Southern Ocean deep-water carbon export enhanced by natural iron fertilisation

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It is now well proven that addition of iron to high-nutrient low-chlorophyll regions induces phytoplankton blooms that take up carbon[1-3]. However, carbon export from the surface layer, and particularly the ability of the ocean and

sediments to sequester carbon for many years, remains poorly quantified[3]. Through the CROZEX experiment[4] in the Southern Ocean, we show that annual particulate carbon fluxes out of the surface layer and three km below a large, highly productive, naturally iron-fertilised region of the SubAntarctic Southern Ocean are 2-3 times larger than those from an adjacent HNLC area and have been so throughout the Holocene. This supports the hypothesis that increased iron supply to the glacial SubAntarctic may have directly enhanced carbon export[5]. The CROZEX sequestration efficiency[6] (amount of carbon sequestered below the depth of winter mixing for a given iron supply) of 8600 mol:mol was 18 times greater than that of an induced bloom which reached its export phase[7] but 77 times smaller than that of a natural bloom, KEOPS[8]. Large losses of purposefully added Fe can explain the lower efficiency of an induced bloom[6]. The discrepancy from KEOPS may result in part from an underestimate of horizontal iron supply.

In many open ocean regions there is low phytoplankton biomass despite a large macronutrient reservoir[3]. The Southern Ocean is the most biogeochemically significant of these HNLC regions due to its large spatial extent and influence on global nutrient cycles[9]. Mesoscale iron (Fe) enrichment experiments have demonstrated that Fe addition modifies phytoplankton processes, enhancing diatom biomass[10, 11] and increasing atmospheric CO_2 drawdown[1]. Observing bloom decline and quantifying the sequestration of photosynthetically fixed carbon resulting from Fe addition has more rarely been achieved[7, 12].

An alternative way to determine the role of Fe in regulating the biological carbon pump in the Southern Ocean is to study regions of high phytoplankton biomass stimulated by natural Fe inputs from shallow topography or islands. Recently KEOPS[8] demonstrated enhanced carbon export to below 200 m in the naturally iron-fertilized bloom over the Kerguelen Plateau. The Crozet Islands and Plateau (hereafter Crozet), located in the Polar Frontal Zone at the northern boundary of the

Southern Ocean is another region characterized by a marked annual phytoplankton bloom (Fig. 1). The SubAntarctic Front (SAF) of the generally eastward flowing Antarctic Circumpolar Current turns north past Crozet (Fig. 1), then east again when it encounters the Agulhas Return Current[13]. Thus south of Crozet HNLC conditions prevail[4], while north of Crozet an annual bloom covering 120000 km^2 (the size of Ireland and 50 times larger than the SOFeX bloom[2, 11]) results from Fe supplied from Crozet[14]. Fe enrichment over the light-limited winter period leads in spring to a strong north-south gradient in phytoplankton biomass (Fig. 1), productivity, community structure[15], dissolved inorganic carbon (DIC) uptake[16] and nitrate uptake[17], once stratification and increased solar irradiance reduce the mixed layer below the critical depth[18]. Weak circulation in the bloom region is such that water has a residence time there of ~60 days[4].

During austral summer 2004/5 we conducted an extensive oceanographic research programme (CROZEX) around Crozet[4] to test the hypotheses that the north-south gradient in chlorophyll *a* (chl *a*) is induced by natural Fe fertilisation and causes enhanced organic carbon flux into the deep ocean. To capture this flux, sediment traps were moored north (M10), east (M5) and south (M2, M6) of Crozet (Fig. 1). Short sediment cores were collected at M5, M6 and M10. Weak eastward flow past M2 and M6 and the absence of upstream blooms[13] characterised these HNLC "control" (-Fe) sites south of the bloom. M10 was under the bloom (+Fe) and M5 was under the eastward extension of the bloom. East-southeast flow along the SAF towards M5, the large spatial extent of the bloom combined with weak circulation within it and the predominance of *Eucampia antarctica* (a diatom that responded strongly to iron enrichment[19]) in the 3000m M10 and M5 traps (but absence from M2 and M6 traps) confirm that M10 and M5 traps received export flux from the iron-enhanced bloom. KEOPS and CROZEX are compared in Supplementary Table 1.

