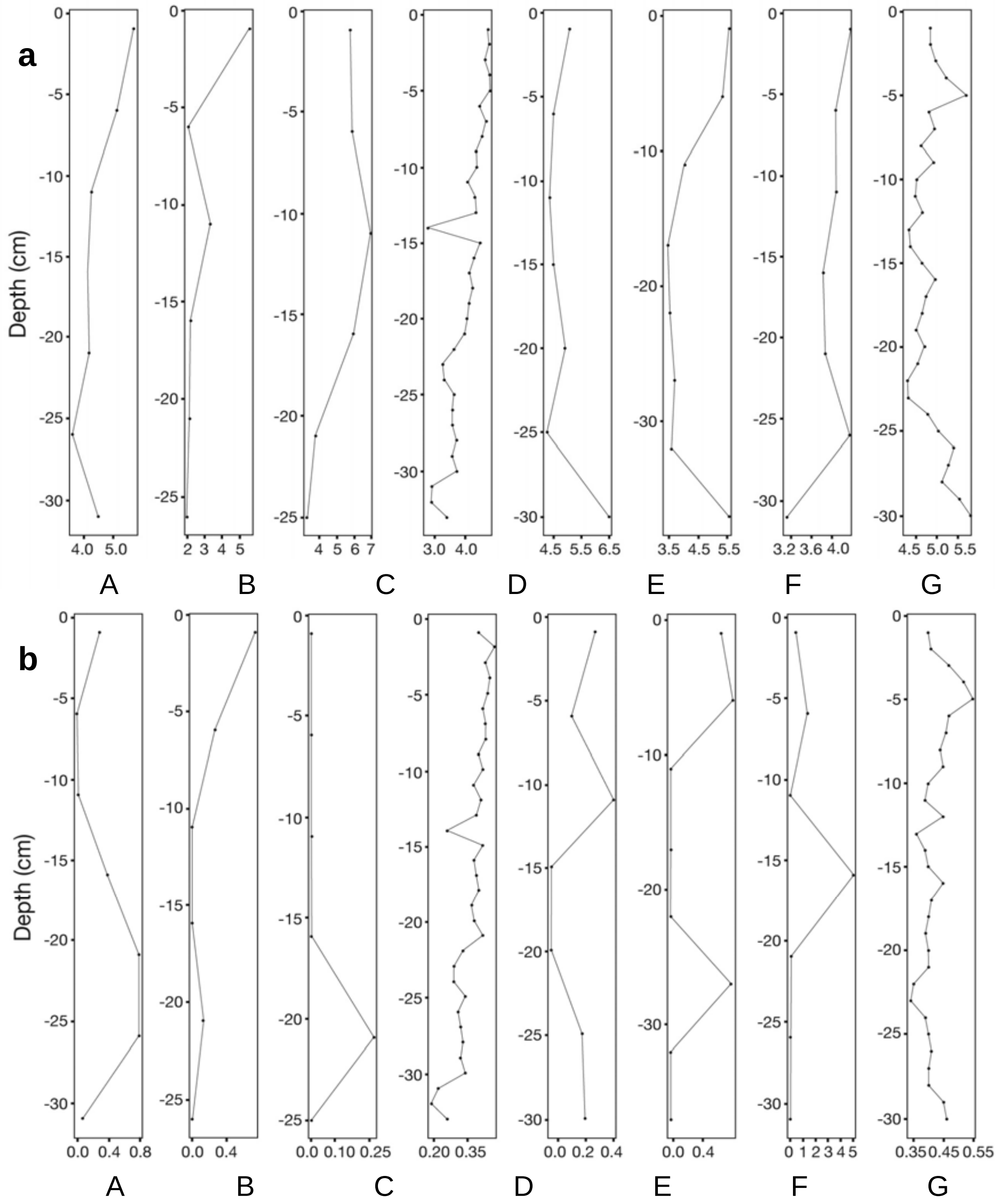

Figure 4. Vertical variation of a) Organic carbon (%) and b) Organic nitrogen (%) in the sampled cores (see Fig.1 for location of samples).

