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Biogenic barium in suspended and trapped material as a tracer of export production in the tropical NE Atlantic (EUMELI sites)

C. Jeandel [a,*], K. Tachikawa [a], A. Bory [b], F. Dehairs [c]

[a] *LEGOS (UMR 5566, CNES/CNRS/UPS), Géodésie Spatiale, Observatoire Midi-Pyrénées, 14 Ave E. Belin, F-31400, Toulouse, France*
[b] *LSCE, Domaine CNRS, Ave de la Terrasse, F-91190, Gif-Sur-Yvette, France*
[c] *Vrije Universiteit Brussel, ANCH, Pleinlaan 2, B-1050, Brussel, Belgium*

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Abstract

Biogenic barium (bio-Ba) was measured in trapped and suspended particles at both the mesotrophic (M) and oligotrophic (O) EUMELI sites, in the tropical NE Atlantic. Trap data (2500 m depth) were used to calculate the exported production (ExP), using the relationship established by François et al. [François, R., Honjo, S., Manganini, S., Ravizza, G., 1995. Bio-Ba fluxes to the deep sea: implications for paleoproductivity reconstructions. Global Biogeochem. Cycles 9, 289–303.]. We find 12 ± 4 and 1.6 ± 0.4 gC/m^2/year at sites M and O, respectively. These values are consistent with: (1) the measured total primary productions at both sites and (2) the measured exported carbon estimated by the "instantaneous" sampling of drifting traps in two seasons. At site O, our estimate compares well with the ExP deduced from measured particulate organic carbon (POC) at 2500 m [François et al., 1995; Sarnthein, M., Winn, K., Duplessy, J.-C., Fontugne, M., 1988. Global variations of surface ocean productivity in low and mid-latitudes: influence on CO$_2$ reservoirs of the deep ocean and atmosphere during the last 21,000 years. Paleoceanogr. 3, 362–399.]. At site M, there is an offset in flux timing and estimated ExP fluxes do not compare well with primary production observations. These observations suggest that advected refractory carbon is present in the traps and/or that organic matter yielding large POC fluxes is different from that favoring bio-Ba formation and transport. In particular, fecal pellets might play a main role in the bio-Ba synthesis and vertical transfer. In suspended particles, the vertical distribution of bio-Ba could be related to phytoplanktonic and/or heterotrophic activity. Based on the meso-pelagic bio-Ba maxima, we estimated that 1.4–1.5 and 0–0.1 gC/m^2 of exported carbon is remineralized during the month of June, just below the mixed layer at sites M and O, respectively. The ExP calculated using trapped bio-Ba flux (François et al., 1995) is discussed with regards to the fraction of this ExP remineralized at mesopelagic depths. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oceanography; Export production; Proxy; Biogenic barium; Flux; Tropical Atlantic

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1. Introduction

In the marine environment, biogenic barium (bio-Ba) formation is directly related to plankton activity and to surface water productivity (Goldberg and

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[*] Corresponding author. Tel.: +33-5-6133-2933; fax: +33-5-6125-3205.
E-mail address: catherine.jeandel@cnes.fr (C. Jeandel).

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Arrhenius, 1958; Chow and Goldberg, 1960; Dehairs and Goeyens, 1989; Dymond et al., 1992; François et al., 1995; Dymond and Collier, 1996; Paytan et al., 1996). Bio-Ba is the fraction of particulate Ba of biological origin and is mostly made of barite in the water column (Dehairs et al., 1980). Therefore, trapped and sedimented barite fluxes are used to reconstruct the modern and paleo-productivity, respectively. Legeleux and Reyss (1996) clearly showed that bio-Ba is mostly formed in the upper 250 m of the water column. However, surface ocean waters are highly undersaturated with respect to barite (Church and Wolgemuth, 1972; Jeandel et al., 1996; Monnin et al., 1999). Two pathways have been proposed to explain the production and occurrence of barite in the oceanic water column. The first one proposes that barite precipitates within saturated microenvironments. Barium is taken up by plankton and plankton detritus (active uptake and/or adsorption). Plankton mortality leads to the formation of aggregates. High Ba contents and sulphate concentrations, resulting from the oxidation of reduced organic sulphur compounds or dissolution of celestite, induce barite oversaturation in the aggregates and lead to the ''abiotic precipitation'' of barite crystals (Chow and Goldberg, 1960; Dehairs et al., 1980; Bishop, 1988; Stroobants et al., 1991; Dymond and Collier, 1996). The second pathway involves active biological precipitation. This has not been considered as a major source of barite because the evidence of this process has not been observed in pelagic marine organisms. However, recent work by Bertram and Cowen (1997) indicates that some ovoid crystals (one of the most common forms of barite microcrystals in the ocean) might be precipitated by active biological processes. If they are dense enough, barite-containing aggregates will settle and reach the sediments, thereby bringing information that can be directly related to the surface ocean productivity. Based on empirical relationships between bio-Ba or barite and productivity, the accumulation of bio-Ba or barite in sediments has been used to reconstruct paleo-productivity (Dymond et al., 1992; Gingele and Dahmke, 1994; François et al., 1995; Nürnberg, 1995; Frank, 1996; Paytan et al., 1996; Nürnberg et al., 1997). The present paper provides data from sediment traps and suspended matter that confirm the relationship between bio-Ba collected in trap samples and surface productivity in the tropical NE Atlantic.

During the transit through the water column, bacterial activity may decompose part of the barite-carrying aggregates. Thus, barite crystals may be released to the ambient seawater. This process is thought to be responsible for the ubiquitous occurrence of a suspended bio-Ba maximum in mesopelagic waters (Dehairs and Goeyens, 1989; Dehairs et al., 1980, 1992, 1997). The water column stock of barite crystals is likely to reflect both the magnitude of the export flux and the extent of the heterotrophic oxidation of particulate organic carbon (POC) in subsurface and intermediate waters (Dehairs et al., 1992, 1997). Therefore, two types of information can be obtained: one based on the relationship between trapped and/or sedimented barite fluxes and export production (François et al., 1995); the second is based on the relationship between suspended bio-Ba, export C flux and its remineralization at mesopelagic depths (Dehairs et al., 1997). During the EUMELI program, both sedimenting particles and suspended particles were sampled, allowing for a comparison of both approaches. It is expected that the second one will provide fluxes less than or equal to those estimated from the first relationship. This paper reports sediment trap and suspended bio-Ba as well as POC fluxes in the deep water of the mesotrophic and oligotrophic EUMELI sites. We use these observations to: (1) compare and evaluate different approaches to reconstruct export production using bio-Ba; (2) discuss the process leading towards barite formation; (3) improve our knowledge of bio-Ba as a tracer of present-day productivity.

2. Sampling and analytical procedure

2.1. Sampling

All samples were collected during the EUMELI program, which took place between 1991 and 1992 in the Northeastern Tropical North Atlantic. Three different sites were explored (Fig. 1): the eutrophic site (E site: 20°32′N, 18°37′W) is the closest to the continental margin (about 200 km off the African

