

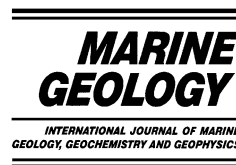


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Reconstructing export production at the NE Atlantic margin: potential and limits of the Ba proxy

Nathalie Fagel^{a,*}, Frank Dehairs^b, Rolf Peinert^c, Avan Antia^c, Luc André^d

^a *Clay and Paleoclimate, Geology Department, Université de Liège, B18 Sart-Tilman, Allée du 6 Août, B-4000 Liège, Belgium*

^b *Analytical Chemistry Department, Vrije Universiteit Brussel, B-1050 Brussels, Belgium*

^c *Institut für Meereskunde, D-24105 Kiel, Germany*

^d *Mineralogy and Geochemistry Department, Royal Museum for Central Africa, B-3080 Tervuren, Belgium*

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Abstract

Barium (Ba), aluminium (Al), and zirconium (Zr) were measured in sediment trap material deployed at two margin settings of the NE Atlantic: the Bay of Biscaye at Goban Spur and the NW Iberian Margin. The Particulate Organic Carbon (POC)/Ba ratios of the trapped material in both margin environments are clearly higher compared to the open ocean. Although lateral advection of POC may partly explain these higher POC/Ba ratios for margin systems, it is clear that the yield of authigenic particulate Ba during organic matter degradation in the water column is lower in margin environments. In order to assess export production in margin settings we optimised transfer functions based on trapped Ba fluxes that were originally elaborated for open ocean settings. Calculations of export production based on trapped Ba flux and POC/Ba ratio were compared with calculations based on trapped POC flux only. Export production based on Ba flux show greater internal consistency amongst traps along the same mooring, suggesting that this approach has advantages over the one based on POC flux only. Estimated export productions are of the same order of magnitude as estimates of new production, but systematically fall short of the latter. This systematic discrepancy needs further investigation.

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1. Introduction

The water column flux of particulate excess Ba (Ba_{xs} = authigenic barite and other biogenic Ba phases) has been used to compute export production via the application of different algorithms

(Dymond et al., 1992; François et al., 1995, Nürnberg, 1995). These algorithms rely on the vertical evolution of the Particulate Organic Carbon (POC)/ Ba_{xs} ratio in sediment trap samples. For the open ocean environment, the approaches based on the Ba_{xs} flux as predictor variable produce results similar to those based on the POC flux. However, it has been argued that under conditions of potential POC advection, such as existing in the vicinity of margin systems, Ba_{xs} rather

* Corresponding autor. Tel.: +32-4-366-2209;
Fax: +32-4-366-2202.

E-mail address: nathalie.fagel@ulg.ac.be (N. Fagel).

than POC would be the appropriate predictor for export production (François et al., 1995).

In the present study, selected geochemical data (Al, Ba, and Zr) for sediment trap material collected along the Iberian Margin are discussed and compared with results for the Goban Spur area (northern Gulf of Biscay) published earlier (Fagel et al., 1999; Dehairs et al., 2000). By comparing these areas of the NE Atlantic Margin, which contrast in terms of shelf and slope morphologies, we aim at evaluating: (1) the regional variability of the impact of lateral advection on trap fluxes, and (2) the feasibility of export production calculation in close-to-margin settings, as based on trapped Ba_{xs} fluxes. The latter objective requires verifying whether the higher POC to Ba flux ratios we reported earlier for the Goban Spur Margin as compared to the open ocean (Dehairs et al., 2000) are local features, or to the contrary, are characteristic for the broader region, therefore

justifying the development of a transfer function specific for the margin environment.

1.1. Site description

Between July 1997 and December 1998, sediment traps were deployed at 600 m and 1100 m depth at two sites off the Iberian Margin (OMEX II programme): site IM2 at the upper slope and site IM3 at the lower slope (Fig. 1; Table 1). Prior to this study sediment trap work had been conducted off the Goban Spur Margin, in the northern Gulf of Biscay (OMEX I programme). For the Goban Spur area three mooring sites were studied between July 1993 and September 1995 (Fig. 1; Table 1): site OM2 at the upper slope; site OM3 at the base of the continental slope, and site OM4 in the abyssal plain (Antia et al., 1999).

The Iberian Margin is characterised by a narrow shelf adjacent to a steep slope cut by deep

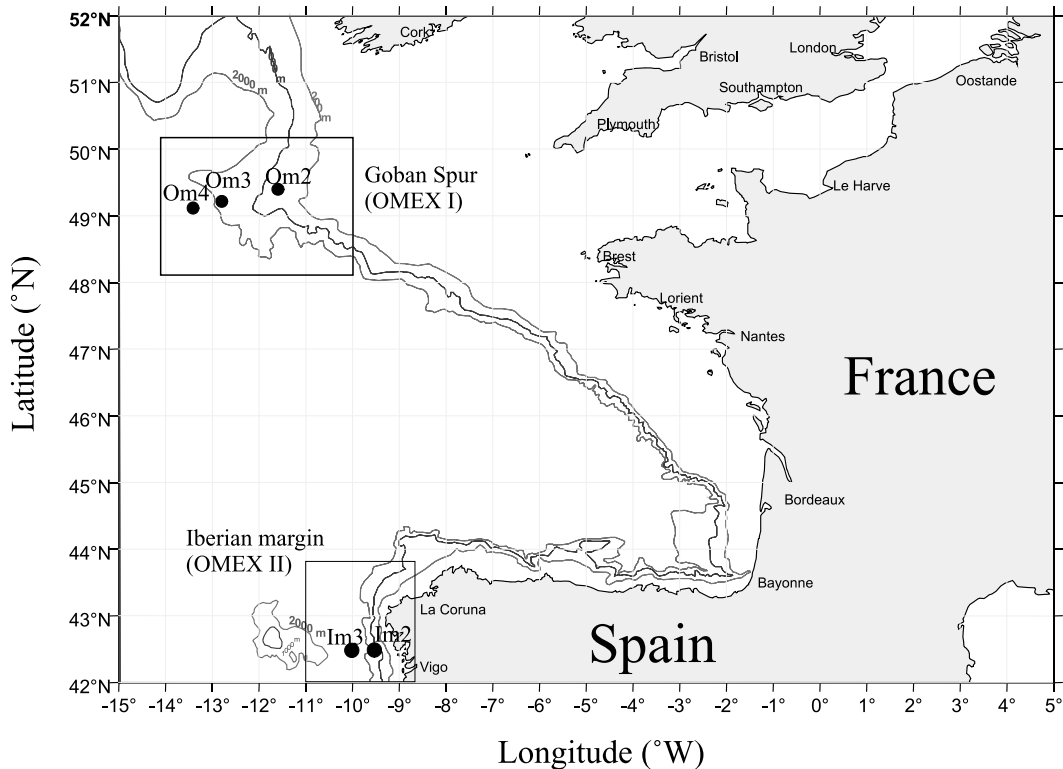


Fig. 1. Location of the sediment trap mooring sites at northern Iberian Margin (sites IM2 and IM3, OMEX II, 1997–2000) and at Goban Spur in the northern Gulf of Biscay (sites OM2, OM3 and OM4; OMEX I, 1993–1996). Water depth in metres.

