**Paleoproductivity changes and upwelling
variability in the *Galicia Mud Patch* during the
last 5000 years: geochemical and microfloral
evidence**

Bernárdez, P.^{1,2,*}, González-Álvarez, R.², Francés, G.², Prego, R.¹,
Bárcena, M.A.³, Romero, O.E.⁴

¹ Grupo de Biogeoquímica Marina, Instituto de Investigaciones Marinas (IIM-CSIC).C/
Eduardo Cabello 6, 36208 Vigo, Spain

² Departamento de Geociencias Marinas y Ordenación del Territorio, Facultad de
Ciencias del Mar, Campus Lagoas-Marcosende s/n. Universidad de Vigo, 36310, Vigo,
Spain

³ Departamento de Geología, Facultad de Ciencias, Universidad de Salamanca, 37008,
Salamanca, Spain

⁴ Instituto Andaluz de Ciencias de la Tierra (CSIC-Universidad de Granada), Granada,
Spain

*Corresponding author. Grupo de Biogeoquímica Marina, Instituto de Investigaciones
Marinas (IIM-CSIC). C/ Eduardo Cabello 6, 36208 Vigo, Spain.

Tel.: +34 986 231930; fax: +34 986292762.

E-mail: pbernard@iim.csic.es

24 **Abstract.** The Holocene paleoclimatic history of the Galician continental shelf
25 (NW Spain) has been investigated through the analyses of diatom remains, as
26 well as geochemical and sedimentological parameters. Diatoms, other siliceous
27 compounds, and biogenic silica (BSi) and metals content were analysed from a
28 gravity core recovered from the *Galicia Mud Patch*, NW Iberian Peninsula,
29 covering the last 5000 years. Results were integrated together in a multiproxy
30 study in order to determine the climatic and the oceanographic influence on the
31 paleoproductivity conditions that have occurred in the region.

32

33 Downcore changes in diatom assemblages composition and abundance reflect
34 changes in diatom production related to long/short-term variations in climate,
35 regional oceanography, upwelling strength, and river influx off the coast of Galicia
36 and Portugal. As displayed by the diatom taxa record, paleoclimatic variability
37 was related to different atmospheric conditions, particularly the relative strengths
38 and position of the Azores High and Iceland Low pressure cells. Metals and
39 microflora fluctuations are interpreted as changes in the riverine influence and
40 upwelling intensity paced by oceanographic, atmospheric and climatic changes.

41 Lack of diatoms between 4700–3300 and 1800–1200 cal. yr BP could be linked
42 to early diagenetic processes taking place in the sediment after burial.

43

44 All tracers considered, biogenic barium (Ba_{excess}), metals and diatom
45 assemblages, show consistent profiles displaying a general increase of the
46 marine productivity for the last 1200 cal. yr BP. River run-off due to high
47 precipitation conditions in the catchment area is an additional important source of
48 nutrients to the surface waters promoting diatom production. In this way,

49 microflora indicates that during 800 and 500 cal. yr BP high production is
50 triggered by influx of river-derived nutrients under conditions of SW winds and
51 storms due to a NAO negative-like phase. The biosiliceous and geochemical
52 signatures of sediments from the last 500 cal. yr BP indicate conditions of
53 enhanced upwelling and increased phytoplanktonic production associated to the
54 intensification of northerly winds. Upwelling strengthening in this area, attributed
55 to recent global warming, could provoke an increase in phytoplankton biomass
56 and the consequent biological, climatological and socioeconomical impacts.

57

58 The imprint of the anthropic activities has been recorded by the increasing Pb/Al
59 ratios for the last 400 cal. yr BP. The oceanographic changes recorded in
60 Galician shelf are correlative with other marine and terrestrial paleoenvironmental
61 records in the NW Iberian Peninsula.

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65 **Keywords:** metals, diatom assemblages, Late Holocene, paleoproductivity, NW
66 Iberian Peninsula

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68 1. BACKGROUND, STUDY SITE AND OBJECTIVES

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71 Paleoenvironmental reconstruction allows an understanding of the processes that
72 drive climate and ocean changes and affect biological systems. In recent years,
73 increasing interest has been shown in the study of Holocene climate variations.
74 The Galician-Portuguese area is, together with the Peruvian, Californian, and
75 northwestern African systems, one of the major coastal upwelling regions of the
76 world ocean (Wooster *et al.*, 1976). The position of both pressure systems acting,
77 the Iceland Low and the Azores High, determines the intensity and direction of
78 the coastal winds leading to a marked seasonal cycle and, therefore, a
79 seasonally-controlled hydrography (Wooster *et al.*, 1976). Moreover, on a
80 millennial-centennial scale, atmospheric conditions, that is the position, strength
81 and the atmospheric sea level pressure difference between both pressure
82 systems (NAO index), control the patterns of precipitation and upwelling in the
83 area (Figure 1).

84

85 Upwelling events mainly occur from April to October (Fraga, 1981), when the
86 Azores anticyclone moves northwards and the N–NNE winds along the coast
87 exert a southwards surface stress that causes Ekman transport offshore (Blanton
88 *et al.*, 1987; Álvarez-Salgado *et al.*, 1993). Upwelling forces the nutrient-rich
89 Eastern North Atlantic Central Water (ENACW) towards the coast during most of
90 spring and summer (Fraga, 1981). In contrast, in winter the Iceland Low
91 strengthens and centers over the northern North Atlantic. As a result,
92 downwelling-favourable southerly winds prevail along the coast (Wooster *et al.*,

1976; Fraga, 1981) and lead to the development of the downwelling regime (Vitorino *et al.*, 2002a,b) and a persistent poleward flow (*Iberian Poleward Current*, IPC) along the continental slope (Peliz *et al.*, 2003). Moreover, the *Western Iberian Buoyant Plume* (WIBP), a fresher surface water lens flowing northwards, is also well developed during this season (Peliz *et al.*, 2002) due to high river runoff related to high rainfall. In this way, the Galician-Portuguese region off the Iberian Peninsula is a suitable area to assess climatic conditions and productivity implications.