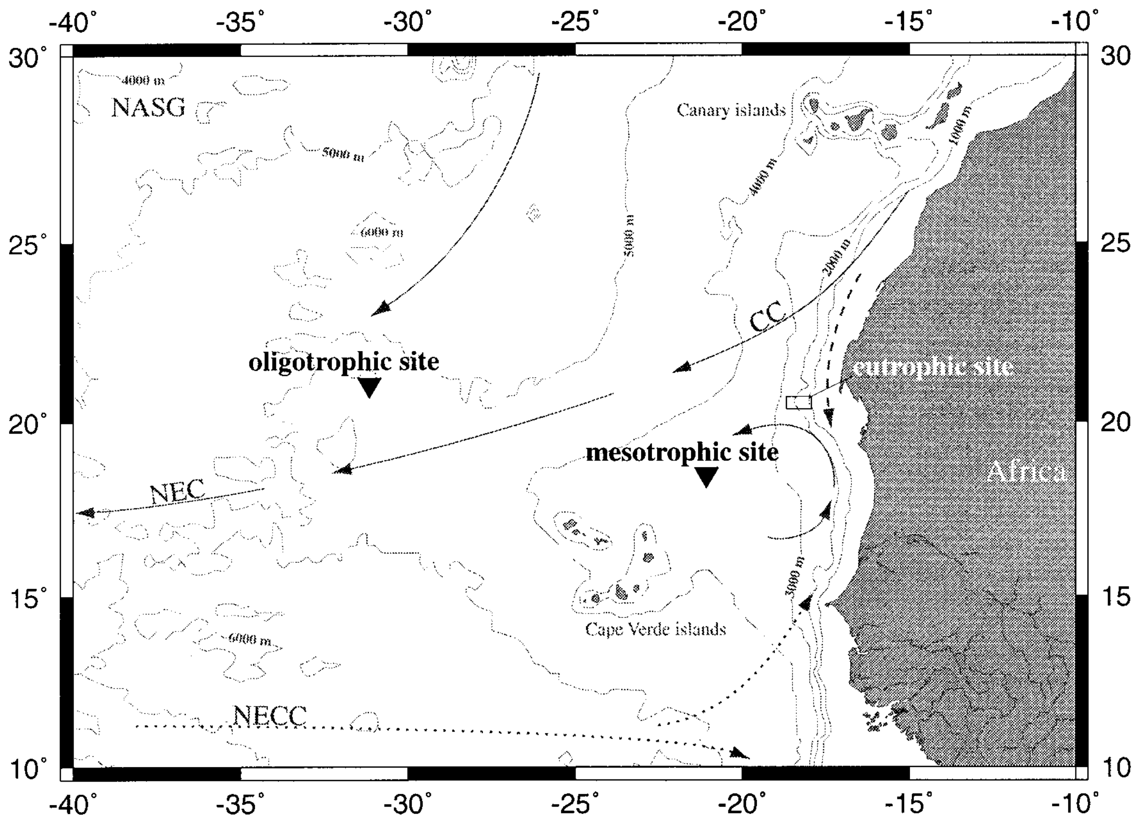

Fig. 1. Location of the EUMELI sampling sites (F-JGOFS). The main surface currents are identified (CC: Canary Current, NEC: North Equatorial Current, NECC: North Equatorial Counter Current, NASG: North Atlantic Subtropical Gyre).

continent), and is characterized by the largest dust flux (up to 15 g/m^2/year; Rea, 1994). This site is within the Mauritanian upwelling region and the primary productivity (650 gC/m^2/year) is the highest of the three sites (Morel, 1996). The mesotrophic site (site M: 18°30′N, 21°07′W) and the oligotrophic site (site O: 21°04′N, 31°12′W) are described in detail by Tachikawa et al. (1997). Briefly, the dust flux is estimated at 6–15 g/m^2/year and at 4–5 g/m^2/year at sites M and O, respectively (based on sedimentation rate; Rea, 1994). The respective primary productivities are 350 and 120 g C/m^2/year (Morel, 1996).

Sediment traps (Technicap PPS 5) were deployed at 2500 m depth at sites M and O from February 1991 to May 1992 (the sampling interval was 10 days). Because of fish invasion of the traps deployed at site M (eggs and fish remains observed in the trap, N. Leblond, pers. commun.), samples were available for only 8 months (February–September 1991).

During the deployment, the trapped material was stored in cups filled with seawater and a buffered 5% formaldehyde solution to limit degradation. On land, after the removal of swimmers, the trapped material was split into subsamples following the method described by Heussner et al. (1990). Subsamples were then either rinsed with de-ionized water and centrifuged, or filtered (0.4 μm) and rinsed with ammonium formate (NH_4CO_2H) before being lyophilized (Leblond et al., 1995). The ^{210}Pb analysis of the supernatants of the trapped material shows that loss of material due to dissolution is very low (Legeleux et al., 1996).

Marine suspended matter was collected using large volume filtration pumps (ISP, Challenger Oceanics Mark I; 31–995 litres) on Durapore membranes

Table 1
Element fluxes measured in trapped material (2500 m) at the mesotrophic and oligotrophic EUMELI sites

Sample #	Date	Mass (mg/m^2/day)	Bio-Ba (μg/cm^2/year)	POC (μg/cm^2/year)	Al (μg/cm^2/year)	%POC	%Bio-Ba of total Ba	POC/bio-Ba (g/g)
Mesotrophe 2500 m								
II-2 M1	12 Feb 91	57	–	102	–	5	–	–
II-2 M2	13 Feb 91	99	1.26	176	99	5	63	140
II-2 M3	23 Feb 91	309	3.14	646	200	6	68	206
II-2 M4	05 Mar 91	681	7.90	2459	398	10	73	311
II-2 M5	15 Mar 91	577	5.25	2497	258	12	73	476
II-2 M6	25 Mar 91	603	4.65	4538	226	21	73	977
II-2 M7	04 Apr 91	318	4.03	1593	192	14	74	396
II-2 M8	14 Apr 91	109	2.22	289	118	7	72	130
II-2 M9	24 Apr 91	178	2.92	582	146	9	73	199
II-2 M10	04 May 91	115	2.05	351	108	8	72	171
II-2 M11	14 May 91	121	2.89	415	136	9	74	144
II-2 M12	24 May 91	508	4.85	4743	151	26	81	979
II-2 M13	03 Jun 91	467	6.41	4058	151	24	85	633
II-2 M14	13 Jun 91	505	6.83	1239	264	7	77	181
II-2 M15	23 Jun 91	265	4.11	520	141	5	80	126
II-2 M16	03 Jul 91	168	5.28	366	169	6	81	69
II-2 M17	13 Jul 91	96	2.37	176	102	5	76	74
II-2 M18	23 Jul 91	85	1.57	199	85	6	71	127
II-2 M19	02 Aug 91	132	3.09	351	142	7	74	113
II-2 M20	12 Aug 91	86	2.38	213	91	7	78	90
II-2 M21	22 Aug 91	85	1.93	210	96	7	73	109
II-2 M22	01 Sep 91	177	1.97	367	186	6	59	186
II-2 M23	11 Sep 91	149	3.09	270	234	5	64	88
II-2 M24	12 Sep 91	98	2.05	234	155	7	64	114
Average Meso standard deviation (σ)		**250 ± 197**	**3.58 ± 1.81**	**1108 ± 1453**	**167 ± 73**	**9 ± 6**	**73 ± 6**	**263 ± 264**
Oligotrophe 2500 m (EUMELI 2)								
II-2 O1	18 Feb 91	–	–	–	–	–	–	–
II-2 O2	19 Feb 91	–	–	–	–	–	–	–
II-2 O3	23 Feb 91	8	–	17	–	6	–	–
II-2 O4	05 Mar 91	22	–	42	–	5	–	–
II-2 O5	15 Mar 91	20	0.32	–	12	–	77	–
II-2 O6	25 Mar 91	27	0.57	58	23	6	77	102
II-2 O7	04 Apr 91	15	0.30	39	12	7	77	131
II-2 O8	14 Apr 91	18	0.39	45	17	7	75	115
II-2 O9	24 Apr 91	25	0.71	41	25	5	79	59
II-2 O10	04 May 91	40	0.84	106	33	7	77	126
II-2 O11	14 May 91	29	0.62	62	22	6	79	100
II-2 O12	24 May 91	33	0.55	46	19	4	79	83
II-2 O13	03 Jun 91	37	0.72	63	26	5	78	87
II-2 O14	13 Jun 91	43	0.80	95	28	6	79	119
II-2 O15	23 Jun 91	64	1.13	104	38	4	80	92
II-2 O16	03 Jul 91	46	0.91	74	31	4	80	81
II-2 O17	13 Jul 91	30	0.63	49	20	5	81	78
II-2 O18	23 Jul 91	36	0.89	79	30	6	80	88
II-2 O19	02 Aug 91	44	0.89	106	30	7	80	119
II-2 O20	12 Aug 91	39	1.02	46	32	3	81	45
II-2 O21	22 Aug 91	41	1.20	54	37	4	81	45
II-2 O22	01 Sep 91	45	0.99	52	33	3	80	52
II-2 O23	11 Sep 91	36	0.80	68	31	5	77	85
II-2 O24	12 Sep 91	31	–	75	–	7		–