Table 1

Location and operation period of the sediment trap moorings during the OMEX I (1993–1996, Goban Spur) and OMEX II (1997–2000, Iberian Margin) programmes

| Site | Programme | Cruise | Site name | Location | Latitude (°N) | Longitude (°W) | Water depth (m) | Trap depth (m) | Trap record |
|----------------|-----------|---------------------------|-----------|-------------------------|---------------|----------------|-----------------|----------------|---|
| Iberian Margin | OMEX II | R/V <i>Pelagia</i> | IM2 | near-shelf, lower slope | 42°38.4' | 9°42.1' | 1500 | 600 | July 1997–December 1998 |
| | | | IM3 | off-shelf, slope base | 42°37.7' | 10°1.7' | 2245 | 1100 600 | July 1997–February 1998 July 1997–November 1998 |
| | | | | | | | | 1100 | July 1997–November 1998 |
| Goban Spur | OMEX I | R/V <i>Discovery</i> D217 | OM2 | shelf break | 49°11' | 12°49' | 1460 | 600 | July 1993–August 1994 |
| | | | OM3 | slope base | 49°05' | 13°25' | 3650 | 1050 580 | July 1993–September 1994 July 1993–May 1994 |
| | | | | | | | | 1440 | July 1993–September 1993 |
| | | | OM4 | abyssal plain | 49°02' | 13°42' | 4470 | 3260 4000 | July 1993–September 1994 September 1994–September 1995 |

canyons. During summer, the area is characterised by intense wind-induced upwelling at the shelf edge, enhancing primary production and carbon export to the sediments (van Weering et al., 2002). During the OMEX II investigation period, the yearly new production was estimated at 100–120 gC m⁻² y⁻¹ (Brion et al., 2003). The maximum tidal currents (15–25 cm s⁻¹) are directed northwards, parallel to the slope, and are sufficiently strong to resuspend particles throughout an important part of the tidal cycle and keep larger particles in suspension. Such tidal currents, together with internal waves, generate significant turbidity at the shelf edge and the upper slope (Thomsen et al., 2002). Seasonal hydrodynamic conditions control the development of nepheloid layers on the shelf. During summer, any transport of fine particles in nepheloid layers is confined to the shelf edge. In winter, intense downwelling and resuspension during storms induce enhanced transport of resuspended shelf-derived particles over the shelf edge. The extension of intermediate nepheloid layers over the upper slope is evidenced by the high mass fluxes recorded by the IM2 and IM3 traps in winter, especially during March 1998 (Antia et al., 1999).

Sediment accumulation along the sediment trap transect varies from 315 to 2296 g m⁻² y⁻¹ on the shelf to 31–98 g m⁻² y⁻¹ on the middle and upper slope. On the steep upper slope, however, sediment accumulation is close to zero (van Weering

et al., 2002). Epping et al. (2002) report that sedimentary carbon oxidation rates are low compared to other upwelling areas (e.g. the Chilean and Peruvian upwelling). Organic carbon oxidation rates in the sediments decrease with water depth, from 11 on the shelf to 2 gC m⁻² y⁻¹ at 5000 m (Epping et al., 2002). Anaerobic oxidation ranges from 10 to 40% on the shelf and decreases to <10% below 2000 m, with 5–9% due to sulphate reduction.

In comparison, the Goban Spur Shelf extends as a broad gently sloping platform with a sudden upper slope break at 1400 m (van Weering et al., 1998). An important cross-shelf transport of fine particles occurs permanently within a bottom nepheloid layer (Thomsen and van Weering, 1998). Sediment mass accumulation rates are lower compared to the Iberian Margin (van Weering et al., 1998): from >58 g m⁻² y⁻¹ on the shelf to 26–30 g m⁻² y⁻¹ on the slope. The upper slope break is characterised by a minimum value of 16.5 g m⁻² y⁻¹, reflecting the occurrence of winnowing at that location (van Weering et al., 1998). This part of the slope acts as a source for off- and along-slope transport of fine particles in intermediate and bottom nepheloid layers (Thomsen and van Weering, 1998; van Weering et al., 1998). Input of resuspended and laterally advected material induced an increase of mass flux with depth (Antia et al., 1999).

New production, estimated to range between

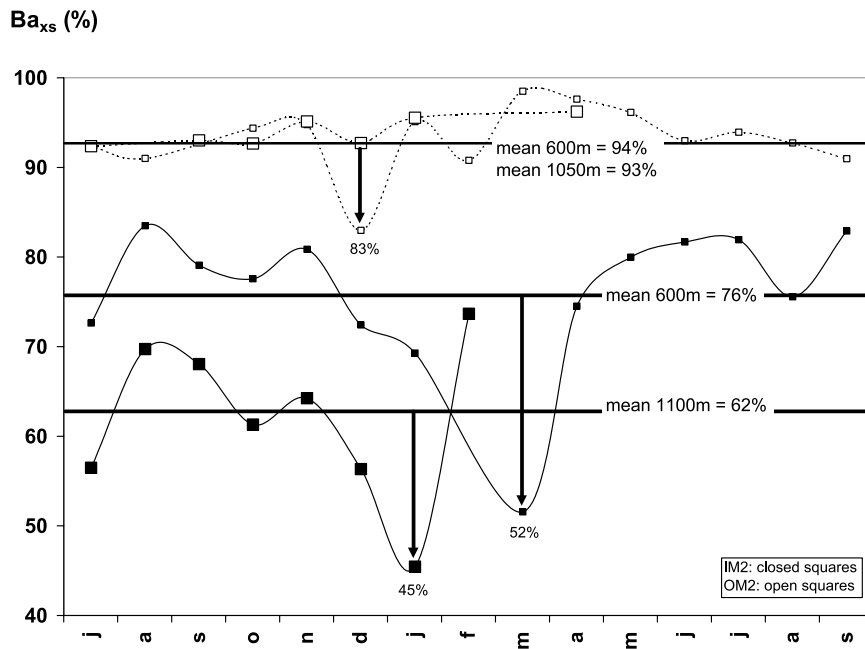


Fig. 2. Iberian Margin and Goban Spur; monthly-averaged evolution of the relative contribution of Ba_{xs} to total Ba for the 600-m and 1100-m traps at site IM2 (black squares) and site OM2 (open squares; data from Fagel et al., 1999). Note that the sampling intervals are different at both margin sites (see Table 1). The size of the symbols is indicative of the water depth. The horizontal lines represent the monthly averaged Ba_{xs} value for each trap. The arrows point to major detrital dilution events related to winter storms.

50–80 $gC\ m^{-2}\ y^{-1}$ (Joint et al., 2000), was up to a factor 2 lower than reported for the Iberian Margin studied here. For Goban Spur sediments between 200 and 1500 m, Lohse et al. (1998) report sedimentary carbon oxidation rates ranging between 6.6 and 18.8 $gC\ m^{-2}\ y^{-1}$. Such rates are larger than those measured at the Iberian Margin (see above). Oxidic degradation accounts for 68–90% of the total organic carbon oxidation on the upper slope, reaching more than 90% on the lower slope, while sulphate reduction accounts for 7–21% in shelf and upper slope sediments, and less than 5% deeper on the lower slope (Lohse et al., 1998).