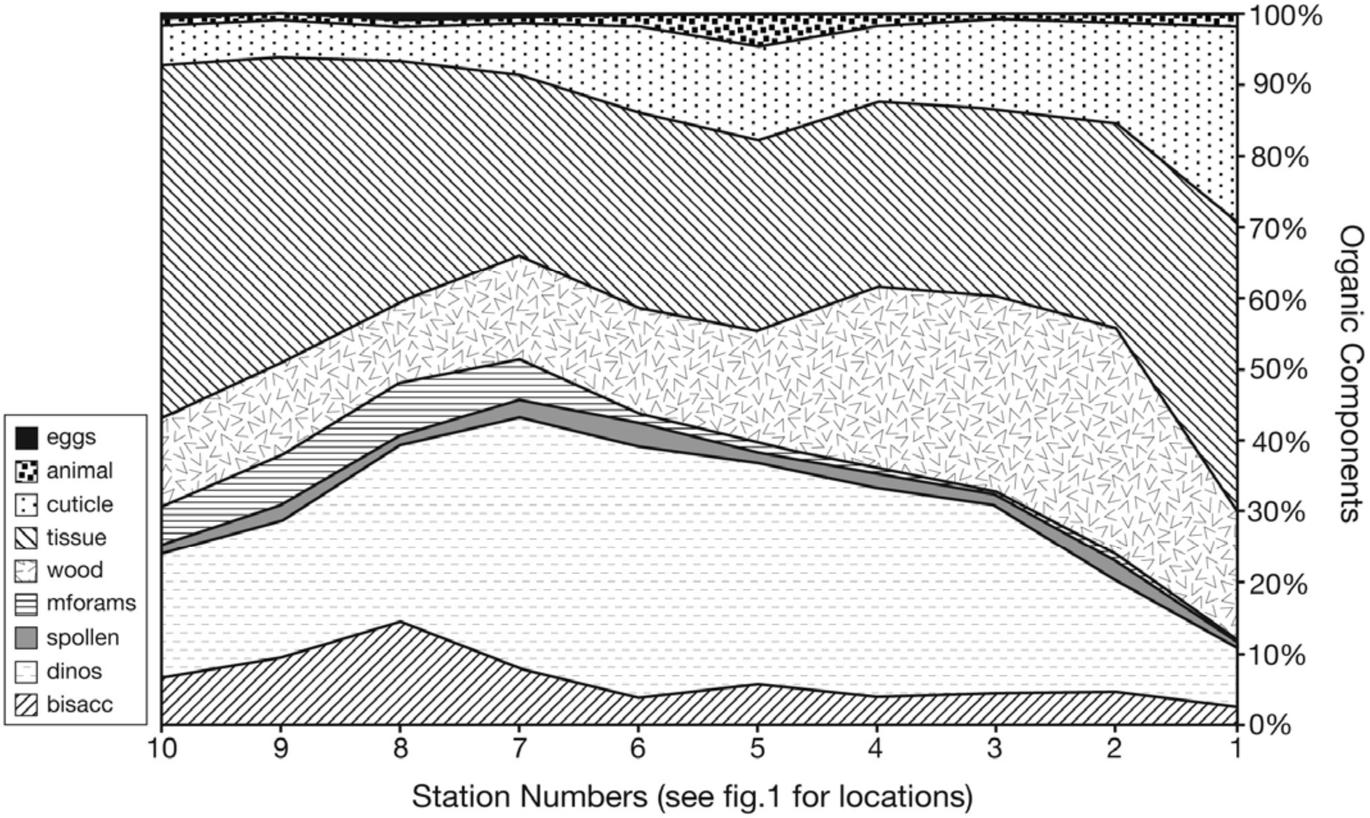

Figure 5. Variation of organic components from seaward to landward (see Fig.1 for location of samples).