Table 1 (*continued*)

Sample #	Date	Mass (mg/m^2/day)	Bio-Ba (μg/cm^2/year)	POC (μg/cm^2/year)	Al (μg/cm^2/year)	%POC	%Bio-Ba of total Ba	POC/bio-Ba (g/g)
Oligotrophe 2500 m (EUMELI 3)								
III-2 O1	25 Sep 91	10	–	23	–	6	–	–
III-2 O2	29 Sep 91	21	0.54	41	17	6	81	76
III-2 O3	09 Oct 91	23	0.68	39	22	5	81	58
III-2 O4	19 Oct 91	19	0.62	28	18	4	82	46
III-2 O5	29 Oct 91	16	0.53	39	14	7	83	73
III-2 O6	08 Nov 91	17	0.50	33	16	5	81	66
III-2 O7	18 Nov 91	39	0.69	73	24	5	80	106
III-2 O8	28 Nov 91	47	1.00	82	37	5	78	82
III-2 O9	08 Dec 91	31	0.79	53	28	5	79	67
III-2 O10	18 Dec 91	30	0.82	47	29	4	79	57
III-2 O11	28 Dec 91	37	0.84	47	33	4	77	55
III-2 O12	07 Jan 92	42	1.09	65	42	4	78	59
III-2 O13	17 Jan 92	32	0.89	48	33	4	78	54
III-2 O14	27 Jan 92	29	0.79	43	28	4	79	54
III-2 O15	06 Feb 92	25	0.69	39	25	4	79	57
III-2 O16	16 Feb 92	59	1.58	100	59	5	78	63
III-2 O17	26 Feb 92	48	1.02	82	38	5	78	81
III-2 O18	07 Mar 92	44	1.22	88	39	6	81	72
III-2 O19	17 Mar 92	36	1.04	73	34	6	80	70
III-2 O20	27 Mar 92	40	0.99	73	39	5	77	73
III-2 O21	06 Apr 92	64	1.37	124	64	5	74	91
III-2 O22	16 Apr 92	85	1.85	156	83	5	75	84
III-2 O23	26 Apr 92	46	1.11	67	48	4	76	60
III-2 O24	06 May 92	36	–	–	–	–	–	–
Average Oligo standard deviation (σ)		**35 ± 15**	**0.85 ± 0.3**	**63 ± 28**	**31 ± 12**	**5 ± 1**	**78 ± 2**	**78 ± 20**

(0.65-μm porosity, 142-mm diameter). The filters were rinsed with de-ionized water to eliminate sea salt. They were then dried and stored in sealed Petri dishes until analysis.

2.2. Analytical procedure

Trap samples were analyzed in two different laboratories (LEGOS and LSCE) following similar methods. About 10–100 mg of each sample were totally dissolved using either a HNO_3/HF mixture in sealed Teflon bombs for at least 8 h on a hot plate at 100°C (LEGOS), or a HNO_3/HCl/HF mixture in pressure controlled Teflon bombs (maximum about 150 psi) for 1 h using microwave heating (LSCE). At both laboratories, aliquots (10%) of the resulting solutions were diluted with 2% HNO_3 for multi-element (including Al and Ba) analysis (Bory, 1997; Tachikawa et al., 1997).

Filtered particles, analyzed at LEGOS only, were totally dissolved using a strong acid digestion (Landing and Lewis, 1991), and diluted with 2% HNO_3. The same elements were analyzed as for the trap material (Tachikawa et al., 1999). These authors verified that the acid digestion quantitatively dissolves all elements, including Ba.

Element concentrations were determined by Inductively Coupled Plasma Mass Spectrometer (ICP/MS: ELAN 5000), using indium as an internal standard (Valladon et al., 1995; Tachikawa et al., 1997, 1999) or by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES Thermo Jarel Ash Polyscan 61 E; Bory, 1997). Blank contributions corresponded to about 1% and 2% of the Ba and Al signals in the suspended matter and below 1% for both elements in the trapped material. In both laboratories, the reproducibility of analysis was better than 5% for Al and Ba measurements. The com-

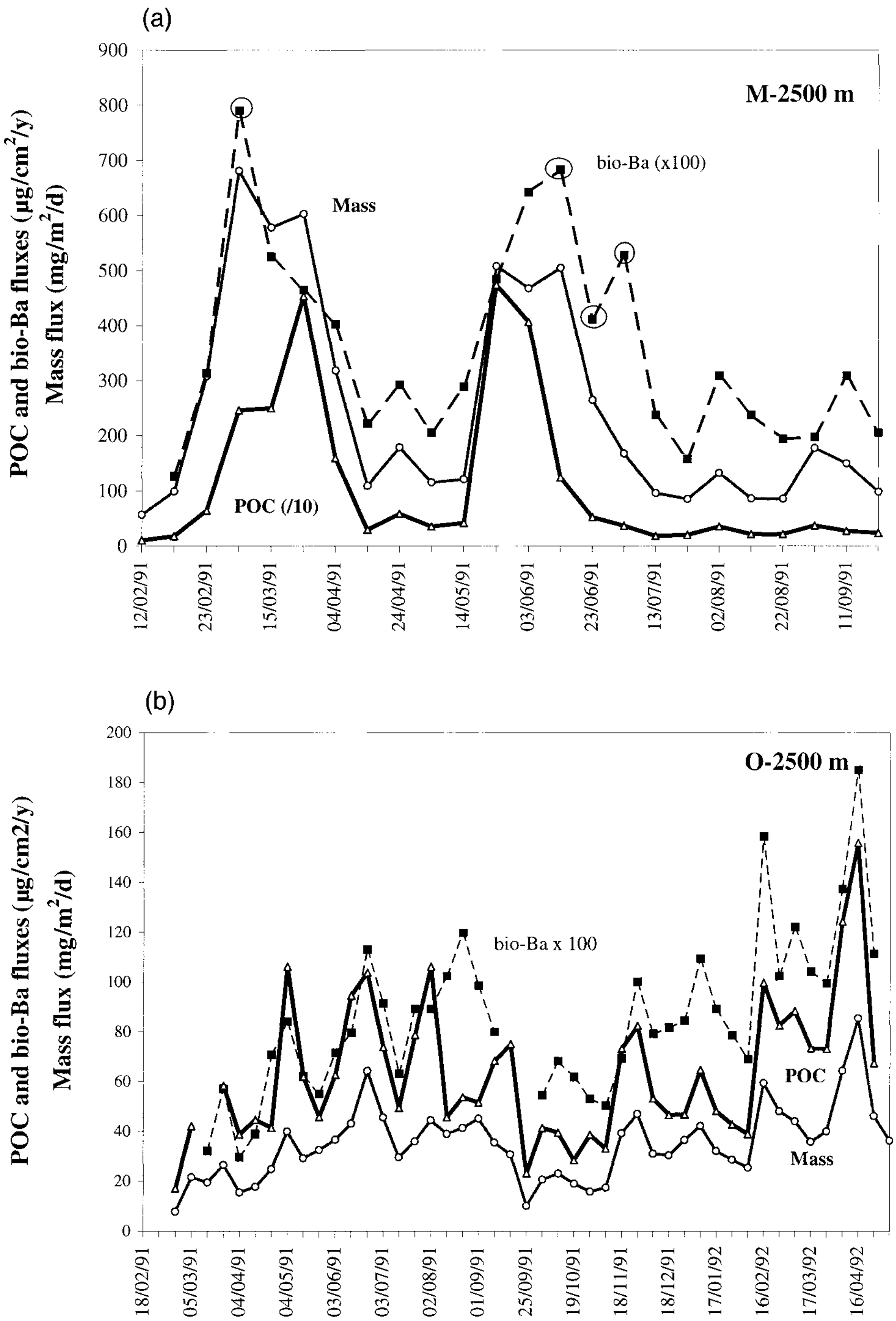

Fig. 2. Temporal variation of the mass (mg/m^2/day, open circles, solid line), POC (μg/cm^2/year, open triangles, thick line) and bio-Ba (μg/cm^2/year, black squares, dashed line) fluxes at EUMELI sites M (a) and O (b). Bio-Ba fluxes were multiplied by 100 (both figures) and POC fluxes were divided by 10, in panel (a) only. Encircled data (a) correspond to samples with low POC/bio-Ba ratios (M4, M14, M15 and M16).