101

These hydrodynamic and oceanographic features affect the primary production of this region. Primary production in these upwelling areas is high due to the influx of nutrients in spring and summer to the surface waters controlling phytoplankton activity, and especially that of diatoms, which increases drastically (Abrantes and Moita, 1999). However, during winter, supply of nutrients may come from the riverine runoff of the Atlantic Rivers draining hinterland. Diatom assemblages have been used as qualitative indicators of primary production, changes in paleo-upwelling intensity, as well as other environmental variables such as temperature and salinity. In the studied area, different diatom groups are linked with the various surface and subsurface water masses, freshwater inputs and hydrological fronts generated by the upwelling processes (Abrantes and Moita, 1999).

113

Depositional systems of continental shelves are natural archives of data on changes in past environmental conditions. A high number of paleoenvironmental tracers can be extracted from their sediments. The sediment cover of the narrow shelf west of Galicia is composed mostly by thin Pleistocene-Holocene units

118 (López-Jamar *et al.*, 1992). The morphology and extent of this shelf sedimentary
119 environment is controlled by storm surges, supply of sediments, currents and a
120 structural control (Jouanneau *et al.*, 2002; Dias *et al.*, 2002a,b). The present sea-
121 floor surface sediments are dominantly silty clay with some areas of muddy sand
122 sediments and gravels at the ría mouths near the coast (Dias *et al.*, 2002;
123 Jouanneau *et al.*, 2002). Large values of suspended fine sediment to the shelf
124 are supplied by the main river systems (Miño-Douro), and other small rivers and
125 streams along the coast, forming the *Galicia Mud Patch*. Therefore,
126 sedimentation on this margin is highly influenced by terrigenous inputs from rivers
127 draining the hinterland. The nature of sediments that accumulate in the Galician
128 continental shelf results from the combination of several main mechanisms as
129 summarized: (i) the supply of terrestrial material from the main river-systems
130 draining the area; (ii) the dispersal of the material due to the acting of current
131 systems and hydrographic conditions; (iii) the rate of primary production in the
132 surface waters and the subsequent accumulation of biogenic material (organic,
133 calcareous and siliceous) in the sediment; (iv) and the dissolution processes
134 throughout the water column, at the sediment-water interface, and within the
135 sediment.

136

137 In this way, Galician shelf sediments contain geochemical, faunal and floral
138 tracers of terrestrial input, primary productivity, physico-chemical conditions of the
139 surface waters and terrestrial vegetation (González-Álvarez and Francés, 2005;
140 González-Álvarez *et al.*, 2005; Martins *et al.*, 2005; Martins *et al.*, 2006a,b;
141 Martins *et al.*, 2007) which show that this area is highly sensitive to climatic
142 fluctuations. Little information about the history of the marine paleoproductivity

143 and paleoclimatology exists in this area, being some studies restricted to the Rías
144 Baixas (Diz *et al.*, 2002; Desprat *et al.*, 2003; Álvarez *et al.*, 2005; Muñoz-Sobrino
145 *et al.*, 2007). The understanding of upwelling variability and the ecological
146 consequences during the late Holocene remains poorly studied.

147

148 In this paper we present a 4700-yr record of the climatic changes in the western
149 Galician continental shelf. This sediment record provides the opportunity for high-
150 resolution reconstruction of past marine environmental conditions in this
151 temperate zone. We analysed the core sediment samples on the basis of a
152 multivariable study based on sedimentological data, bulk sediment composition,
153 biogenic silica content, diatoms and concentration of several metals.

154

155 The general objectives of this work are to identify the variations in siliceous
156 production and to assess the intensity of upwelling and productivity off Galician
157 coast during the last 5000 years. We also investigate how oceanographic and
158 biological processes (e.g., upwelling, surface water dynamics, nutrients input,
159 primary productivity) in the euphotic zone control the production, export, and
160 burial of some paleoenvironmental proxies (e.g., the biosiliceous compounds and
161 metals). We also examine the production recording potential of the diatom
162 assemblages in the context of seasonal changes of the biological productivity
163 associated with the upwelling cycles. The results obtained are discussed in
164 relation to previous research in the study area. We focus on the timing and the
165 magnitude of the main production events during the Late Holocene and their
166 relation to global climatic events and regional correlations.

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169 **2. DATA ACQUISITION AND METHODS**

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172 **2.1. Core location and sampling**

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175 The material used in this work was obtained from a 260 cm-length gravity core
176 SMP02-3 (42°02.207'N, 9°02.363'W), retrieved from a water depth of 121 m in
177 the core of the *Galicia Mud Patch* offshore Galician coast during a cruise onboard
178 R/V Mytilus in October 2002 (Figure 1).

179

180 Core was stored at 4°C until it was longitudinally splitted in two equal parts (Ø 9
181 cm). The core was visually described, logged, photographed, X-rayed and sub-
182 sampled at constant intervals. The working-halves of the gravity core were cut
183 into 1-cm thick slices. Each slice was then separated into subsamples and stored
184 in plastic bags for different analyses. One half was studied with regard to various
185 sedimentological studies and the other half was used for micropaleontological
186 fossils identification and biosiliceous material counts, bulk component analyses
187 and metal determinations. Samples for siliceous microfossil analysis were
188 collected at the same depth intervals as sediment subsamples used for
189 geochemical determinations.

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191

192 **2.2. Procedures and analyses**

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195 **Chronological control**

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198 AMS ^{14}C dating of foraminiferal tests (~10 mg carbonate) recovered from several
199 levels of the core were performed at the Geochron Laboratories (Massachusetts,
200 USA) and at the AMS facility of the Aarhus University (Denmark) (Figure 2).

201

202 Ages are given in calibrated years before present (cal. yr BP) to facilitate
203 comparison of the present results with other records of different origins. The raw
204 ^{14}C ages were corrected from the global reservoir effect (apparent surface-water
205 age $\delta R=376\pm 46$) and, therefore reported as cal. yr BP with the Calib 5.0.1
206 software (Stuiver and Reimer, 1993 modified version 2002;
207 <http://calib.qub.ac.uk/calib/>) using the Marine04 calibration dataset for
208 radiocarbon ages younger than 26,000 ^{14}C years (Hughen *et al.*, 2004). A
209 calibrated age range within 2σ confidence limits (95% probability) was obtained
210 (Figure 2). The dates used in figures and discussion represent the intercept of
211 radiocarbon age with the calibration curve. No local-reservoir effect was applied
212 ($\Delta R=0$) as shown by Abrantes *et al.* (2005).