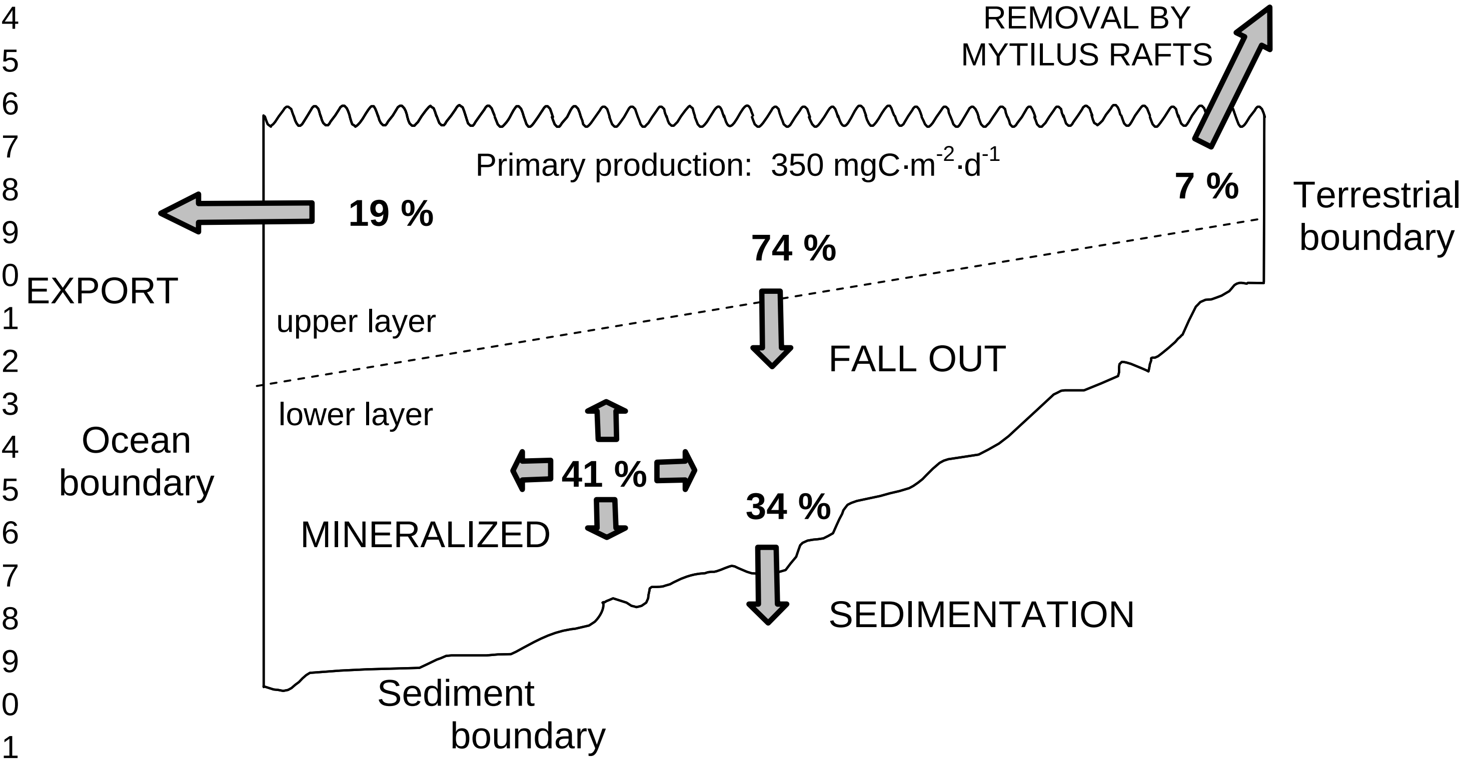

Figure 6. Autochthonous POC production and fluxes in the Ria Vigo

Table 1. Annual ranges and average values of discharges, POC concentrations and loads of the main terrestrial contributors to the Ria of Vigo.