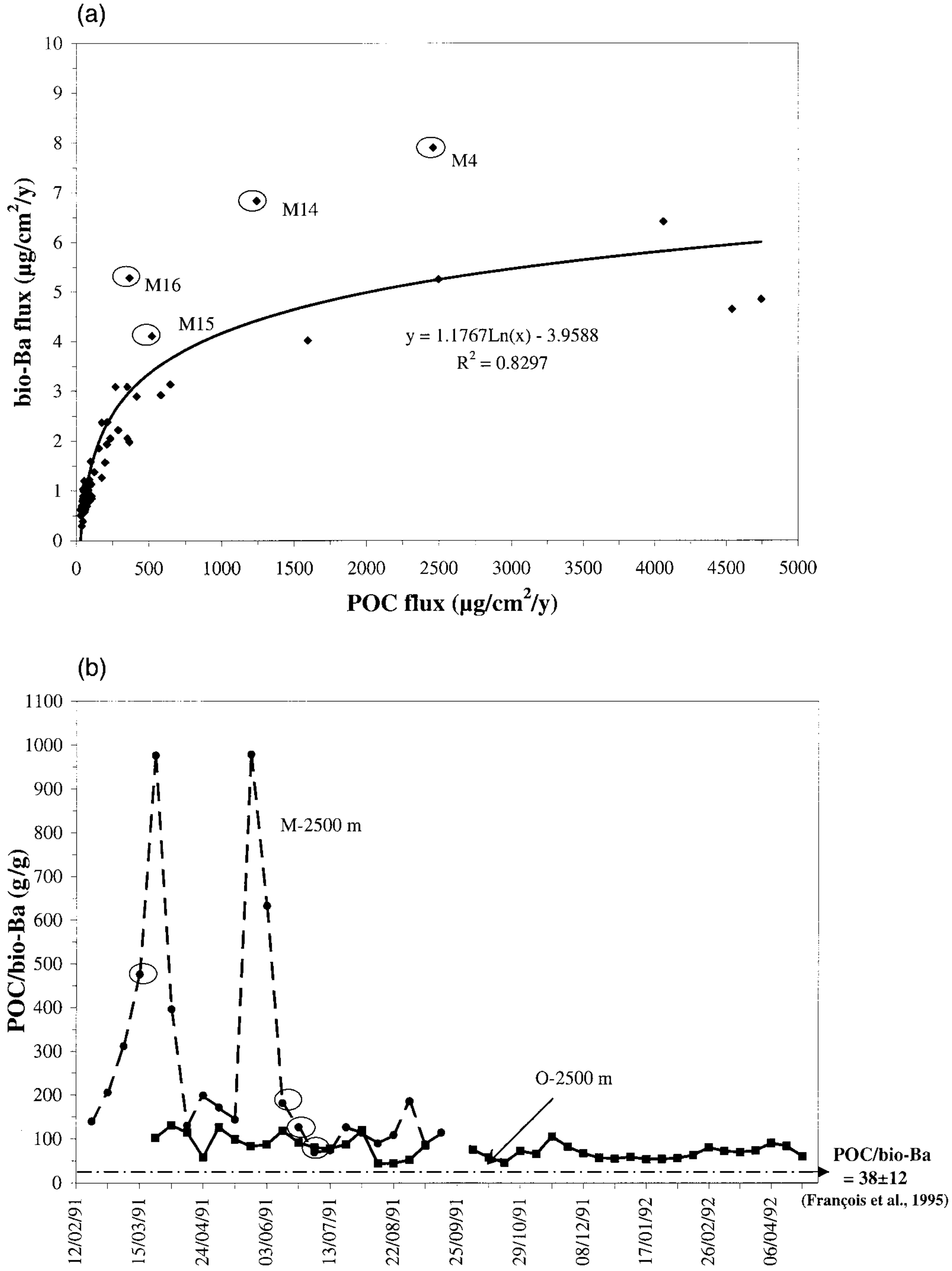

Fig. 3. (a) Relationship between the bio-Ba and the POC fluxes, at sites M and O. Encircled data correspond to the same samples as in Fig. 2a. (b) Temporal variation of the POC/bio-Ba ratio at site M (dashed line) and site O (solid line). The value of 38 ± 12 g/g represented by the arrowed dashed line is calculated using the following relationship proposed by François et al.,1995 (the error bar of 12 corresponds to the 1 standard deviation value, estimated at 2500 m using Fig. 10 of François et al., 1995): POC/bio-Ba = $4787z^{-0.616}$. Encircled data correspond to the same samples as in Fig. 2a and panel (a).

plete analytical methods were tested by measuring geological standards (BE-N, MAG 1 and BCSS-1). The accuracy is better than 5% for suspended matter and better than 3% for trapped material. These values are better than analytical uncertainties of each measurement based on the counting statistics. The reproducibility of the whole analytical procedure including homogeneity of the samples was established by independent replicates of some samples. It is also within the above error bars. The measurements of both laboratories have been compared. Results obtained on independent subsamples are in good agreement. Therefore, data from both labs were combined in order to provide the most complete set of results.

3. Results and discussion

Results are presented in Table 1 and Figs. 2 and 3 for the sediment trap material, and in Table 2 and Figs. 4 and 5, for the suspended particles. To make the comparison with other published data easier, our mass flux and element fluxes are shown in mg/m^2/day and μg/cm^2/year.

Throughout this work we will discuss the behavior of bio-Ba, deduced from the Ba measured in our samples using the equation

$$(\mathrm{Ba})_{\mathrm{bio}} = (\mathrm{Ba})_{\mathrm{meas}} - (\mathrm{Al})_{\mathrm{meas}}((\mathrm{Ba}/\mathrm{Al})_{\mathrm{ref}}) \qquad (1)$$

where $(\mathrm{Ba})_{\mathrm{meas}}$ and $(\mathrm{Al})_{\mathrm{meas}}$ are measured bulk concentrations and $(\mathrm{Ba}/\mathrm{Al})_{\mathrm{ref}}$ is the average crustal ratio for these elements. This calculation subtracts the lithogenic Ba contribution from the total Ba of the samples. Following the compilation proposed by Dymond et al. (1992), the $(\mathrm{Ba}/\mathrm{Al})_{\mathrm{ref}}$ ratio ranges between 0.005 and 0.010. We adopted the average value of 0.0075. The range of uncertainty on this value results in an average error of less than 5% for the majority of the filtered particles, where bio-Ba consists of more than 83% of total Ba (Table 2).