213

214

215 **Bulk biogenic component analyses**

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217

218 Sediment composition was analyzed on bulk sediment and ground subsamples.
219 One portion of each 1-cm slice was used for the bulk geochemical analysis with a
220 sampling interval of 6 cm. CaCO_3 , organic carbon and nitrogen are standard
221 parameters measured on cores taken for marine studies. These tracers were
222 measured on LECO carbon element analyzers. Total carbon (TC) content and
223 total nitrogen (TN) were measured with the CN-2000 analyzer using samples that
224 had not been ashed prior to analysis. The total inorganic carbon (TIC) was
225 obtained by acid digestion of a portion of the sediment in a LECO CC-100
226 connected to the CN analyser. Organic carbon (TOC) was calculated as TC
227 minus TIC. Calcium carbonate (CaCO_3) concentration was calculated multiplying
228 the total inorganic carbon (TIC) content by the factor 8.33 supposing that all the
229 inorganic carbon is calcium carbonate.

230

231 The extraction of amorphous silica particles was made following a soda-
232 hydrolysis technique based on Mortlock and Froelich (1989). Standard deviation
233 for this method is ± 0.2 , indicating good reproducibility (Bernárdez et al., 2005).
234 The resulting extract was determined for the dissolved silicate concentration on
235 the basis of molybdate-blue spectrophotometry at 812 nm (Hansen and Grashoff,
236 1983) by means of a continuous flow analyser AutoAnalyser Technicon II. Data
237 are expressed as weight of Si (e.g., biogenic silicon) and opal content was
238 calculated as $2.14 \times \text{Si}$. This conversion does not account for the bound-water
239 content (2–15% depending on the type and age of the material; Mortlock and
240 Froelich, 1989) of the opal, which is difficult to predict.

241

242 All the results are given in weight percent of dry, salt-free sediment. The
243 proportion of non-organic, non-opaline and non-calcareous constituents is
244 regarded as the siliciclastic or terrigenous sediment fraction and it is calculated
245 as the residual from 100% of the calcium carbonate, total nitrogen and organic
246 carbon and opal sum.

247

248

249 **Analytical procedures for metal determinations: Ba, Cu, Mn, Pb, Al, Fe**

250

251

252 For chemical analyses of the metal contents, the dry bulk and homogenised
253 samples were subjected to total acid digestion. Approximately 40–50 mg of
254 sediment was weighted directly into Teflon® pressure vessels. The samples
255 underwent an acid digestion using a mixture of concentrated HNO₃, and HF using
256 6 ml HNO₃ (65%) and 2 ml HF (48%) in a Milestone MLS 1200 Mega microwave
257 oven following the EPA 3052 guideline (EPA, 1996) for siliceous-type matrices.
258 Handling and analysis of samples were carried out in a clean laboratory (ISO
259 class 7-8) and plastic labware employed for sampling, storage and sample
260 treatment was previously acid-cleaned (HNO₃ 10%) for at least 48 h and washed
261 throughout with Milli-Q water.

262

263 Fe, Al, Mn and Ba were determined using flame atomic absorption spectrometry
264 (FAAS) technique with a Varian 220FS apparatus. The concentrations of Cu and
265 Pb were measured by means of electrothermal atomic absorption spectrometry
266 (GF-AAS) using a Varian 220 apparatus equipped with Zeeman background

267 correction. The accuracy of the analytical procedure was tested by repeated
268 analyses of certified reference materials (CRMs), PACS-2 from the National
269 Research Council of Canada (Table 1), excepting for Ba. In this case, accuracy
270 was determined analysing a control sample with a known concentration of Ba and
271 checking the reproducibility. RSD for Ba is 5.72%. The results obtained agree
272 well with the certified values. Relative Standard Deviations (RSDs) were typically
273 lower than 10% excepting Cu (14.8%) (Table 1).

274

275 The excess/biogenic Ba concentration (Ba_{excess} or Ba_{bio}) was calculated following
276 the equation (1) (normative method). Ba/Al aluminosilicate ratio is required to
277 assess the biogenic barium, in particular in sediments with high detrital
278 background (Reitz *et al.*, 2004). This ratio is presumed to be representative of the
279 terrigenous input and serves as a correction factor for subtracting Ba associated
280 to terrigenous inputs (Gingele and Dahmke, 1994). After detrital barium is
281 accounted for, the remaining one is attributed to biogenic barite and linked to the
282 productivity in surface waters (Gingele and Dahmke, 1994; Dymond and Collier,
283 1996; Gingele *et al.*, 1999).

284

285 A normative approach on conservative elements like Al is commonly used to
286 assess the detrital barium background:

287

288
$$Ba_{\text{excess}} = Ba_{\text{total}} - Ba_{\text{terr}} = Ba_{\text{total}} - (Al \times Ba / Al_{\text{det}}) \quad (1)$$

289

290 Ba should be affected by early diagenesis (McManus *et al.*, 1994; McManus *et*
291 *al.*, 1998; Paytan *et al.*, 1996; Schenau *et al.*, 2001), but in this work we will

292 designate the biogenic barium as barium excess (Ba_{excess}) since we consider that
293 the diagenetic remobilization is discarded and the terrigenous component was
294 excluded by normalization to Al (Schenau *et al.*, 2001). Ba/Al_{det} ratio can be
295 estimated independently and is constant in time and source. Due to the
296 impossibility of determining a regional ratio, we simply use the global average
297 crustal ratio (0.0037, Reitz *et al.*, 2004; Table 2).

298

299

300 **Siliceous microfossils preparation: Diatom counting and relative species**
301 **percentages**

302

303

304 The sediment samples for diatom identification were prepared by a standard
305 method devised by Abrantes (1988). Suspension volume and volume used to
306 mount the glass slides were known. A 500 μL of slurry (after mixing the solution
307 for homogenization) across a 18×18 mm circular cover slips, placed in a circular
308 Petri dish ($\varnothing$ 47 mm) was pipetting, and they were left to dry at room
309 temperature. When evaporation is complete and cover slips are dry, they were
310 removed and fixed on onto permanently labelled smear slides using the high
311 refractive mounting medium Permount™ (Fisher Scientific).