1.2. Materials and methods

1.2.1. Sampling and analysis

Sediment trap sampling conditions are described in von Bodungen et al. (1991). For the Goban Spur trap samples, analytical techniques have been detailed elsewhere (Fagel et al., 1999;

Dehairs et al., 2000). We have followed a similar procedure for the Iberian Margin samples. Briefly, aliquots of cup suspensions (1/16th of total amount) were filtered under pressure of filtered air on Nuclepore polycarbonate membranes with a pore size of 0.4 μm . The aliquots represented between 50 and 100 mg of dry matter, what is 3–100 times more than for the Goban Spur samples. Filters were digested in a tri-acid mix (HCl/HNO₃/HF) at 80°C.

Major elements were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES, ARL, IRIS, 35000C). Trace element contents were determined by Inductively Coupled Plasma Mass Spectrometry (ICP–MS, VG Elemental, PlasmaQuad, PQ2 Plus). With a mean dilution factor of 1650, the qualitative (3 standard deviations of the blanks) and quantitative detection limits (defined as 9 standard deviations of the blanks) range between 50 and 500 $\mu g\ g^{-1}$. For Ba and Zr, concentrations in solution exceed 20–300 times the quantitative detection level. Besides the

data for Ba, Al and Zr reported here, additional data for major elements (Iberian Margin) and trace elements (both Goban Spur and Iberian Margin) were provided to the BODC database (<http://www.pol.ac.uk/bodc/omex>) or are available from the authors upon request.

Biogenic, or excess Ba (Ba_{xs}), was calculated as bulk Ba content minus lithogenic Ba. The Ba_{xs} phase in suspended matter is mainly associated with barite (Dehairs et al., 1980) but also with calcium carbonate, strontium sulphate, biogenic silica and organic matter (Dymond et al., 1992; Schroeder et al., 1997). Lithogenic Ba is calculated using a reference crustal Ba/X ratio with the element X assumed to be exclusively of lithogenic origin (e.g. Dymond et al., 1992). Al is usually taken as the reference element but since Al data were not available for all samples from Goban Spur, Zr was used as the lithogenic reference (Fagel et al., 1999). In the present study we also used Zr as the lithogenic reference element. We considered a Ba/Zr (wt/wt) ratio for shale = 3.095, which is the value for Post-Archean Australian Shales (Ba = 650 ppm and Zr = 210 ppm; Taylor and McLennan, 1985). The concentrations of Ba_{xs} calculated using either Al or Zr as lithogenic references differ only by a few percent (Fagel et al., 1999).

2. Results

2.1. Trace element contents and fluxes

For the Iberian Margin the Al, Zr and Ba contents of the individual cup samples vary by a factor of 27–60 ($1600 < Al < 94\,000$ ppm; $2.7 < Zr < 72$ ppm; $28 < Ba < 1190$ ppm) (Table 1). This range of variation is higher than that observed for the Goban Spur traps (Fagel et al., 1999). On average, at the Iberian Margin, Ba_{xs} represents < 90% of total Ba (IM2: av. 76 and 62% at 600 and 1000 m, respectively; IM3: av. 83 and 80% at 600 and 1100 m, respectively). The Ba_{xs} fraction varies widely over the year and decreases to below 50% in January and March 1998 (Fig. 2). Events with decreased relative Ba_{xs} contribution also occur in summer (see July 1997,

Fig. 2) but the depletion is less pronounced. At Goban Spur Ba_{xs} fractions accounted, in general, for > 90% of total Ba (Fagel et al., 1999).

Monthly averaged Ba_{xs} fluxes for the Iberian Margin vary between 16 and 2490 $\text{nmol m}^{-2} \text{d}^{-1}$ (Table 2). The highest Ba_{xs} fluxes are generally recorded during summer (Table 2; Fig. 3A). Zr fluxes usually range between less than 2 and 523 $\text{nmol m}^{-2} \text{d}^{-1}$, but they can reach higher values, with a maximum of 1364 $\text{nmol m}^{-2} \text{d}^{-1}$ (IM3, 1100 m, January 1998). A slight difference is observed between sites IM2 and IM3 with, in general, higher Zr fluxes for the upper slope IM2 site. Three samples lay off the main regression trend, with up to 10 times higher Zr fluxes (600 and 1000 m for January 1998 and 600 m for March 98). They coincide with major decreases of the Ba_{xs} fraction during winter (Fig. 2).

Zr fluxes at Goban Spur are distinctly lower and less variable compared to the Iberian Margin (usually around 50 $\text{nmol m}^{-2} \text{d}^{-1}$ and exceptionally up to 120 $\text{nmol m}^{-2} \text{d}^{-1}$; Fagel et al., 1999). As a result, the Goban Spur sites are characterised by larger and also less variable Ba_{xs} fractions than those at the Iberian Margin. The cases of sites IM2 and OM2 are compared in Fig. 2.

2.2. POC/ Ba_{xs} ratio

Monthly averaged POC/ Ba_{xs} ratios (Table 2) at IM3 600 m show a clear seasonal evolution with higher ratios during summer–autumn (Fig. 4). Extremely high POC/ Ba_{xs} values were reached in August, September and November 1997 (ratios of 1705, 1777 and 2552, respectively), but such high values were not observed in 1998 (Table 2; Fig. 4). For both sites this seasonality has largely disappeared at 1100 m (Table 2). POC/ Ba_{xs} ratios, averaged over the whole sampling period, decrease with depth, but at site IM3 this decrease is small.

3. Discussion

3.1. Importance of lateral advection

At Goban Spur, input of advected material into

Table 2
Data for IM2 and IM3 mooring sites at the Iberian Margin (OMEX II)