Table 2
Total aluminium, barium and bio-Ba concentrations in suspended matter (stars indicate samples for which volumes of filtered water are doubtful)

Sample #	Depth (m)	Al (nmol/l)	Ba (pmol/l)	Bio-Ba (pmol/l)	Bio-Ba (% of total Ba)	E_F (Ba)
E-site (20°32′ N, 18°37′ W), June 92						
E33	10	117 ± 9	343 ± 31	169 ± 72	49	0.4 ± 0.1
E41	20	48 ± 4	2031 ± 138	1961 ± 29	97	5.6 ± 1.2
E32	50	28 ± 3	324 ± 23	284 ± 17	87	1.6 ± 0.4
E40	100	16 ± 1	238 ± 18	213 ± 10	90	1.9 ± 0.5
E37	500	23 ± 1	337 ± 25	304 ± 14	90	2.0 ± 0.5
E36	1000	12 ± 1	290 ± 20	273 ± 7	94	3.4 ± 2.5
E38	1600	54 ± 4	277 ± 21	197 ± 33	71	0.7 ± 0.2
E39	1800	16 ± 1	103 ± 7	79 ± 10	77	0.8 ± 0.2
M site (18°30′ N, 21°07′ W), June 92						
M27	10	22 ± 1	63 ± 6	31 ± 13	49	0.4 ± 0.1
M30	20	8 ± 0.4	17 ± 2	5 ± 5	29	0.3 ± 0.1
M11	50	8 ± 0.5	195 ± 16	183 ± 5	94	3.3 ± 0.8
M26	100	7 ± 0.4	112 ± 10	102 ± 4	91	2.2 ± 0.5
M29*	250	16 ± 0.8	414 ± 30	390 ± 10	94	3.4 ± 0.9
M10*	1000	14 ± 0.7	167 ± 13	147 ± 8	88	1.6 ± 0.4
M12	2500	4 ± 0.2	33 ± 3	27 ± 2	83	1.1 ± 0.3
O site (21°04′ N, 31°12′ W), June 92						
O8	10	5 ± 0.3	17 ± 2	10 ± 3	58	0.5 ± 0.3
O7	50	4 ± 0.4	20 ± 2	14 ± 2	70	0.7 ± 0.2
O6	100	4 ± 0.3	13 ± 2	7 ± 2	56	0.4 ± 0.1
O5*	250	1 ± 0.1	26 ± 2	24 ± 1	94	3.2 ± 0.8
O9	1000	4 ± 0.3	72 ± 5	67 ± 2	92	2.6 ± 0.6

E_F (Ba) corresponds to the Ba-enrichment factor.

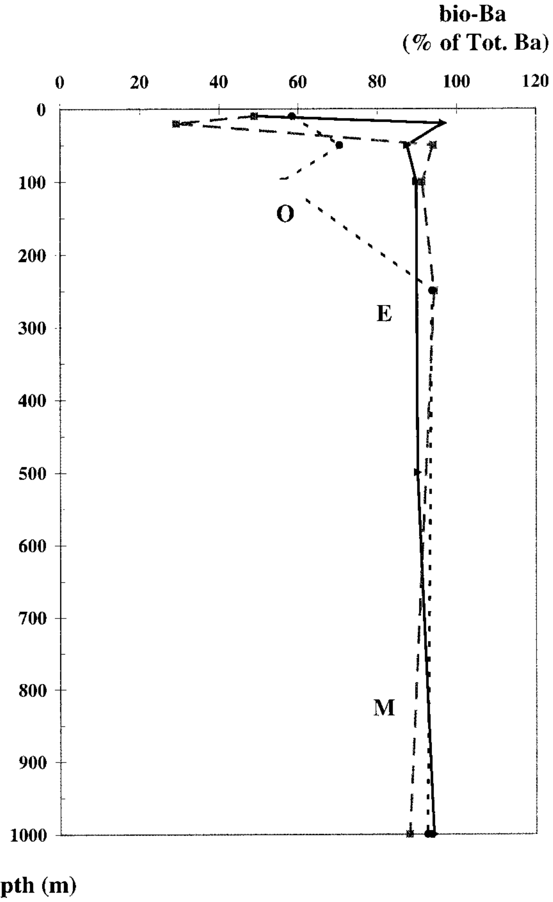

Fig. 4. Vertical profiles of the percentage of biogenic Ba (%bio-Ba = bioBa/total Ba × 100) in the filtered suspensions at the three EUMELI sites (solid line: site E, broken line: site M, small black dotted line: site O).

Lithogenic Ba contribution is larger for samples filtered close to the surface, increasing the average uncertainties in bio-Ba estimates to 35% (when bio-Ba fraction is of 49%) and even 80% (when bio-Ba fraction drops down to 29% at site M, see Table 2). With the trapped material, the related uncertainties are 13% and 9% for the M and O samples, where bio-Ba consists of 73% and 79% of total Ba, respectively (Table 1).

Exported carbon flux (ExP) was estimated using the trapped material bio-Ba fluxes and carbon respiration rate (which represents part of the ExP) was estimated from the concentrations in the meso-pelagic bio-Ba maxima, applying the Dehairs et al. (1997) relationship. These estimates are compared to each other and to observed POC fluxes.

3.1. Trapped bio-Ba fluxes and export production

This section discusses the results obtained for the sediment traps deployed at 2500 m at sites M and O (Table 1). Fig. 2a and b represent the temporal variation of the mass, bio-Ba and POC fluxes at both sites. At site M, two periods of high fluxes are observed, in March and May–June, which are probably related to an increase of surface biological activity. During the first major event, the bio-Ba and mass flux variations occur simultaneously, whereas the POC maximum occurs somewhat later. This situation is reversed during the second event, with the POC peak coinciding with the first peak of the mass flux, whereas the bio-Ba peak occurs later (Fig. 2a). At site O, the mass flux is 4–8 times lower than

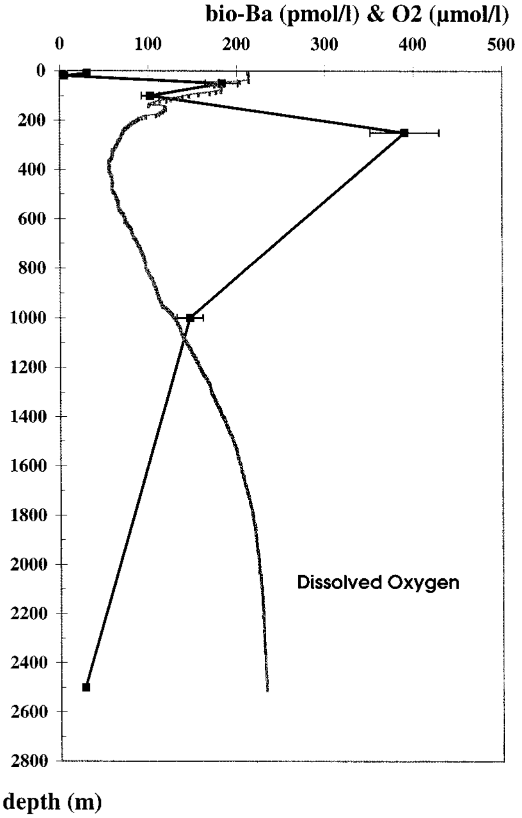

Fig. 5. Vertical profiles of suspended bio-barite and dissolved oxygen, measured at site M during the EUMELI-4 cruise (June 1992).

at site M. Seasonal variations are also different, being characterized by many small peaks all over the year, with larger events during spring/summer. The coherence of temporal variations in bio-Ba, POC and mass fluxes is excellent for this site. For sites M and O combined, the best fit between the bio-Ba and POC fluxes is a logarithmic relationship: for high POC fluxes, bio-Ba fluxes tend towards constant values (Fig. 3a). Such tendency has previously been observed for Ba in the Equatorial Pacific (Dymond and Collier, 1996), and for ^{210}Pb and Al at EUMELI sites (Legeleux et al., 1996; Bory and Newton, 2000). Four points lies above the logarithmic plot, characterized by significantly higher bio-Ba fluxes than expected for the measured POC fluxes (encircled in Fig. 3a). They correspond to samples M4 (5 March), M14 (13 June), M15 (23 June) and M16 (3 July); they also exhibit bio-Ba proportions of 73%, 77%, 80% and 81%, around the average for site M (Table 1). These samples were collected at the beginning of the first bloom (March) and the end of the second bloom (June and July): their low POC/bio-Ba values reflect the incoherence in timing between the POC and bio-Ba peaks during bloom episodes (Fig. 2a).