312

313 Light microscopes (LEICA DMLB and Zeiss) with phase contrast optics and a
314 magnification up to 1000× was used for quantification and diatom identification.
315 Several non-overlapping transverses across the cover slips were examined
316 depending on the diatom concentration. For each sample, at least 300 diatom

317 valves were counted to ensure proper assessment of diatom abundance and
318 composition. Although 300 valves is generally regarded as the optimum number
319 needed for quantitative interpretations, the scarcity of preserved diatoms within
320 the sedimentary record in several levels of the core prevented this in all but a few
321 samples. However, in micropaleontological studies based on the interpretation of
322 the proportional distribution of the dominant taxa (>3%) counts of around 100
323 specimens are sufficient (Fatela and Taborda, 2002). The counting procedure
324 and definition of diatom counts and total number estimates followed those of
325 Schrader and Gersonde (1978). Specimens representing more than one-half of
326 the valve were counted as one and for pennate diatoms, such as *Thalassionema*
327 spp., each pole was counted as one-half specimen. Remaining fragments were
328 not counted as one specimen. Diatoms were identified to the lowest taxonomic
329 level possible, based principally on the keys of Hustedt (1930), Hustedt (1959),
330 Hartley (1996) Hasle and Syvertsen (1996) and Witkowski *et al.* (2000). Each
331 individual was identified to the species level, otherwise they were assigned to a
332 genus on the basis of Round *et al.* (1990). Data concerning the ecology of the
333 diatom taxa were compiled from previous references in addition to several
334 specific bibliographies, and, species were divided into freshwater, benthic and
335 marine planktonic species.

336

337 Number of diatom fragments, silicoflagellates, sponge spicules, phytoliths,
338 crysophycean cysts and radiolaria per gram of sediment was also assessed, as
339 well as palynomorphs abundance (data in Bernárdez *et al.*, in press). For
340 evaluation of the state of preservation of diatom valves, the preservation index
341 defined by Abrantes (1988) was calculated.

342

343

344 **3. PALEOENVIRONMENTAL PROXIES**

345

346

347 **3.1. Chronostratigraphical features**

348

349

350 Lithological characteristics of the core and the age model based on the ^{14}C AMS
351 planktonic foraminiferal dates are shown in Figure 2. The record spans from 4700
352 cal. yr BP to present, assuming that sample 0–1 cm corresponds to 0 cal. yr BP.
353 Sedimentation rate was quite variable over the age range studied, ranging
354 between 0.12 and 1.39 mm yr⁻¹ (Figure 2), but it sharply increases during the last
355 1200 years (0–150 cm). This abrupt increase coincides with a change in
356 sedimentary units (Figure 2).

357

358

359 **3.2. Sediment composition**

360

361

362 **Bulk biogenic components**

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365 Sediments are predominately siliciclastic with the terrigenous fraction clearly
366 dominating. Biogenic fraction represents a low proportion, consisting of

367 calcareous remains of gastropods, bivalves and foraminifers, and siliceous
368 microfossils. Visual core description, colour variation, and X-ray data do not show
369 either significant evidences of sediment disturbance, only some bioturbation at
370 specific levels.

371

372 Concentrations of biogenic silica (BSi) reveal consistently high values at the
373 bottom of the core compared to those obtained in the upper muddy sequence.
374 Opal content falls in the range between 1.18 and 2.07 wt.%, accounting on mean
375 for the 1.61 dry weight percent of the core sediment. Biogenic silica, as well as
376 TOC constitutes a small source of biogenic components to the sediments, being
377 CaCO_3 the major component of the marine derived biogenic sediments. TOC and
378 BSi show a similar profile, displaying a strong peak around 700 cal. yr BP (Table
379 3).

380

381

382 **Metals content**

383

384

385 The major components of the core sediments are Si, which represents 227 mg g^{-1}
386 as a mean value ($85\text{--}364 \text{ mg g}^{-1}$), and Al ($33\text{--}119 \text{ mg g}^{-1}$, averaging 71 mg g^{-1})
387 (Bernárdez *et al.*, in press). Low Al values are found between 4700 and 4000 cal.
388 yr BP. An increasing trend is recorded towards the top of the core peaking
389 around 2000 cal. yr BP. Maximum values occur between 800 to 500 cal. yr BP.

390

391 Fe (ranging from 18 to 49 mg g⁻¹) is also an important contributor to the sediment.
392 Good linear correlation between Fe and Al (Bernárdez *et al.*, press) implies that
393 Fe/Al downcore variability is reduced, excepting for a small peak in the lower Unit
394 1 around 4200–3900 cal. yr BP (Figure 3).

395

396 Mn content shows high downcore variability (0.09–0.48 mg g⁻¹). Higher amounts
397 are found at 790–524 cal. yr BP and around 2000 cal. yr BP (Figure 3). Mn/Al
398 ratio displays relatively stable values between 0.004 and 0.005, excepting at the
399 bottom of the core where ratios oscillate around 0.003. As observed for Fe/Al
400 ratio, Mn/Al ratio shows a progressive decrease from 1200 cal. yr BP up to 200
401 cal. yr BP (Figure 3).

402

403 Pb is one of the minor components of the core sediments. This metal is detected
404 in the range of 2–39 µg g⁻¹. Pb displays very low values in the lower part of the
405 core, increasing progressively up to 3300 cal. yr BP. From 1200 cal. yr BP to
406 present, Pb content progressively increases up to reach the maximum value in
407 recent times (Figure 3). Pb/Al ratio follows the same trend to that found for Pb
408 content in the lower part of the core, and around 3330 cal. yr BP values stabilize
409 around 0.0003. From 400 cal. yr BP to present this ratio progressively increases
410 reaching the maximum value at present (Figure 3).

411

412 Cu levels in the core vary from 3 to 27 µg g⁻¹, peaking around 1800–1990 cal. yr
413 BP and 790–520 cal. yr BP. From 1200 to 800 cal. yr BP, very low and stable
414 values are found (Figure 3). Cu/Al distribution presents low variability. Only a

415 small peak on the Cu/Al ratio is recorded around 2000 cal. yr BP and also at the
416 top of the core (Figure 3).
417
418 Barium in marine sediments occurs as biogenic barite or is associated with
419 aluminosilicates. The Ba/Al detrital ratio is the crucial factor in the Ba_{bio} calculated
420 from Ba_{total} . We have decided to use the most recent global average crustal ratio
421 (0.0037, Reitz *et al.*, 2004, Table 2). The amount of biogenic barium in the
422 sediment ranges from 3.9 ($mg\ g^{-1}$) to almost nothing. Ba_{excess} exhibits a distinct
423 profile, with two major peaks around 1800 cal. yr BP and 834–524 cal. yr BP
424 (Table 2, Figure 4). In fact, values increase progressively from the bottom of the
425 core towards the top. Total Ba content follows the same trend, although values
426 are slightly higher, between 0.12 and 0.44 $mg\ g^{-1}$ (Table 2, Figure 3). Total Ba
427 versus Al follows the same trend to that found for total barium from the bottom of
428 the core up to 1200 cal. yr BP. During the last 1200 years Ba/Al ratio slightly
429 increases, reaching the highest values during last 200 years (Figure 3).