| Site and depth | Month | Mass Flux ^a (mg m ⁻² d ⁻¹) | POC ^a (mg m ⁻² d ⁻¹) | Al (ppm) | Zr (ppm) | Ba (ppm) | Ba _{xs} ^b (ppm) | Ba _{xs} (%) | F _{Ba_{xs}} (nmol m ⁻² d ⁻¹) | F _{Zr} (nmol m ⁻² d ⁻¹) | POC/Ba _{xs} (wt/wt) |
|-----------------------|-----------------------|---|---|-------------|-------------|-------------|--|-------------------------|---|--|---------------------------------|
| <i>IM2</i> | | | | | | | | | | | |
| 600 m | Jul-97 | 943 | 33 | 52703 | 34 | 382 | 277 | 73 | 1908 | 350 | 124 |
| | Aug-97 | 39 | 6 | 8075 | 5 | 100 | 84 | 83 | 24 | 2 | 1705 |
| | Sep-97 | 55 | 11 | 17574 | 11 | 145 | 114 | 79 | 46 | 7 | 1777 |
| | Oct-97 | 227 | 12 | 13772 | 9 | 122 | 95 | 78 | 157 | 22 | 558 |
| | Nov-97 | 86 | 19 | 10989 | 7 | 106 | 86 | 81 | 54 | 6 | 2552 |
| | Dec-97 | 166 | 8 | 50163 | 30 | 339 | 245 | 72 | 297 | 55 | 191 |
| | Jan-98 | 1286 | 14 | 66128 | 37 | 379 | 265 | 70 | 2490 | 523 | 42 |
| | Mar-98 ^c | 1281 | 49 | 61148 | 61 | 387 | 199 | 52 | 1864 | 852 | 190 |
| | Apr-98 | 94 | 7 | 36983 | 36 | 416 | 310 | 74 | 213 | 38 | 235 |
| | May-98 | 52 | 4 | 26256 | 22 | 339 | 271 | 80 | 102 | 13 | 276 |
| | Jun-98 | 60 | 6 | 32599 | 31 | 531 | 434 | 82 | 189 | 20 | 213 |
| | Jul-98 | 26 | 3 | 27694 | 25 | 438 | 358 | 82 | 68 | 7 | 279 |
| | Aug-98 | 339 | 27 | 37873 | 34 | 400 | 302 | 76 | 746 | 127 | 265 |
| | Sept-98 | 56 | 4 | 20394 | 19 | 342 | 284 | 83 | 115 | 11 | 225 |
| | Nov-98 | 8 | 2 | 19668 | 19 | 802 | 729 | 91 | 43 | 2 | 393 |
| | Dec-98 | 9 | 1 | 22091 | 18 | 311 | 256 | 82 | 16 | 2 | 255 |
| | 1100 m | Jul-97 | 282 | 15 | 15137 | 13 | 95 | 54 | 56 | 111 | 42 |
| Aug-97 | | 42 | 2 | 19000 | 17 | 149 | 104 | 70 | 32 | 8 | 433 |
| Sep-97 | | 29 | 1 | 32579 | 23 | 239 | 163 | 68 | 34 | 7 | 231 |
| Oct-97 | | 129 | 10 | 23574 | 22 | 170 | 104 | 61 | 98 | 31 | 768 |
| Nov-97 | | 64 | 2 | 65894 | 55 | 472 | 303 | 64 | 141 | 38 | 121 |
| Dec-97 | | 121 | 5 | 34089 | 29 | 204 | 115 | 56 | 102 | 39 | 334 |
| 6 Jan-98 ^c | | 2256 | 79 | 52998 | 55 | 244 | 73 | 30 | 1205 | 1364 | 476 |
| 21 Jan-98 | | 317 | 24 | 76307 | 52 | 403 | 242 | 60 | 559 | 181 | 306 |
| Fev 98 | 90 | 4 | 49538 | 29 | 337 | 248 | 74 | 162 | 28 | 194 | |
| <i>IM3</i> | | | | | | | | | | | |
| 600 m | Jul-97 | 52 | 6 | 26477 | 18 | 370 | 314 | 85 | 119 | 10 | 341 |
| | Aug-97 | 169 | 14 | 19456 | 13 | 209 | 167 | 80 | 207 | 25 | 477 |
| | Sep-97 | 22 | 3 | 19199 | 11 | 256 | 220 | 86 | 35 | 3 | 557 |
| | Oct-97 | 53 | 5 | 11164 | 9 | 181 | 151 | 84 | 59 | 6 | 569 |
| | Nov-97 | 73 | 11 | 15833 | 14 | 320 | 281 | 88 | 149 | 11 | 517 |
| | Dec-97 | 106 | 10 | 15528 | 9 | 272 | 242 | 89 | 187 | 11 | 370 |
| | 6 Jan-98 ^c | 670 | 28 | 70376 | 49 | 207 | 56 | 27 | 273 | 361 | 742 |
| | 21 Jan-98 | 269 | 11 | 42109 | 23 | 249 | 167 | 67 | 328 | 68 | 250 |
| | Feb-98 | 159 | 8 | 62022 | 36 | 396 | 277 | 70 | 322 | 64 | 191 |
| | Mar-98 | 316 | 41 | 12564 | 11 | 330 | 295 | 89 | 681 | 39 | 436 |
| | Apr-98 | 75 | 10 | 21783 | 21 | 591 | 526 | 89 | 289 | 17 | 243 |
| | May-98 | 126 | 12 | 14335 | 13 | 254 | 210 | 83 | 193 | 19 | 456 |
| | Jun-98 | 28 | 3 | 11352 | 11 | 222 | 187 | 84 | 38 | 4 | 610 |
| | Jul-98 | 29 | 4 | 16763 | 16 | 208 | 159 | 76 | 33 | 5 | 874 |
| | Aug-98 | 70 | 8 | 20307 | 21 | 304 | 238 | 78 | 121 | 16 | 453 |
| | Sept-98 | 58 | 7 | 18965 | 18 | 312 | 258 | 83 | 109 | 11 | 477 |
| | Oct-98 | 22 | 2 | 24068 | 24 | 450 | 375 | 83 | 60 | 6 | 275 |
| | Nov-98 | 15 | 1 | 26503 | 24 | 434 | 360 | 83 | 40 | 4 | 245 |
| | 1100 m | Jul-97 | 222 | 67 | 24390 | 17 | 325 | 273 | 84 | 443 | 41 |
| Aug-97 | | 200 | 9 | 53167 | 35 | 545 | 437 | 80 | 638 | 76 | 98 |
| Sep-97 | | 36 | 2 | 45595 | 32 | 367 | 269 | 73 | 71 | 13 | 184 |
| Oct-97 | | 39 | 4 | 11132 | 8 | 120 | 101 | 84 | 28 | 3 | 999 |
| Nov-97 | | 25 | 2 | 17282 | 11 | 224 | 191 | 85 | 35 | 3 | 459 |
| Dec-97 | | 50 | 2 | 36078 | 26 | 382 | 303 | 79 | 111 | 14 | 139 |
| Jan-98 | | 146 | 5 | 69258 | 43 | 442 | 311 | 70 | 331 | 68 | 116 |
| Feb-98 | | 22 | 3 | 31411 | 21 | 289 | 224 | 78 | 37 | 5 | 531 |
| Mar-98 | 386 | 30 | 19173 | 17 | 320 | 269 | 84 | 757 | 70 | 283 | |
| Apr-98 | 72 | 5 | 20152 | 17 | 373 | 321 | 86 | 168 | 13 | 214 | |
| May-98 | 67 | 4 | 15260 | 13 | 243 | 203 | 83 | 99 | 9 | 289 | |
| Jun-98 | 43 | 4 | 14944 | 13 | 252 | 212 | 84 | 67 | 6 | 394 | |

Table 2 (Continued).

| Site and depth | Month | Mass Flux ^a (mg m ⁻² d ⁻¹) | POC ^a (mg m ⁻² d ⁻¹) | Al (ppm) | Zr (ppm) | Ba (ppm) | Ba _{xs} ^b (ppm) | Ba _{xs} (%) | F _{Ba_{xs}} (nmol m ⁻² d ⁻¹) | F _{Zr} (nmol m ⁻² d ⁻¹) | POC/Ba _{xs} (wt/wt) |
|----------------|---------|---|---|-------------|-------------|-------------|--|-------------------------|---|--|---------------------------------|
| | Jul-98 | 112 | 8 | 34793 | 33 | 378 | 276 | 73 | 225 | 41 | 251 |
| | Aug-98 | 83 | 6 | 21530 | 19 | 254 | 192 | 76 | 116 | 17 | 353 |
| | Sept-98 | 61 | 4 | 21045 | 19 | 232 | 174 | 75 | 77 | 12 | 421 |
| | Oct-98 | 20 | 2 | 32993 | 28 | 399 | 314 | 79 | 45 | 6 | 299 |
| | Nov-98 | 31 | 2 | 15844 | 15 | 210 | 164 | 78 | 37 | 5 | 345 |

Monthly-averaged Al, Zr, Ba, Ba_{xs} concentrations in ppm; Ba_{xs} in %; mass and POC fluxes in mg m⁻² d⁻¹ (data from Antia et al., 1999); Ba and Zr fluxes in nmol m⁻² d⁻¹; weight ratio of POC vs. Ba_{xs}. For IM2 1100 m and IM3 600 m, we report the values for the two individual cups (6/01/1998 and 21/01/1998). For those two mooring sites, the January 1998's estimate is only based on the cup collected the 21st January.