3.1.1. Temporal variations in the POC/bio-Ba ratio

Variations of the POC/bio-Ba mass ratio with time and at both sites are presented in Fig. 3b. For comparison, we also reported the POC/bio-Ba values predicted by the relationship proposed by François et al. (1995): POC/bio-Ba = 38 ± 12 g/g at 2500 m (see the figure caption). The POC/bio-Ba ratio reaches values close to 1000 during bloom events at site M, while at site O, the values are less variable and never exceed 130. The yearly average calculated for site O is 78 ± 20 (Table 1), slightly higher than the model ratio of 38 (François et al., 1995). This could reflect: (1) that the statistical relationship applied to the subset of all the data chosen by these authors does not apply here; (2) a poorer preservation of bio-Ba in the NE Atlantic water column which is largely undersaturated with regards to barite (Monnin et al., 1999) compared to other oceanic environments; (3) a slight influence of excess carbon from terrigenous origin, advected from the shelf and slope regions; (4) an inherited error due to a deviation between Ba/Al in actual terrigenous matter and the ratio used here, although the lowest Ba/Al ratio observed today (0.0055) still yields elevated POC/bio-Ba ratios.

The high POC/bio-Ba values observed at site M (only 450 km from the coast) could argue in favor of the assumption that the high POC/bio-Ba ratios found in trapped materials close to the continent reflect a contribution of refractory POC laterally transported in deep waters from shelf and slope sediments (François et al., 1995). Unfortunately, we do not have POC/bio-Ba values for any of these inferred shelf sediments, to assess the reliability of this hypothesis. The influence of such a lateral advection was observed in the deep OMEX traps, off the mid-European margin, as discussed in Antia et al. (in press). A study of the EUMELI current-meter data indicates that an east–west component, which may transport suspended material from the African shelf, is only significant at 250 m depth and becomes weaker with depth: at 2500 m, it is insignificant (Bory, 1997; Bory et al., 2000; Tachikawa et al., 1999). Therefore, if advection of refractory carbon occurs, it would mostly occur in the surface layers. The mesoscale dynamics in the upwelling area could lead to the surface advection of filaments of productive waters, towards the EUMELI area (Berthon, 1992), and also the Canary Islands area (Neuer et al., 1997; Ratmeyer et al., in press). These advected waters could also transport refractory carbon from the shelf area. The highest POC/bio-Ba ratios are observed in spring. If these ratios result from advection of refractory carbon, they are expected to be most significant when turbulence and wind stress are enhanced: this happens during spring in this area, when the marine trade winds become active and strong (Tomzcack, 1977; Chiapello et al., 1995). Indeed, the timing of high POC/bio-Ba occurrence correlates with high east–west current periods.

On the other hand, Dymond and Collier (1996) suggest that POC/bio-Ba ratios are determined by the variability in surface ecosystem parameters (productivity as well as community composition) and not due to contamination by refractory POC. These authors observe variations of a factor of 2–3 in POC/bio-Ba ratio in the equatorial Pacific, whereas our site M values vary by up to a factor of 10. A close look reveals that the samples which are characterized by POC/bio-Ba ratios above 500 (first peak: 15 March to 4 April; second peak: 14 May to 3 June), correspond to periods of very high POC fluxes. The POC concentration increases from an average of 9.3–20.6% (in March) and to 25.6% (in May). However, these high POC fluxes occur about 15 days after (in March) or before (in May) the bio-Ba peak. This offset in timing between the POC and bio-Ba peaks is reflected by relatively low POC/bio-Ba ratios for samples M4, M14, M16 and, to a lesser extent, M15 (circled in Figs. 2a, 3a and b); on the opposite, samples M6 and M12 are characterized by high POC/bio-Ba ratios (Table 1 and peaks of Fig. 3b). ''Sticky-gelatinous'' organic material was observed in the traps when the highest POC/bio-Ba ratios were recorded, mostly in cups M5–M9 and M12–M13 (N. Leblond, pers. commun.). High POC fluxes could then be related to the occurrence of gelatinous zooplankton. Such gelatinous zooplankton (e.g., salps) would induce large sinking velocities (about 500 m/day; Bory, 1997; Bory et al., 2000). When present, such plankton may have two effects on the bio-Ba/POC relationship: (1) they prevent the precipitation of barite crystals because of the fast transit time through the water column, or (2) they sink through the water column after (in March) or before (in June) the maximal formation of bio-Ba, and thus they are essentially decoupled from the bio-Ba flux. Such observations suggest that organic matter yielding barite formation is different from that forming the main POC flux in this area.

Another observation argues against horizontal transport of shelf-derived material. At both sites, Al and bio-Ba fluxes are linearly correlated (Al Flux = 42.4 (bio-Ba Flux) + 2.3, $r^2 = 0.84$ for 64 values, unit: $\mu g/cm^2/year$). This correlation holds even when bio-Ba fluxes are *decoupled* from POC fluxes (the four samples encircled in Figs. 2a, 3a and b). As bio-Ba and Al trace biogenic and terrigenous fluxes respectively, no co-genetic origin can explain this co-variation. Such a relation can be obtained either if transfer processes are dominant in controlling both tracer stocks in the surface waters or if bio-Ba is precipitated in the material transferring Al. Bory et al. (2000) show that the largest amounts of swimmers occur after the large POC event and co-vary with the $CaCO_3$ *and* lithogenic peaks. Comparison with our data shows that swimmer, $CaCO_3$ and lithogenic maxima are also consistent with the bio-Ba peaks. The $CaCO_3$ maximum cannot be attributed to coccolithophores at that time. It probably corresponds to zooplanktonic foraminifera, which would reflect zooplankton abundance above the traps (Bory et al., 2000). If the quantity of swimmers collected in the traps is assumed to be also related to the surface zooplanktonic activity, we suggest that zooplankton (mostly copepods, Leblond, pers. commun., but also foraminifera) could be responsible for this late and weaker POC export. Animals could graze and package lithogenic particles and export them via their fecal pellets (Bory and Newton, 2000; Bory et al., 2000). This also suggests that fecal pellets are micro-environments promoting barite formation, in agreement with Bishop's (1988) hypothesis. A relation between copepod fecal pellets and Al fluxes has previously been observed in the Mediterranean Sea, although bio-Ba was not determined in that work (Buat-Menard et al., 1989).

These results would thus support the hypothesis that POC/bio-Ba flux variations observed at 2500 m are a result of changes in surface water biological processes as well as export production (Dymond and Collier, 1996). Enhanced bio-Ba fluxes are not always related to large POC flux events. They could be related to export of fecal pellets, which would represent the main carrier (and/or site of formation) of the bio-Ba to the deep ocean sediments.

3.1.2. Bio-Ba as a tracer for export production

We calculated the ExP (g/m^2/year) on the basis of the bio-Ba flux ($F_{\text{bio-Ba}}$) and the relationship proposed by François et al. (1995):

$$\mathrm{ExP} = 1.95(F_{\text{bio-Ba}})^{1.41} \tag{2}$$

This equation assumes that $F_{\text{bio-Ba}}$ is independent of depth and is completely controlled by surface water processes.

The results can be compared to carbon export (ExP) calculated from POC flux (Fc) in the EUMELI trapped material at 2500 m, and the relationship proposed by Sarnthein et al. (1988):

$$\mathrm{ExP} = \exp\{(\ln\ \mathrm{Fc} + (0.5537 \ln z) - 3.023)/0.6648\} \tag{3}$$

where z designates the water column depth (2500 m) and Fc is the measured POC flux at z.

ExP at each station was calculated from the yearly averaged bio-Ba, POC fluxes (Table 1) and Eqs. (2) and (3).