430

431

432 **Diatoms**

433

434

435 The frequency of the major species amounts to mean around 80% of the total
436 species percent throughout the core, including mainly species of the genera
437 *Chaetoceros*, *Leptocylindrus*, *Paralia*, and *Thalassionema*. *Chaetoceros* resting
438 spores (R.S.) (mostly *Chaetoceros affinis*), are the main component of the diatom
439 assemblage, ranging from 20 up to 70% for the last 500 cal. yr BP. Their

percentage progressively increases from the bottom to the top of the core.

Chaetoceros cinctus R.S. has the same profile as found for *C. affinis* R.S. but relative percentages are very low (0–3%). *Chaetoceros diadema* R.S. represents also a high contribution of the total *Chaetoceros* spores. Downcore pattern of this species shows high abundances (~6%) around 1000–700 cal. yr BP (Figure 4).

Leptocylindrus danicus R.S. represents the 8–30% of the assemblage. Higher percentages around 30% are found at 3300, 2200 and 1200 cal. yr BP. From this age to the top of the record values become stable (around 18%) (Figure 4).

Paralia sulcata relative abundance varies from 5 to 43%, although a high amount of this species is observed at around 1200–960 cal yr BP and around 400 cal. yr BP. The degree of preservation of the assemblage calculated from the margin dissolution of this species follows the same pattern to that found for *P. sulcata*. Higher abundances are found when preservation is poor (Figure 4).

Thalassionema nitzschioides relative abundance varies between 2–6%. Higher values (averaging 11.7%) are found from 3300 to 2200 cal. yr BP. A strong peak, with values up to 10% between 878–524 cal. yr BP, is also recorded (Figure 4).

456

457

458 **4. DISCUSSION**

459

460

Knowledge on the seasonal diatom succession and its record in the sediments of the Galician shelf is limited. There are only a few studies regarding diatom water column assemblages of the Portuguese-Galician shelf (Bode and Varela, 1998; Abrantes and Moita, 1999; Bode *et al.*, 2002). Interpretation of the diatom

assemblages in the core is mainly based on the ecological characteristics of the species described in Abrantes (1988) and Bao *et al.* (1997).

From the study of the record archived in core SMP02-3, different sediment conditions are inferred for the last 5000 years. Two periods barren of diatoms have been identified (4700–3300 and 1700–1200 cal. yr BP), intercalated between periods where diatoms are present (Figure 4). Diatom barren sequences in the Galician shelf record may reflect lower production, combined with more intense dissolution of diatom frustules. We suggest that the low diatom abundances observed in some samples result from severe dissolution, indicating a diagenetic control. Fe and Mn contents are indicative of early stages of diagenesis (Froelich, 1979) especially in organic matter-rich environments. Normalization of these chemical elements to Al (Hanson *et al.*, 1993) reports the separation of metal concentrations into natural (marine-derived and terrestrial-derived) and other fractions (e.g. anthropogenic). In this way, variations in the Fe/Al and Mn/Al ratios in our record point to different reducing/oxidizing conditions within the sediment. Both periods barren of diatoms (Figure 3) record the highest values of the Fe/Al and Mn/Al ratios, therefore they are representative an oxic environment promoted by coarser sediments, which favours the biogenic silica dissolution. Profile of relative abundance of *P. sulcata* shows that even heavily silicified forms disappear from the sedimentary record (Figure 4). This species has been related to enhanced upwelling conditions (Abrantes, 1988; Abrantes, 1991; Bárcena and Abrantes, 1998) and linked to vertically-mixed water column and high surface water salinity (McQuoid and Nordberd, 2003 and references therein). In our record, higher abundances of *P. sulcata* coincide with

490 high values of the preservation index. Therefore, as reported by Bao *et al.* (1997)
491 in the Galician shelf surface sediments, abundance of this species is mostly
492 related to preservation conditions.

493

494 On the contrary, the anoxic-suboxic conditions which lead to the reduction of Mn
495 and Fe are indicated by low values of Fe/Al and Mn/Al ratios. The remobilization
496 of Fe and Mn and the increase of the reduced species in solution occur when
497 dissolved oxygen is consumed in pore-waters after organic matter
498 remineralization. In our record, during the last 1200 cal. yr BP sediment grain size
499 is finer and a high influx of organic matter occurs (Table 3), therefore, anoxic
500 conditions in the sediment are well established. Most of the diatom assemblages
501 remain in this suboxic-anoxic environment, getting preserved. Similar
502 geochemical patterns have been already observed in a nearby core (Martins *et*
503 *al.*, 2006b; Martins *et al.*, 2007), pointing to depressed levels of oxygen and early
504 diagenetic changes in muddy sediments between 2200–1200 cal. yr BP and
505 500–0 cal. yr BP. However, imprecision in their age model impedes the
506 correlation of both records.

507

508 Despite the preservation effects on the diatom assemblage, we consider that
509 downcore variations in diatom abundance are the result of changes in primary
510 production. Clear trends are observed when looking at the individual species
511 data.