^a Data from Antia et al. (1999).

^b Excess-Ba calculated using Zr as the lithogenic reference element (Fagel et al., 1999).

^c Cup not taken into account in the mean calculation.

the traps below 1000 m was clearly evidenced (Antia et al., 1999; Wollast and Chou, 1998). This advection was sustained by nepheloid layers fed by sediment resuspension at the shelf break during occasional winter storms (McCave et al., 2001; van Weering et al., 1998). Advection had a strong impact on fluxes of POC and lithogenic matter. For the 1440 m trap at site OM3, Antia et al. (1999) estimated that about 40% of the POC was advected, and Fagel et al. (1999) report highest lithogenic fluxes for the same OM3 site at 1440 and 3260 m. Furthermore, the co-variation of Ba_{xs} and Zr fluxes (i.e. increasing fluxes with water depth and enhanced winter fluxes) indicates that part of the trapped Ba_{xs} was also advected (Fagel et al., 1999; Dehairs et al., 2000). To avoid erroneous export production estimations in margin systems, the advective input of POC and Ba_{xs} to the traps must be corrected.

For the Iberian Margin, we observe larger contributions of lithogenic Ba in the trapped material (Fig. 2) than at Goban Spur. The fact that these larger lithogenic Ba fractions, in general, go along with enhanced Zr fluxes (i.e. enhanced lithogenic fluxes) emphasises the general occurrence of stronger advective transport at the Iberian Margin, as compared to Goban Spur. Furthermore, discrete events of large reductions of the Ba_{xs} fraction during winter are more salient at the Iberian Margin than at Goban Spur. This is particularly true for the January and March 1998 events (Fig. 2) which could be traced back to storm action (Antia and Peinert, 1999). From Fig. 3A, it

clearly appears that these reduced Ba_{xs} fractions during winter at the Iberian Margin are associated with unusually high Zr fluxes that were not observed at Goban Spur. This increased contribution of advected material to the trapped material at the Iberian Margin probably results from the narrowness of the shelf and the proximity of the mooring sites to the shelf break, where storm-induced resuspension of sediments is particularly important in winter (van Weering et al., 2002; Vitorino et al., 2002). From the relationship between Ba_{xs} and Zr fluxes at the Iberian Margin (Fig. 3A), it is not clear whether lateral supply of Ba_{xs} occurred also outside the peak advection events in January and March 1998.

3.2. Evolution of POC/Ba_{xs} ratios with depth and season

Decreasing POC/Ba_{xs} flux ratios with depth (Fig. 5) have been reported for various parts of the world ocean, e.g. the North Atlantic (François et al., 1995; Dymond et al., 1992), the Equatorial Pacific (Dymond et al., 1992; Dymond and Collier, 1996), the South Pacific (Klump, 1999). A decrease of POC/Ba ratio essentially reflects decreasing POC fluxes with depth due to mineralisation, but can also result from increasing Ba_{xs} fluxes with depth, as is frequently observed. In the latter case ongoing formation of barite in micro-aggregates sinking through the water column might be the mechanism involved. Klump (1999) suggests that the evolution of POC/Ba_{xs} ratios

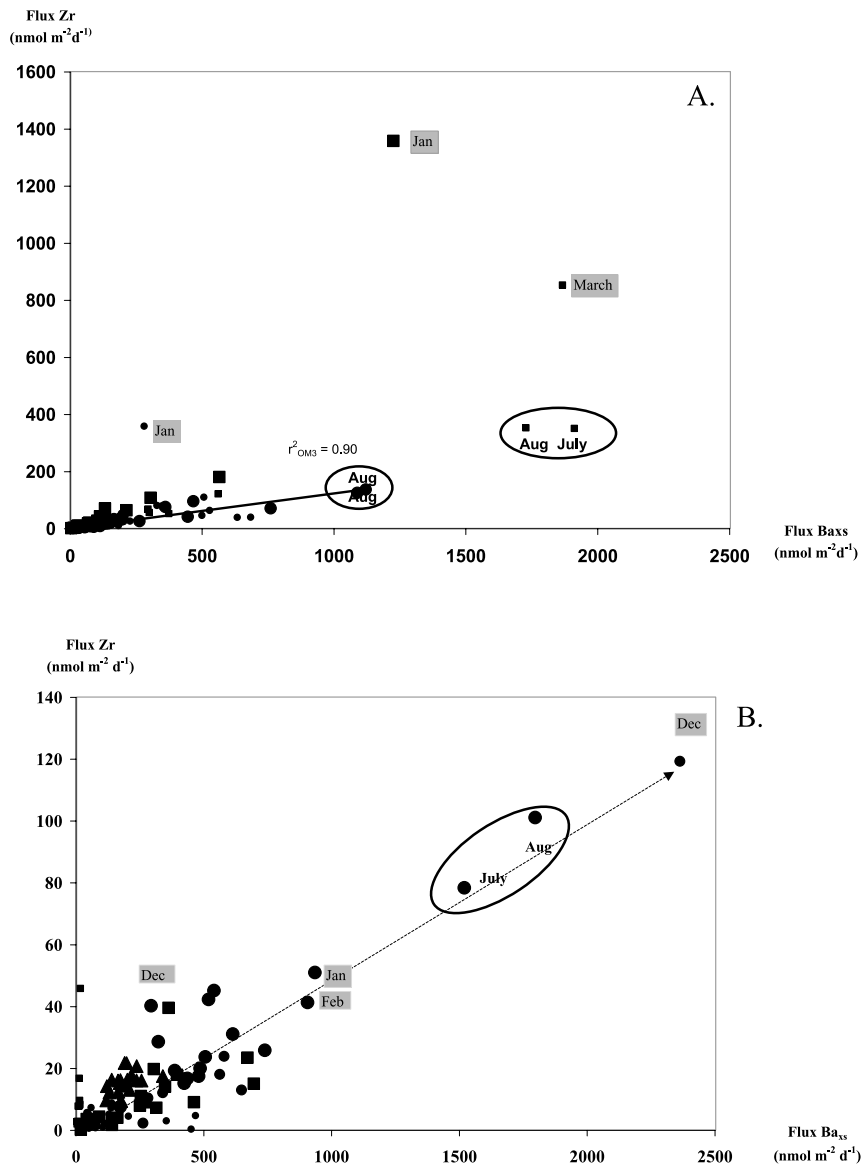


Fig. 3. Iberian Margin and Goban Spur; monthly-averaged Zr fluxes vs. Ba_{xs} fluxes in sediment trap material along the NW European continental margin. Enhanced Ba_{xs} fluxes related to higher productivity during summer are circled. The size of the data point increases with trap depth. Note all the individual cup data are plotted. (A) For the Iberian Margin, shaded squares (January, March 1998) highlight unusually high Zr fluxes, reflecting lithogenic material input. Squares: IM2; circles: IM3. The heavy line represents the linear regression trend for site IM3. (B) For the Goban Spur, shaded squares (December 1993; January, February 1994) highlight unusually high Zr fluxes, reflecting lithogenic material input. Squares: OM2; circles: OM3; triangles: OM4. The dashed arrows emphasise the general seasonal evolution of the fluxes for OM3.

mainly reflects an increase of Ba_{xs} with depth, based on the fact that Ba_{xs} enrichment in margin sediments (Namibia and Chile) increases with water column depth.