A large discrepancy is observed for site M between the two approaches. Estimates of the annual carbon fluxes exported from the surface, based on the bio-Ba flux, is 12 ± 4 gC/m^2/year (the error bar reflects the 1 standard deviation (σ) on the average annual Ba flux). Estimates based on POC data yield 20 times higher fluxes, reaching 267 ± 400 gC/m^2/year. This result is generally consistent with the high POC/Ba ratios at M. The ExP estimates from site O yield more consistent values: 3.6 ± 1 gC/m^2/year from POC (Eq. 3) and 1.6 ± 0.4 gC/m^2/year from the bio-Ba flux (Eq. 2); note that ExP calculations based on total POC are still slightly higher than those based on bio-Ba, in agreement with the slightly larger POC/bio-Ba value than these suggested by François et al. (1995). We compared these export fluxes to primary production measured directly onboard during the fall of 1991 and the spring of 1992 at the same sites (^{14}C incubation method; EUMELI 3 and 4 cruises). At site M, the ExP estimated from bio-Ba represents between 2.6% and 5% of the measured primary production (456 gC/m^2/year in spring and 237 gC/m^2/year in fall, Dandonneau, pers. commun.; Morel, 1996). ExP estimated from total POC ranges from 1 to 3 times larger than the primary production. At site O, ExP based on bio-Ba represents less than 2% of the measured primary production (120 and 102 gC/m^2/year in spring and fall) and the ExP estimate from total POC flux corresponds to 3.3% of primary production. These calculations suggest that more carbon is recycled in the upper mixed layer at site O than at site M. This is consistent with the respective oligotrophic and mesotrophic character of these sites. Averaged ExP estimated from bio-Ba fluxes are in good agreement with average new production estimates for mesotrophic upwelling areas and for oligotrophic tropical gyres (Berger et al., 1989).

At site M, there is a clear inconsistency between ExP values deduced from the measured POC and bio-Ba fluxes. Furthermore, ExP based on POC flux is too large compared to the measured primary production. This discrepancy is worse when calculations are made on a 10-day timescale (e.g., more than 2000 gC/m^2/year for cups M6 and M12 with POC data, about 17 gC/m^2/year with Ba data). We should recall here that François' relationship (Eq. 2) was initially calibrated using Eq. 3 (Sarnthein et al., 1988) for open ocean sites not influenced by advection from the margin and slope (see François et al., 1995). Therefore, the discrepancy between both ExP estimates yields two hypotheses: either the enhanced surface production does not induce bio-Ba formation, or the large POC flux measured at 2500 m does not reflect surface productivity according to the Sarnthein relationship. Large POC/bio-Ba ratios may indicate that some trophic conditions prevent barite formation (see Section 3.1.1). However, the fact that the calculated ExP values and sometimes the POC flux measurements (see Table 1) can be larger than the measured total primary production strongly suggests that (i) under the ecosystem considered, the Sarnthein et al. (1988) relationship does not hold, or (ii) *refractory* POC imported via advected filaments contaminates the surface carbon stock (ingestion or aggregation of this refractory carbon by gelatinous organisms could yield rapid vertical transport of POC). In both cases, the ExP calculations would be biased. The bio-Ba estimate produces results that may be more consistent with expected export based on primary production observations. These assessments are corroborated by the consistency between the ExP calculated at the oligotrophic site O (which is also likely not influenced by advected refractory POC) using both approaches.

Future work will apply the relationships discussed here to the *sedimented* bio-Ba and POC, and check if they could constrain paleo-productivity in the EUMELI area (Jeandel et al., 1998).

3.2. Suspended particulate Ba and productivity

3.2.1. Suspended bio-Ba distribution

Average suspended bio-Ba concentrations in the water column decrease from site E to site O, which is consistent with the primary production gradient between these sites (Table 2). Fig. 4 presents the depth distribution of the bio-Ba fraction (% of total Ba) on the suspended material at the three sites. The most striking feature is that the contribution of lithogenic Ba to the suspended Ba stock is restricted to the upper 10 m at site E and 20 m at site M whereas it could reach 250 m at site O (the poor vertical resolution of the sampling at this site prevents us from precisely establishing the depth at which this lithogenic contribution vanishes). Below these depths at all the sites, the bio-Ba fraction represents more than 80% of the Ba stock. We calculated Ba enrichment factors for each sample (E_F(Ba) is the ratio between the measured Ba/Al ratio and the crustal reference of 0.0075 ± 0.0025 as discussed in Section 2). Significant Ba enrichments are observed between 20 and 1000 m at site E, between 50 and 1000 m at site M and between 250 and 1000 m at site O (Table 2). We compare these results to those of Tachikawa et al. (1999), who calculated the Mn and Rare Earth enrichments (REE) on the same filtered samples. At all sites, Mn and REE enrichments in the suspended particles occur immediately below the surface, yielding maxima at shallower depths than the bio-Ba ones (e.g., at 50 m at site O). As these data were obtained off the Saharan desert, the alumino-silicate fraction likely reflects a Saharan dust input (Tachikawa et al., 1999). Tachikawa et al. (1999) hypothesized that Mn and REE enrichments are related to bacterial activity coupled to chemical adsorption on particles. Hence, Ba enrichment might be linked to different biological or chemical processes, that might occur deeper in the water column. They can be related to the chlorophyll-a (chl-a) concentration maximum at the three sites. In June 1992, chl-a contents are as high as 7 μg/l at 15 m at site E; they show a maximum of 2 μg/l around 50 m at site M, whereas at site O, the maximum (0.5 μg/l) is centered around 125 m (Claustre and Marty, 1995; Morel, 1996). The consistency between chl-a concentrations and Ba enrichments is not the result of physical properties of the water as shown by CTD and nephelometer data (Vangriesheim et al., 1993; Claustre and Marty, 1995). Legeleux and Reyss (1996) proposed that barite formation occurs in the upper 250 m of the water column, but the precise formation mechanism is not understood yet: the debate is still open between the ''abiotic precipitation'' of barite crystals (Chow and Goldberg, 1960; Dehairs et al., 1980; Bishop, 1988; Stroobants et al., 1991) and the active biological precipitation (Bertram and Cowen, 1997). Our observations could suggest that active phytoplankton uptake is a significant process. On the other hand, the depth of chl-a maxima could reflect a layer of increased degradation of organic matter, heterotrophic activity and potential ''micro-environments'' for barite formation and/or Ba adsorption. In either case, we suggest that bio-Ba is forming in particulate organic matter (POM) (including, possibly, live plankton), which is correlated with the chl-a maximum.

3.2.2. Mesopelagic bio-Ba maximum

At sites M and O, the profiles of suspended bio-Ba (June 1992; EUMELI 4) show relatively low surface values (31 and 10 pmol l^{-1}, respectively). At site E, the surface bio-Ba content is 169 pmol l^{-1}

but reaches 1961 pmol l^{-1} at 20 m. At sites M and O, concentrations increase with depth eventually leading to a bio-Ba maximum at 250 m (site M). Despite an increase with depth, at site O concentrations in general remain very low and no mesopelagic bio-Ba maximum is discerned. At site E, bio-Ba concentrations first decrease between surface and 100 m but subsequently increase to reach a maximum at 500 m. Deeper in the water column concentrations decrease again, with bio-Ba generally less than 100 pmol l^{-1} at depths > 1000 m. The maxima at sites E and M occur in the same general depth range as the oxygen minima. Oxygen concentrations decrease to 55 μmol kg^{-1} (700 m) at site E and 85 μmol kg^{-1} (375 m) at site M. At site O the oxygen minimum is less pronounced (120 μmol kg^{-1}; 650 m; oxygen data are from Taillez et al., 1994).