512

513 The high input of allocthonous diatoms (benthic and freshwater groups) at 800–
514 500 cal. yr BP to the shelf leads to the maximum abundance of the diatom

515 valves. A strong peak in the relative percentage of *T. nitzschioides* and *C.*
 516 *diadema* occurs at this age. *T. nitzschioides* responds to a weakened upwelling
 517 and/or high fluvial input discharge (Pokras and Molfino, 1986; van Iperen *et al.*,
 518 1987; Abrantes, 1988; Bao *et al.*, 1997). In this way, *T. nitzschioides* is present in
 519 significant percentages where runoff influence is detected by the presence of
 520 freshwater, benthic species and other riverine input tracers (Bernárdez *et al.*, in
 521 press). The downcore profile of *C. diadema* also follows the same pattern,
 522 reaching the highest abundances (~6%) at 1000–700 cal. yr BP (Figure 4).
 523 Although ecological preferences of *C. diadema* R.S. are not extensively
 524 investigated, a few studies report the appearance of this species during spring
 525 blooms (Tiselius and Kuylenstierna, 1996; McQuoid and Nordberg, 2006) and
 526 high nutrient concentrations (Rebolledo *et al.*, 2005). In our case, the clear
 527 relationship between the percentage of the freshwater assemblage and *C.*
 528 *diadema* R.S. suggests high influx of river-derived nutrients to the shelf.
 529
 530 It has been assumed that upwelling is the main mechanism for enhancing
 531 primary production off Galicia. However, influence of river runoff during winter
 532 has not been properly assessed. Prego and Bao (1997) indicated that upwelling
 533 is the main forcing controlling the silicate concentrations in the Galician
 534 continental waters during summer, but they also pointed to the possible influence
 535 on productivity of silicate derived from freshwater inputs during winter. deCastro
 536 *et al.* (2006) also suggested that high freshwater discharge fertilizing the area can
 537 induce a phytoplankton bloom in the Galician shelf. This is in apparent
 538 contradiction to Bode *et al.* (2002), who have suggested that relatively low
 539 numbers of diatoms in Galician waters occur under high runoff.

540

541 Ba_{excess} is commonly used as a tool for the reconstruction of paleoproductivity
542 although some authors have discussed its validity (e.g., Anderson and Winckler
543 2005). In core SMP02-3, high correlation between Ba and Al in bulk sediment
544 reveals that the barium comes from several different sources and some of the
545 barium is associated with terrigenous aluminosilicate materials. The non-
546 terrigenous barium follows the same profile to that found for other
547 paleoproductivity indicators, such as TOC and opal (Table 3, Figure 4). Maximum
548 values of Ba_{excess} (Figure 4) coincide with strong humid periods reported by
549 Bernárdez *et al.* (in press): around 2000 cal. yr BP during the Roman Warm
550 Period (RWP) and at 800–500 cal. yr BP. During the RWP we can not evaluate
551 the primary production and the oceanographic conditions since it is one of the
552 periods barren of diatoms. However, we can conclude that at 800–500 cal. yr BP
553 primary production is enhanced.

554

555 Downcore values of total Cu are within the range reported for the recent
556 sediments deposited in the western Galician shelf (Araújo *et al.*, 2002; Corredeira
557 *et al.*, 2005). Two strong peaks are observed around 2000 cal. yr BP and at 800–
558 500 cal. yr BP paralleling the pattern found for total Ba (Figure 3). These Cu
559 peaks are related to strong input of detrital materials from continental soils and
560 weathered rocks, since when normalising to Al values Cu/Al profile becomes
561 stable, except for maximum values found at 2000 cal. yr BP. Cu is an essential
562 micronutrient for phytoplankton being part of the biogeochemical cycles (Sunda
563 *et al.*, 1981). A strong biological uptake for Cu is observed in the Galician shelf
564 waters (Santos-Echeandía *et al.*, 2005) since Cu concentrations in the

565 suspended particulate matter are in the range of dissolved values. Peak in Cu/Al
 566 around 2000 cal. yr BP and in recent sediments could be linked to more
 567 biological activity and diatom productivity in surface waters that can raise its
 568 content in the sediments.
 569
 570 *Chaetoceros* R.S. are heavily silicified and characteristic of turbulent waters rich
 571 in nutrients of upwelling areas (Abrantes, 1988; Pitcher, 1990; Abrantes and
 572 Moita, 1999; Romero and Hebbeln, 2003). Under present-day conditions in the
 573 western Iberian shelf, *Chaetoceros* spp. proliferate in spring and summer when
 574 upwelling is well developed (Abrantes and Moita, 1999). As one of the main
 575 contributor to diatom community in our record (Figure 4), it is suggested that the
 576 presence of these spores is linked to more frequent upwelling events and high
 577 nutrient input. There are important amounts of different spore morphotypes of the
 578 diatom genus *Chaetoceros*. One of these high nutrient input indicators is *C.*
 579 *cinctus*. It is absent from the record, but appears during the last 500 cal. yr BP,
 580 reflecting the upwelling intensification. *C. affinis* presents the same pattern, a
 581 species also related to the coastal upwelling phenomena off Chile (Romero and
 582 Hebbeln, 2003).
 583
 584 Ecologically, *L. danicus* blooming is related to nutrient depletion, upwelling
 585 relaxation and the breakage of summer stratification after the mixing period
 586 (Varela *et al.*, 2001; Bárcena *et al.*, 2001; Bárcena *et al.*, 2004). A strong
 587 decrease in the abundance of *L. danicus* is recorded at recent times, when high
 588 nutrients and enhanced productivity by upwelling intensification are recorded.
 589 Ba_{excess} also exhibits high values (~2.5 mg g⁻¹) during the last 500 cal. yr BP

590 (Figure 4). However, these values do not reach those found during the humid
591 period. Therefore we can conclude that primary productivity at 800–500 cal. yr
592 BP is triggered by river-derived nutrients, which could be supplied in higher
593 amounts than those derived from upwelled waters.

594

595 The intensification of the upwelling in the Galician-Portuguese margin during
596 approximately the last 1000 cal. yr BP is a well known fact (Soares, 1993; Diz *et*
597 *al.*, 2002; González-Álvarez *et al.*, 2005; Lebreiro *et al.*, 2006; Martins *et al.*,
598 2006a; Soares and Dias, 2006; Martins *et al.*, 2007; Muñoz-Sobrino *et al.*, 2007).
599 Meeker and Mayewski (2002) have also pointed that at ca.1400 AD the Iceland
600 Low was deeper, and cool and dry conditions were recorded at these latitudes.
601 Moreover, Mayewski *et al.*, (2004) indicate that from 600 cal. yr BP to present a
602 bipolar cooling exists and more humidity in the tropics. Our record confirms this
603 interpretation, however high temporal resolution in the upper part of our core
604 allows us to enclose the enhancement of the upwelling regime for the last 500
605 years.