	Fluvial	Oitaven	Alvedosa	Lagares	Fraga	Maior	Ullo
Flow	range	1.0 – 173.6	0.11 – 9.58	0.21 – 18.45	0.02 – 2.35	0.02 – 2.35	0.04 – 4.33
(m^{3}·s^{-1})	average	16.33	1.63	3.68	0.41	0.40	0.74
[POC]	range	0.08 – 0.74	0.10 – 1.42	0.14 – 5.89	0.16 – 0.57	0.07 – 0.50	0.08 – 1.44
(mg·L^{-1})	average	0.18	0.37	1.14	0.33	0.26	0.45
POC Load	range	0.1 – 87.7	0.1 – 26.8	0.7 – 3.3	0.3 – 3.0	0.01 – 0.2	0.1 – 0.4
(g·s^{-1})	average	3.52	2.06	1.05	0.87	0.06	0.12
	STP	Arcade	Redondela	Teis	Vigo	Cangas	Moaña
Flow	range	0.010 – 0.033	0.058 – 0.087	0.052 – 0.110	1.70 – 2.29	0.040 – 0.099	0.069 – 0.118
(m^{3}·s^{-1})	average	0.017	0.073	0.071	1.953	0.061	0.086
[POC]	range	0.12 – 6.55	0.35 – 15.3	0.82 – 68.9	0.39 – 12.6	0.18 – 10.5	0.19 – 6.21
(mg·L^{-1})	average	1.62	3.70	29.1	5.07	2.60	1.72
POC Load	range	0.01 – 0.07	0.01 – 0.93	0.05 – 4.98	0.74 – 23.4	0.01 – 0.54	0.02 – 0.48
(g·s^{-1})	average	0.03	0.26	2.00	9.71	0.14	0.15

Table 2. POC loads of individual water courses:

$$F = a \cdot Q^2 + b \cdot Q + c$$

POC fluxes, F, are in g s^{-1} with discharges, Q, in m^3 s^{-1}. R^2 is the correlation coefficient between F and Q.

Type	Source	a	b	c	R^2
Fluvial	Oitaven	0.0024	0.088	0.03	0.999
	Alvedosa	0.350	-0.587	0.28	0.995
	Lagares	0.0019	0.080	0.68	0.749
	Fraga	-0.338	1.95	0.25	0.901
	Maior	-0.0360	0.163	0.01	0.924
	Ullo	-0.0222	0.170	0.03	0.787

Table 3. Grain counts of organic matter components in the surface sediments of the Ria of Vigo. Number of grains counted was 400.

Component	St.1	2	3	4	5	6	7	8	9	10
bisac	11	19	18	16	23	15	32	58	38	27
dinos	33	62	105	117	125	141	140	99	76	69
spollen	4	11	6	8	6	13	10	5	9	5
mforanms	0	3	2	2	5	5	23	30	28	21
wood	72	128	110	103	63	60	59	45	52	50
tissue	163	115	109	104	107	110	101	136	172	199
cuticle	110	56	51	43	53	48	29	19	21	22
animal	6	6	3	6	17	7	3	4	4	4
eggs	1	0	0	1	2	1	3	4	0	3
lycos	6	7	5	8	7	9	10	16	15	16

Table 4. Mineral carbon, total organic carbon (TOC), and Rock-eval parameters for selected box-corer samples from San Simón Bay.

Station	Mineral carbon weight %	TOC %	ROCK-EVAL parameters					
			mgHC / g rock		mg CO_2 / g rock	T max	mg / g TOC	
			S_1	S_2	S_3	(ºC)	iH	iO
B	0.48	5.87	0.06	16.20	9.45	417	275	160
D	0.80	4.43	0.12	13.31	7.45	415	300	168
E	0.89	4.46	0.15	13.40	8.04	415	300	180
F	1.00	4.68	0.22	14.73	8.55	409	314	182
G	1.03	4.28	0.26	12.00	7.75	414	280	181
H	0.95	4.39	0.10	12.05	0.10	414	274	184