The POC/ Ba_{xs} ratios for the Iberian and Goban Spur Margin systems studied here are systematically higher than the ratios for the open ocean (Fig. 5). For stations close to margins, François

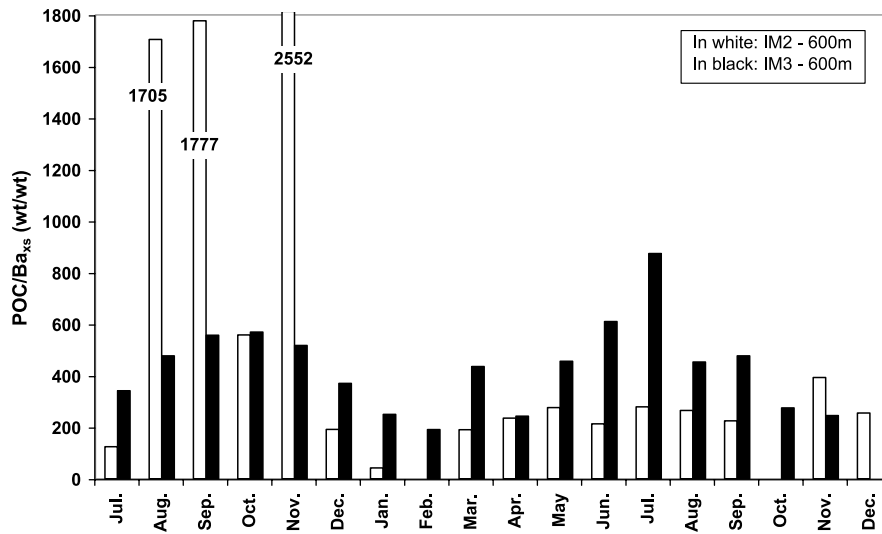


Fig. 4. Iberian Margin; seasonal evolution of monthly-averaged POC/Ba_{XS} ratio (wt/wt) in sediment trap material for the 600-m traps at sites IM2 and IM3 (data from Table 2).

et al. (1995) attribute higher POC/Ba_{XS} ratios to advection of refractory detrital POC from nearby shelf and slope and argue that advection of detrital carbon would go without significant advection of Ba_{XS}. Therefore, the trapped Ba_{XS} flux in margin systems would still be associated with degradation of organic matter produced in local surface waters and thus the Ba_{XS} flux rather than the POC flux would allow for proper estimation of export production in regions where strong advection of POC can be expected. The higher POC/Ba_{XS} ratios for the 1100-m traps at IM2 and IM3 (Fig. 5) as compared to other margin sites including Goban Spur, are likely to reflect larger advection of POC, possibly due to shelf morphology.

More recently Dehairs et al. (2000) and McManus et al. (2002) reported that higher POC/Ba_{XS} ratios in margin systems are probably not solely due to POC advection, but also to a different POC to Ba stoichiometry in these high flux environments. This may be related to the type of biogenic aggregates in which authigenic Ba accumulates and which are controlled by the compositions of the phytoplankton and the grazer communities. It is likely that differences in morphology and size of aggregates exist between margin sites. Indeed, Thomsen et al. (2002) report larger sizes of biogenic aggregates at the Iberian

Margin compared to Goban Spur. For margin areas in general and for the Iberian Margin in particular, the water column transit time of such aggregates must thus be shorter and, as a conse-

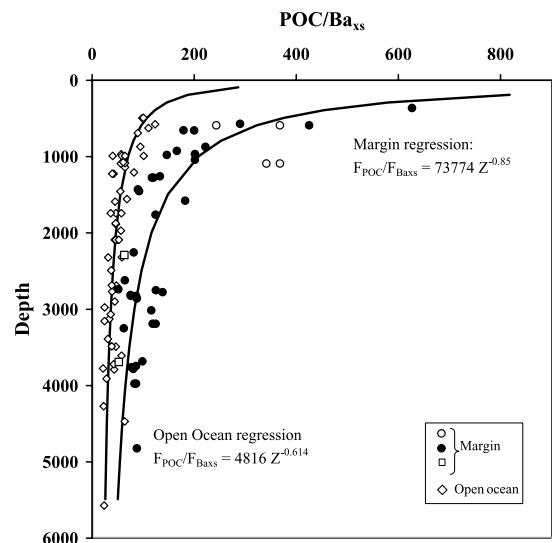


Fig. 5. Depth distribution of POC/Ba_{XS} ratios; comparison between Iberian Margin data (open circles) with other areas reported in literature. Closed circles: margin data from François et al. (1995); Dehairs et al., 2000. Squares: Southeast Pacific Margin data from Klump (1999); diamonds: open ocean sites from François et al. (1995); Dymond et al. (1992).

quence of shorter maturation times, the yield of Ba_{xs} in these aggregates would be smaller for the Iberian Margin than for Goban Spur. Furthermore, we observe a clear seasonal evolution of the POC/ Ba_{xs} ratios at both 600-m traps of the Iberian Margin sites, probably reflecting the seasonal variability of biological factors responsible for barite formation, as suggested also by Dymond and Collier (1996).

3.3. Calculation of export production

Several authors have proposed algorithms relating POC fluxes recorded by sediment traps with primary production and also new or export production (see e.g. Suess, 1980; Betzer et al., 1984; Berger et al., 1987; Pace et al., 1987; Martin et al., 1987; Sarnthein et al., 1988; Christian et al., 1997) and such models have been applied widely (e.g. Bishop, 1989; Bender et al., 1992; Boyd and Newton, 1995; Jickells et al., 1996). However, it was recognised that because of the labile character of POC, reflected by the strongly decreasing POC signal with depth, a more refractory substitute for POC, such as Ba_{xs} would render algorithms for export production more robust (Dymond et al., 1992 and François et al., 1995).

All attempts to use the water column Ba_{xs} flux to estimate export of carbon rely on the vertical evolution of the POC/ Ba_{xs} flux or weight ratio in sediment trap material (Dymond et al., 1992; François et al., 1995; Nürnberg, 1995; Nürnberg et al., 1997):

$$F_{\text{POC}} = a F_{\text{Ba}_{\text{xs}}} Z^b \quad (1)$$

with F = sediment trap flux of POC or Ba_{xs} at depth Z .

Dymond et al. (1992) and more recently Pfeifer et al. (2001) consider coefficients a and b in Eq. 1 to vary as a function of the deep sea dissolved Ba content. However, François et al. (1995) refute this dependency on deep ocean dissolved Ba content, based on their observation that POC/ Ba_{xs} ratios are variable even within single oceanic basins having relatively homogenous deep water dissolved Ba concentrations. François et al. (1995) ascribe variable POC/ Ba_{xs} ratios within single basins rather to advection of POC from shelf and

slope and proximity of mooring sites to the margin (see discussion in Section 3.1). For the global open ocean, not affected by margin effects, they noticed that a single set of a, b coefficients describes quite reliably the depth evolution of POC and Ba_{xs} fluxes. Optimised coefficients a and b in Eq. 1 (using Gaussian non-linear least-squares computation; Sigma Plot) using sediment trap data earmarked as open ocean sites by François et al. (1995) are: $a = 4820$; $b = -0.614$ (the POC and Ba_{xs} fluxes in Eq. 1 in $\mu\text{g cm}^{-2} \text{yr}^{-1}$ units). These values are similar to those reported originally by François et al. (1995).