606

607 This upwelling intensification is observed under a well-described NAO negative
608 regime (Bernárdez *et al.*, in press). This apparent contradiction is explained by
609 the seasonality of the oceanographic processes acting in the region. We could
610 define a predominance of a NAO negative-like phase with SW winds and winter
611 storm conditions during the last 1200 cal. yr BP, but this fact does not imply the
612 ceasing of the upwelling regime during summer. This climatic situation could be
613 blurred by prevailing winter conditions, but during the last 500 cal. yr BP, N–NNE
614 winds and, therefore, the upwelling regime, would predominate in a seasonal

615 scale. Combining both climatic situations, the final result is the increase in
616 productivity, but the diatom assemblages permit to discriminate between both
617 processes.

618

619 Other studies show increased upwelling in recent years in multiple areas around
620 the world and, in particular, in the Canarian-Iberian margin (Bakun, 1990;
621 Anderson *et al.*, 2002; Goes *et al.*, 2005; Santos *et al.*, 2005; McGregor *et al.*,
622 2007) most of them attributed to 20th century global warming and atmospheric
623 CO₂ rise. Temporal resolution of our record does not permit to discriminate
624 enhanced upwelling on a decadal scale, but shows similar patterns to those
625 found by earlier authors on a century-decadal range. This fact has also important
626 implications on diatom productivity since, although dependent on a complex
627 balance of several factors, it is controlled by upwelling. These results imply an
628 increasing in phytoplankton biomass and the response of the ecosystem and the
629 consequent biological, climatological and socioeconomical impacts. Upwelling
630 may continue to strengthen with global warming (McGregor *et al.*, 2007), even in
631 our study area, provoking ecosystem and diatom composition changes.

632

633 On the other hand, it is important to point out that in the recent years a strong
634 increase in the Pb contents occurred (Figure 3). These values are within the
635 range point out by Araújo *et al.* (2002) for surface sediments in the muddy patch.
636 When Pb is normalized with Al, in order to eliminate the natural lithogenic
637 influence, the variability of Pb/Al ratios is lower, but still shows a significant rise in
638 recent times. One of the primary sources of lead into the aquatic domain is
639 atmospheric deposition (Clark, 2001). However, in the Galician shelf the input by

640 rivers flowing at the shelf could also be an important source. Enrichment factors
641 and isotope ratios seem to indicate that atmospheric Pb pollution started around
642 3500–3000 years BP related to human activities (Martínez-Cortizas *et al.*,
643 2002a), but in the NW Iberian Peninsula atmospheric Pb pollution is only
644 apparent since 2500 years BP (Martínez-Cortizas *et al.*, 2002b). A maximum in
645 concentration was found during the Roman colonization and also for the last 300
646 years due to industrial development (Martínez-Cortizas *et al.*, 2002b). A small
647 peak in the concentration of this element during Roman Warm Period is recorded
648 in our core. Moreover, the increase in the Pb/Al ratios occurs approximately
649 during the last 400 cal. yr BP (Figure 3). This result confirms the age model of the
650 core, but we are not able to detect the decreased Pb concentrations for the using
651 of unleaded gasoline also observed in other paleo-records in Galician marine
652 sediments and peat bogs (Cobelo-García and Prego, 2003; Martínez-Cortizas *et*
653 *al.*, 1997). Conversely, the Pb enrichment in the sediments of the core, which
654 provides a high temporal resolution during the recent years, is in good agreement
655 with the Pb enrichment due to industrial and naval development (Martínez-
656 Cortizas *et al.*, 1997; Martínez-Cortizas *et al.*, 2002b).

657

658

659 **5. CONCLUDING REMARKS**

660

661

662 A multidisciplinary study covering sedimentology (texture, organic matter
663 content), geochemistry (major, minor and trace elements), palaeoecology
664 (diatoms, biosilica compounds) and isotopic dating (^{14}C) has been carried out on

665 the gravity core SMP02-3 retrieved from the Galician continental shelf (NW
666 Iberian Peninsula). Paleoproductivity changes in the NW Iberian Peninsula have
667 been inferred from microflora and geochemical distributions of this core. The
668 study of microfossil assemblages and texture, composition and geochemistry of
669 sediments has been proved to yield relevant information on Holocene primary
670 production changes in the NW Iberian Peninsula.

671

672 Disappearance of diatoms during some periods of the core has been related to
673 oxygenation conditions and early diagenetic processes occurring during burial.
674 Despite the presumably large influence of biogenic silica preservation conditions
675 in periods 4700–3300 and 1800–1200 cal. yr BP, relative abundances of diatom
676 species are still reliable tracers of oceanographic and indeed climatic conditions.
677 Based on diatom valves abundance and dominance, the assemblage zones
678 present in the core can be divided in sub-environments that have evolved
679 through time. The sediments are characterized by a dominance of diatoms
680 representative of high nutrient environments, accompanied by coastal planktonic,
681 benthic and freshwater species.

682

683 The geochemical characterization of the sediment core indicates that sediments
684 deposited at the *Galicia Mud Patch* come from three different sources: lithogenic,
685 anthropogenic and biogenic. Peaks in metal concentrations are mainly related to
686 terrigenous inputs from the river plumes, especially at 800–500 cal. yr BP.

687

688 We have pointed that the sediment features (biogenic compounds and chemical
689 features) are triggered by climatic and oceanographic conditions in the Galician

690 area, as well as, by anthropic activities. The sharp rise in the Pb and Pb/Al
691 concentrations occurred during the last 400 cal. yr BP is linked to Pb enrichment
692 due to industrialization.

693

694 With respect to the timing of coupled marine and terrestrial palaeoenvironmental
695 processes and their effect in the primary production, the record presented here
696 shows that:

697

698 (1) High productivity due to nutrient enrichment is recorded during the last 1200
699 cal. yr BP due to both upwelling intensification and river runoff.

700

701 (2) The major wetter event occurring at 800–500 cal. yr BP, related to a NAO
702 negative-like regime, SW winds and storms, provokes a high diatom production,
703 being the river plumes the main source of nutrients to the coastal waters off
704 Galicia.

705

706 (3) This study indicates that *Chaetoceros* R.S. and some morphotypes are useful
707 tracers of paleoupwelling conditions on the NW Iberian margin. The other proxies
708 considered show consistent patterns indicating high productivity in the Galician
709 shelf during the last 500 years, from the onset of the humid event. This fact is due
710 to the intensification of the upwelling phenomena related to prevailing N–NNE
711 winds controlled by the position and strength of the Azores High.