A bio-Ba maximum in mesopelagic waters is rather ubiquitous in the ocean (Dehairs et al., 1980, 1992, 1997; Collier and Edmond, 1984) and probably reflects both the magnitude of the export flux and the extent of the heterotrophic oxidation of POM in subsurface and intermediate waters (Dehairs et al., 1997). Oxygen consumption resulting from heterotrophic respiration can be estimated from mesopelagic bio-Ba stocks as shown for the Southern Ocean by Dehairs et al. (1997). These authors observed an empirical relationship between the seasonal build-up of the mesopelagic bio-Ba stock and oxygen consumption:

$$(\text{bio-Ba})_{\max} = 1790\, J_{O_2} + K \tag{4}$$

where: $(\text{bio-Ba})_{\max}$ is the depth-weighted average bio-Ba concentration (pmol l^{-1}) in the mesopelagic zone where the concentration maximum is located. J_{O_2} is the oxygen consumption rate (μmol l^{-1} day^{-1}) and K is a constant corresponding to the bio-Ba background concentration (pmol l^{-1}).

Calculated oxygen consumption rates are then turned into rates of respired carbon, applying an O_2/C Redfield ratio of 175:125 (Broecker et al., 1985). In this case, the mesopelagic zone was taken to extend between 100 and 400 m, in agreement with other observations (e.g., Dehairs et al., 1980; Collier and Edmond, 1984). The K value corresponds to a concentration which remains in the water column as a residual fraction of the bio-Ba signal generated during previous bloom events. Since the NE Atlantic waters are strongly undersaturated with respect to barite (Monnin et al., 1999), we assume that, because of dissolution, the bio-Ba background signal could drop close to zero between successive annual bloom events ($K \cong 0$–20 pmol l^{-1}). From the data in Table 2, the depth-weighted average bio-Ba contents between 100 and 400 m were 243, 318 and 20 pmol l^{-1} at sites E, M and O, respectively. Applying Eq. (4) to these mesopelagic bio-Ba contents and considering the background Ba contents of either 0 or 20 pmol l^{-1}, we calculate the monthly organic carbon respiration rates between 1.0 and 1.1 gC/m^{-2} at site E; between 1.4 and 1.5 gC/m^{-2} at site M and between 0 and 0.1 gC/m^{-2} at site O. Below these, the values will be compared to other independent estimations of the exported POC fluxes.

3.3. Comparison of export production calculated from mesopelagic bio-Ba and from sediment trap bio-Ba fluxes

For the month of June, we compared POC respiration rates estimated from Eq. (4) with ExP values estimated from Eq. (2) noting that the actual year at which trap and suspended material were collected are different (i.e., 1991 for the trap samples and 1992 for the suspended matter). The calculated respiration rates should represent a fraction of the carbon export flux. At site M, Eq. (4) yields 1.4 gC/m^2 remineralized in the mesopelagic layers for June. The flux of POC exiting the mixed surface layer as estimated from the bio-Ba flux at 2500 m is about 2.3 gC/m^2 for June (Table 3). The remineralized fraction represents about 60% of the total ExP flux and thus a flux of about 0.9 gC/m^2/month is left for export to greater depths. Sediment traps recorded POC fluxes for June of 1.5 ± 0.5 gC/m^2 at 1000 and 2500 m (Bory et al., 2000 and Table 1). For site O, about half of the exported POC flux is remineralized at mesopelagic depths (maximum of 0.1 gC/m^2 remineralized vs. 0.2 gC/m^2 exported for June). The 2500-m trap recorded a POC flux of 0.1 ± 0.03 gC/m^2 (from Table 1) for June, in general agreement with these results.

Table 3
Comparison between calculated and measured export production on a monthly timescale (gC/m^2/month)

Moored trap location	Collecting time for deep traps	Calculated ExP.[a] (gC/m^2/month)	Measured POC Fluxes[b] (gC/m^2/month)	(Date for drifting traps)
Mesotrophic site				
M-2500	1–11 Sep 91	0.4	0.2	(7–8 Oct 91)
M-2500	13–23 Jun 91	2.3	3	(13 Jun 92)
			2	(18–19 Jun 92)
Oligotrophic site				
O-2500	9–29 Oct 91	0.08	0.04	(13–18 Oct 91)
O-2500	3–30 Jun 91	0.2	0.2	(23–25 Jun 92)

For both sets of data, collecting time and dates are given.

[a] From Eq. (2), using bio-Ba fluxes collected at 2500 m during the same season.

[b] Measurements performed directly on drifting sediment trap samples collected at 200 m depth (Raimbault and Garcia, pers. commun.).

3.4. Comparison of export production calculated from sediment trap bio-Ba fluxes and export production directly measured with drifting sediment traps

A last comparison can be made between the exported POC fluxes calculated and the drifting sediment trap results obtained at the surface of each site. During both EUMELI cruises 3 and 4 (in October 1991 and June 1992, respectively), drifting sediment traps were deployed at 200 m, for 1 or 2 days. The POC fluxes in these traps provide a direct estimate of carbon export (Raimbault and Garcia, pers. commun.). However, drifting traps provide only a snapshot of surface biological activity and export for a given area. As this activity is highly variable with time and space, drifting trap results have to be compared cautiously with deep sediment trap data that represent yearly or monthly averages and integrate fluxes from a much larger sampling area. To minimize this problem, ExP calculations were made with Eq. (2) and the bio-Ba flux collected over 10 days or 1 month during the same season. We report the POC fluxes calculated from bio-Ba fluxes together with the POC fluxes measured with the drifting traps (Table 3). Our results show that for the same seasons and sites, the order of magnitude of estimated and measured fluxes are consistent. Once again, we do not consider that the drifting trap results give the best average estimates of the biological activity and export, but the agreement between the calculated and measured fluxes lends further support to the use of bio-Ba fluxes to calculate POC fluxes exported from the surface.

4. Conclusions

This work compares results on bio-Ba trapped fluxes and bio-Ba suspended profiles at the mesotrophic and oligotrophic ''EUMELI'' sites. In the 2500-m trapped material, the POC/bio-Ba ratio is constant over time at the oligotrophic site and its value is slightly larger than that predicted in the literature (François et al., 1995). At the mesotrophic site, the POC/bio-Ba values are much larger than the predicted value and vary strongly with time. Using bio-Ba data and the empirical relationship proposed by François et al. (1995), we estimate the flux of carbon exported annually at 200 m (ExP) at both sites. At site O, the calculated value is in good agreement with: (i) the oligotrophic nature of this site, (ii) the ExP deduced from the measured POC fluxes and the Sarnthein et al. (1988) relationship and (iii) the direct measurements from drifting sediment traps. At site M, the ExP estimated from trapped bio-Ba fluxes is consistent with the mesotrophic characteristics of the site and drifting trap data, but is not in agreement with ExP calculated from the measured POC as well as with the total primary production of this site. Large POC/bio-Ba ratios and high ExP values deduced from POC fluxes at site M could be related to the advection of refractory carbon in spring from the shelf within highly productive filaments coming from upwelling cells. It could also reflect some trophic conditions which prevent barite precipitation and/or the use of Sarnthein et al. (1988) relationships.

Suspended matter profiles suggest that bio-Ba is forming in POM (including, possibly, living plankton), which is correlated with the chl-a maximum. The comparison between Ba and Mn and REE enrichment depths emphasizes that bio-Ba and these trace element distributions are not controlled by the same processes. Mesopelagic bio-Ba maxima are used to estimate the fraction of ExP which is remineralized at these depths, following the assumptions and transfer function of Dehairs et al. (1997). We observe larger mesopelagic bio-Ba maxima, yielding larger carbon remineralization estimates when the surface productivity is higher.

The good agreement between the calculated ExP (using the data of François et al.,1995) and the drifting trap fluxes supports the use of bio-Ba flux time series to calculate POC fluxes exported from the surface of the present-day ocean.

All these results argue in favor of the use of bio-Barite as a tracer of ExP in the present-day ocean, although the established empirical relationships cannot be applied universally and have to be checked and tested carefully for any given location. In addition, applying the bio-Ba proxy for paleo-productivity requires to assess if the same relationships hold for bio-Ba in the sediment, which will be our next step.

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