But, as discussed above, it appears that for high flux environments at margins less Ba_{xs} is synthesised per unit POC exported. Therefore, we optimised the Eq. 1 coefficients specifically for margin areas using the earmarked margin trap data from François et al. (1995) and also the Dymond et al. (1992) Atlantic Ocean data which, according to François et al. (1995), are characteristic of margin systems. From a Gaussian non-linear least square fitting, we obtain quite different regression coefficient values compared to open oceans: $a = 73770$; $b = -0.85$. These values differ from those we published earlier for the same data set and that were obtained from simple trend line plotting (see Dehairs et al., 2000).

A subsequent step to access export production consists in substituting F_{POC} for $F_{\text{Ba}_{\text{xs}}}$ in transfer functions relating F_{POC} at depth Z with export production via Eq. 1. We will compare the F_{POC} -export production relationships proposed by Sarnthein et al. (1988) and Martin et al. (1987):

$$F_{\text{POC}} = c \text{EP}^d / Z^e \quad (\text{Sarnthein et al., 1988}) \quad (2)$$

$$F_{\text{POC}} = F_{\text{POC}100} (Z/Z_{100})^f \quad (\text{Martin et al., 1987}) \quad (3)$$

with F_{POC} = the sediment trap POC flux at depth Z ; EP = export production; $F_{\text{POC}100}$ = the POC flux exiting the upper mixed layer, which is equivalent to export production; Z_{100} = the lower boundary (100 m) of the upper mixed layer.

Regression coefficients (c, d, e, f) in Eqs. 2 and 3 were optimised via least-square fitting (Gaussian non-linear least-squares computation) using the original Sarnthein et al. (1988) data set for sedi-

ment trap POC fluxes and export production: $c = 5.58$; $d = 0.974$; $e = -0.516$; $f = -0.886$. This approach is similar to the one we discussed in a previous paper (Dehairs et al., 2000), but for which we used original (i.e. non-optimised) regression coefficients, as given by Sarnthein et al. (1988) and François et al. (1995).

For Goban Spur, the observed POC fluxes were corrected for advective input and trapping efficiency, as detailed in Dehairs et al. (2000). For the Iberian Margin, the possible effect of advective input on export production calculations was minimised by not taking into account cups with unusual high Zr fluxes and low Ba_{xs} fractions (i.e. see the three high Zr flux cases in Fig. 3A). Trap-

ping efficiencies (as based on ^{230}Th measurements) were assessed for Goban Spur but not for the Iberian Margin. Since shallow traps (<1000 m) tend to under-sample the vertical particle flux (Yu et al., 2001), it is likely that fluxes for the 600-m traps represent minimal values, but we expect data for the 1000-m traps to reflect true fluxes (Antia et al., 1999). We then substituted F_{POC} in Eqs. 2 or 3 by its expression in Eq. 1. Optimisation of regression coefficients in Eqs. 1–3 via Gaussian non-linear least-squares computation has resulted in export production estimates for the Goban Spur that are no greater than a factor of 2 compared to the values we published earlier (see Section 3.4 and Dehairs et al., 2000).

Table 3

Calculated export production along the NE Atlantic Margin, based on POC or Ba_{xs} trap fluxes

| Site and depth | Trapping efficiency | F_{POC} | $F_{\text{Ba}_{xs}}$ | ExpP via F_{POC} | | ExpP via $F_{\text{Ba}_{xs}}$ | |
|-----------------------|---------------------|---|--|---|---|---|---|
| | | ($\text{gC m}^{-2} \text{y}^{-1}$) ^a | ($\mu\text{g cm}^{-2} \text{y}^{-1}$) ^b | ($\text{gC m}^{-2} \text{y}^{-1}$) ^c | ($\text{gC m}^{-2} \text{y}^{-1}$) ^d | ($\text{gC m}^{-2} \text{y}^{-1}$) ^e | ($\text{gC m}^{-2} \text{y}^{-1}$) ^f |
| <i>Goban Spur</i> | | | | | | | |
| <i>OM2</i> | | | | | | | |
| 600 | 0.38 | 1.95 | 0.8 | 10.1 | 9.5 | 14.0 | 13.2 |
| 1050 | 0.85 | 2.10 | 0.7 | 14.6 | 16.9 | 9.0 | 10.5 |
| <i>OM3</i> | | | | | | | |
| 580 | 0.34 | 1.79 | 1.7 | 9.0 | 8.5 | 28.4 | 25.9 |
| 1440 | 0.98 | 2.12 | 1.6 | 17.4 | 22.5 | 20.3 | 26.1 |
| 3260 | 1.05 | 1.28 | 1.2 | 16.0 | 28.1 | 11.3 | 20.0 |
| <i>OM4</i> | | | | | | | |
| 4000 | 0.7 | - | 1.4 | - | - | 12.0 | 22.8 |
| <i>Iberian Margin</i> | | | | | | | |
| <i>IM 2</i> | | | | | | | |
| 600 | n.m. | 3.8 | 1.6 | 19.9 | 18.6 | 27.2 | 25.1 |
| 1000 | n.m. | 2.9 | 0.8 | 19.8 | 22.3 | 11.2 | 12.8 |
| <i>IM 3</i> | | | | | | | |
| 600 | n.m. | 3.3 | 0.9 | 17.2 | 16.1 | 14.3 | 13.4 |
| 1000 | n.m. | 3.4 | 1.0 | 23.2 | 26.0 | 14.0 | 15.9 |

Calculations based on POC fluxes used Eq. 2 (Sarnthein et al., 1988) or Eq. 3 (Martin et al., 1987). Calculations based on Ba_{xs} fluxes used Eq. 1, with a and b coefficients characteristic of margin systems (see text) and Eqs. 2 or 3. The trap at the 1100-m site was operational only from July 1997 until February 1998. All other traps were operational from July 1997 until November or December 1998 (see Table 1).

Trapping efficiency: as given in Antia et al. (1999).

n.m., not measured.

^a F_{POC} corrected for trapping efficiency (Goban Spur only) and advection.

^b Ba_{xs} flux corrected for trapping efficiency (Goban Spur only) and advection of Ba_{xs} .

^c Export production obtained using F_{POC} and Eq. 2.

^d Export production obtained using F_{POC} and Eq. 3.

^e Export production obtained using $F_{\text{Ba}_{xs}}$ and Eqs. 1 and 2.

^f Export production obtained using $F_{\text{Ba}_{xs}}$ and Eqs. 1 and 3.