712

713 In brief, marine productivity in this area is triggered by two processes that
714 increase the nutrient availability for phytoplankton growth: nutrient input by river

715 discharge and/or coastal upwelling. Both processes are linked to changes in the
716 position and strength of the atmospheric pressure systems and NAO regime.
717

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733

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735

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Figure captions

Figure 1. Schematic illustration showing the North Atlantic Oscillation (NAO) regime and the atmospheric situation. Base map of the study area showing the core site (SMP02-3) and the geographical distribution of the sediments containing more than 50% of mud (modified from Dias *et al.*, 2002a).

Figure 2. Sedimentary logs of the core. Distribution of depositional facies are also shown. ¹⁴C AMS raw ages (yr BP) and the result of the calibration (cal. yr BP, in brackets) are also presented.

C: Clay. S: Silt. Sd: Sand. VF: Very fine sand. F: Fine sand. M: Medium sand. Co: Coarse sand.

Figure 3. Profiles of the chemical elements analysed in the core. Total concentration (solid circles) is shown on the left axis and metal/Al normalization (open squares) is shown on the right axis.

Figure 4. Compilation of diatoms and geochemical proxies in the sediment core SMP02-3. Grey areas indicate climatic events discussed in the text. Lithostratigraphic units and AMS ¹⁴C datings (filled triangles) are also displayed.

Table captions

Table 1. Comparison of the analytical results of the certified reference material PACS-2 (NRCC, Canada) with the measured data.

Table 2 Bulk Ba (Ba_{total}), biogenic (Ba_{excess}) and Al concentrations.

Table 3. Content of opal, TOC, calcium carbonate and terrigenous.

PACS-2	Al (mg g ⁻¹)	Fe (mg g ⁻¹)	Mn (mg g ⁻¹)	Cu (µg g ⁻¹)	Pb (µg g ⁻¹)
Measured value	67.6±3.9	41.6±2.0	0.48±0.04	318±47	186±11
Certified value	66.1±5.3	40.9±0.6	0.44±0.019	310±12	183±8

Table 1

depth (cm)	Age cal. yr BP	Al (mg g ⁻¹)	Ba _{total} (mg g ⁻¹)	Ba _{excess} *
0	19	65.47	2.74	2.49
6	214	65.54	2.92	2.68
12	259	79.54	2.70	2.41
18	303	80.42	2.74	2.44
24	347	79.33	2.62	2.33
30	391	84.44	2.61	2.29
36	436	85.14	2.61	2.30
42	480	85.65	2.61	2.30
48	524	118.76	3.99	3.55
54	569	94.46	2.81	2.46
60	613	104.39	3.35	2.97
66	657	115.76	3.71	3.29
72	701	90.89	2.95	2.61
78	746	102.97	3.24	2.86
84	790	98.59	2.93	2.56
90	834	87.20	2.81	2.49
96	878	69.58	2.00	1.75
102	921	58.75	1.61	1.40
108	964	64.85	1.75	1.51
114	1007	66.36	1.54	1.29
120	1051	67.04	2.40	2.15
126	1094	55.85	2.05	1.85
132	1137	56.03	1.89	1.68
138	1180	49.60	1.62	1.43
144	1223	61.26	2.22	2.00
150	1289	61.15	2.18	1.95
156	1464	69.02	2.71	2.46
162	1640	78.91	2.79	2.50
168	1816	89.20	3.20	2.87
174	1991	91.00	2.94	2.60
180	2167	65.42	2.03	1.79
186	2343	67.99	2.36	2.10
192	2518	85.53	2.56	2.24
204	3356	77.38	2.26	1.97
210	3511	54.78	1.57	1.37
216	3667	61.61	1.39	1.16
222	3823	59.81	1.24	1.02
228	3978	37.70	0.34	0.20
234	4134	34.30	0.69	0.56
240	4289	33.85	0.15	0.02
246	4445	33.22	0.00	-0.12
252	4600	36.52	0.00	-0.14
258	4756	36.73	0.00	-0.14

Table 2

* Reitz *et al.* (2004). new global average 0.0037

depth (cm)	Age cal. yr BP	TOC (%)	CaCO ₃ (%)	opal (%)	terrigenous (%)
0	19	1.72	3.92	1.43	92.94
6	214	1.54	3.58	1.38	93.50
12	259	1.70	3.75	1.33	93.23
18	303	1.61	3.79	1.37	93.24
24	347	1.49	3.87	1.49	93.15
30	391	1.52	3.62	1.43	93.43
36	436	1.62	3.29	1.51	93.58
42	480	1.70	3.00	1.44	93.86
48	524	1.62	3.00	1.58	93.80
54	569	1.64	3.21	1.42	93.73
60	613	1.76	2.78	1.48	93.98
66	657	1.86	2.58	1.40	94.16
72	701	2.03	3.28	1.64	93.05
78	746	1.95	3.87	1.85	92.33
84	790	2.13	3.29	1.76	92.83
90	834	1.65	4.58	1.76	92.01
96	878	1.66	4.78	1.67	91.89
102	921	1.58	5.33	1.78	91.31
108	964	1.72	5.21	1.78	91.30
114	1007	1.81	5.41	1.79	90.99
120	1051	1.72	5.33	1.58	91.38
126	1094	1.49	6.21	1.67	90.64
132	1137	1.37	5.83	1.59	91.22
138	1180	1.09	7.16	1.60	90.14
144	1223	1.19	7.30	1.56	89.95
150	1289	1.18	7.41	1.59	89.82
156	1464	1.08	5.66	1.54	91.73
162	1640	1.18	3.12	1.18	94.52
168	1816	1.11	2.25	1.29	95.35
174	1991	1.11	1.79	1.35	95.75
180	2167	1.18	2.25	1.36	95.21
186	2343	1.32	2.37	1.62	94.70
192	2518	1.35	2.62	1.45	94.58
204	3356	1.45	5.25	1.42	91.89
210	3511	1.37	7.25	1.75	89.63
216	3667	1.30	8.66	1.70	88.34
222	3823	1.27	10.08	1.79	86.86
228	3978	1.11	10.95	1.91	86.03
234	4134	1.09	12.50	1.92	84.50
240	4289	0.92	12.20	2.06	84.82
246	4445	1.05	10.70	1.95	86.31
252	4600	0.94	18.91	1.89	78.26
258	4756	0.81	14.41	2.07	82.71

Table 3

Figure 1

Figure 2

Figure 3

Figure 4