3.4. Export production at the two margin systems: discrepancies relative to new production

We calculated export productions using both POC and Ba_{xs} fluxes (Table 3; Fig. 6). For Goban Spur, export production based on F_{POC} (Eqs. 2 and 3) varied between 8.5 and 28.1 $gC\ m^{-2}\ y^{-1}$, showing large discrepancies between estimates based on shallow and deep traps (Table 3). Export production at OM2 appears lower than at OM3. For the Iberian Margin, export production based on F_{POC} varied between 16.1 and 26 $gC\ m^{-2}\ y^{-1}$. Discrepancies between estimates based on POC flux data for successive traps on the same mooring reach a factor of 3.3 (OM3, 600 m; Eq. 2). Estimates obtained via Eqs. 2 and 3 compare

well, but Eq. 3 results are larger, on average, by 13%.

For the calculations based on $F_{Ba_{xs}}$, we use Eq. 1 regression coefficients characteristic of margin sites. Export productions at the Iberian Margin sites (range 11.2–27.2 $gC\ m^{-2}\ y^{-1}$; Table 3) are similar to values for Goban Spur (range 9.0–28.4 $gC\ m^{-2}\ y^{-1}$; Table 3). Internal consistency of $F_{Ba_{xs}}$ -based export productions between traps of the same mooring is better compared to the values based on F_{POC} . This is not the case for the IM2 site. However, we remind that the 1100-m trap at IM2 was only operational over a restricted period (July 1997 to February 1998; Table 1) compared to all other Iberian Margin traps, rendering comparison of fluxes and calculated export produc-

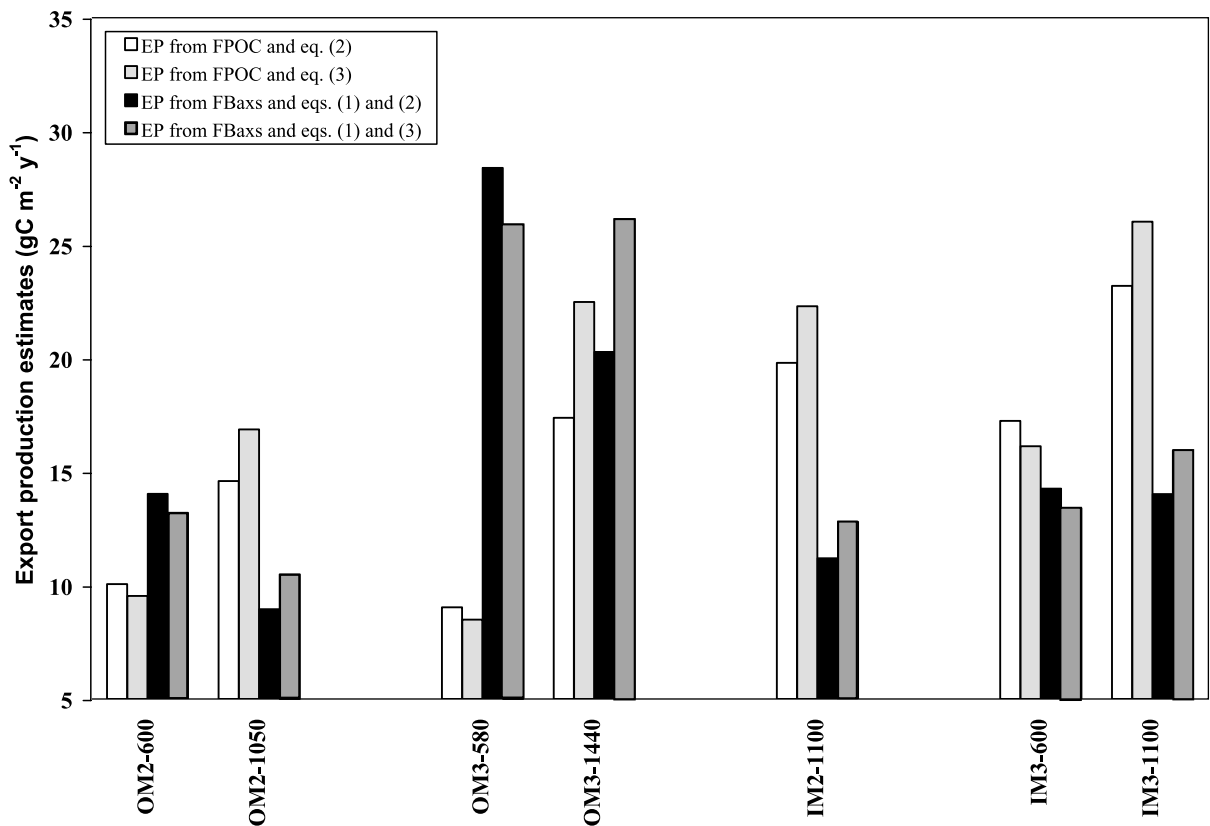


Fig. 6. Comparison of calculated export production at the Iberian Margin and Goban Spur, based on trap POC or Ba_{xs} fluxes. Export productions based on the trapped POC flux were calculated using Eq. 2 (Sarnthein et al., 1988) or Eq. 3 (Martin et al., 1987). For export production calculations based on Ba_{xs} flux, we used Eq. 1 fitted with regression coefficients characteristic of margin systems and Eqs. 2 or 3.

tions with this trap risky. For the deepest traps (OM2, 3260 m; OM4, 4000 m), export production based on $F_{Ba_{xs}}$ are higher by up to a factor 1.9 (OM4, 4000 m) and more consistent with values derived from shallower traps. From our results it appears clearly that calculating export production from $F_{Ba_{xs}}$ is to be preferred. This probably reflects the more refractory character of Ba_{xs} relative to POC with increasing depth in the water column.

Our calculated export productions represent a significant fraction of new production ($\leq 50\%$), but fall short, in general, of accounting for the new production estimates based on ^{15}N uptake experiments. Possible explanations could be, for instance: (1) the utilised algorithms based on trap fluxes are not appropriate because of their inherent large error on predicted fluxes from the surface mixed layer; (2) overestimation of new production because of utilisation of nutrients mineralised on the shelf, which cannot be considered as new nutrients (Chen, 2003); (3) part of the new production is dissolved organic matter that possibly leaves the upper mixed layer by subduction.

4. Conclusions

Export productions at Goban Spur and the NW Iberian Margin were estimated using both particulate organic carbon (POC) and Ba_{xs} fluxes corrected for advection from the shelf break. The main conclusions can be summarised as follows.

(1) Advection appears to consist of pulsed events occurring mainly during winter. For the Iberian Margin, it is possible that advective transport affected only the POC flux and not the Ba_{xs} flux, contrary to the situation at Goban Spur. This possibly reflects the differences in morphology of the two margin systems.

(2) The larger POC/ Ba_{xs} ratios for both investigated margin systems are systematically larger than for open ocean systems. This is possibly related with reduced Ba_{xs} formation per POC unit mineralised as a result of faster particle settling in these margin systems. Furthermore, the strong seasonality of the POC/ Ba_{xs} ratios implies that export production should be calculated based on

yearly averaged fluxes, as stated earlier by François et al. (1995).

(3) This study emphasises the necessity to apply a depth-dependent relationship between POC and Ba_{xs} fluxes using regression coefficients specific for margin systems.

(4) Our results for two NE Atlantic Margin environments show quite similar carbon export fluxes. However, for the same mooring site, estimations based on Ba_{xs} fluxes at different depths show better internal consistency than estimations based on POC fluxes.

(5) It remains unexplained why estimated export production in all cases falls significantly short of new production.

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