It has been shown[14] that the dissolved Fe (DFe; <0.2µm fraction) originates from Crozet with maximum estimated input to the bloom of 550nmol $m^{-2}d^{-1}$

comprising 390, 60 and 100 nmol $m^{-2}d^{-1}$ for the horizontal, vertical and atmospheric fluxes respectively. As the bloom occurs in deep (>2000m) water away from Crozet, horizontal flux dominates DFe supply as expected. A range of 180 - 390 nmol m^{-2} d^{-1} (0.018 - 0.039 mmol m^{-2} integrated over a winter period of 100 days) is estimated (Supplementary Information) for the enhancement in Fe supply to the +Fe region over that to the -Fe region. These are probably underestimates, as additional sources of Fe such as the dissolution of small lithogenic particles[20] will increase Fe supply.

Significant differences were observed in the magnitude, timing, duration and community structure of plankton blooms between the +Fe and -Fe regions. In the -Fe region chl *a* peaked at 0.6 mg m^{-3} in early December (Fig. 2a), when HNLC conditions (nitrate ~ 24 μmol kg^{-1}; silicate ~16 μmol kg^{-1}) prevailed[4]. In the +Fe region chl *a* peaked at over 3mg m^{-3} in October (locally >6 mg m^{-3}, Fig. 1) and was elevated (>1 mg m^{-3}) for 72 days[18] (Supplementary Table 2). Although fertilized by macronutrients from the -Fe region and by winter upwelling in the Polar Frontal Zone, silicate was already becoming limited (<2 μmol kg^{-1}; nitrate 16 μmol kg^{-1}) when first sampled in November[4], indicating silicate:nitrate drawdown of about 2:1, consistent with lower Fe stress than in the -Fe region[19]. Low ambient silicate concentrations, common over much of the SubAntarctic Southern Ocean[11], predisposed a shift in phytoplankton community structure from diatoms to *Phaeocystis*[15]. The bloom peaked <10 days after exceeding 1mg m^{-3} but remained >1mg m^{-3} for another month, potentially sustained by *Phaeocystis* using regenerated Fe and nitrogen[21], as +Fe nitrate values remained ~16 μmol kg^{-1} throughout December and January.

An important difference from purposeful iron enrichment experiments is that Fe concentrations accumulate in the +Fe region during winter. Removal of light limitation in spring[18] determines bloom onset, not Fe addition. Consequently net growth rates in the bloom phase (0.05 day^{-1}, Fig. 2a) are probably light limited and 2-18 times lower than those for artificial experiments (0.10 - 0.90 day^{-1})[3]. Weak

circulation in the +Fe region ensures that neither macronutrients nor Fe can be resupplied to the extensive bloom area during the bloom development period. A possible exception was close to the islands, where a small-area bloom in January[18] may have been fuelled by resupply of Fe and silicate.

The flux of organic carbon from the surface ocean to the ocean interior has been calculated using ^{234}Th at 100 m[22] (Table 1). Following the chlorophyll peak (Fig. 2a) in each region (+Fe and -Fe), mean daily rates of carbon export were similar (16mmol m^2d^{-1}) (Supplementary Table 2). Thus any difference in seasonally integrated export between the two regions depends on the duration of the export events. We estimated export duration by closing the silicate budget, dividing the near surface silicate drawdown (corrected for biogenic silica production) by the opal export rate estimated from ^{234}Th deficits and ^{234}Th/opal ratios. This approach yields export durations (61 and 17 days in the +Fe and -Fe regions respectively) consistent with the observed satellite derived chlorophyll time series (Fig. 2, Supplementary Table 2). The resulting seasonally integrated carbon export in the +Fe region (960mmol m^{-2}) was three times greater (Table 1) than export in the -Fe region (290 mmol m^{-2}), consistent with the independently diagnosed increase in new production[17].

Fluxes of particulate organic carbon (POC) to 3000 m differed remarkably in duration and composition. In the +Fe region (Fig. 2b) POC flux peaked at or before trap deployment in late December, decreasing to near-zero over several months. In the -Fe region POC export was confined to an unusually short but substantial event (Fig. 2b), observed at both M2 and M6 and at two depths (for sinking rates and export flux ranges see Supplementary Information). Substantial silicate drawdown between November and January (Supplementary Table 2) reduced surface silicate to <2.0μmol kg^{-1} at M2 and M6, suggesting that Fe limitation in the -Fe region resulted in heavily silicified diatoms[23] which sank rapidly in January. Despite this event, the longer duration of POC flux over the 2004-5 summer season in the +Fe region resulted in three times greater seasonal export in the +Fe region than the -Fe region (Table 1).

POC flux at 3000 m was 3% (4%) of that at 100m in the +Fe (-Fe) region (Table 1), indicating that remineralization rates were marginally enhanced by Fe availability.

The organic carbon content of the core top (surface mixed layer) sediments sampled several times during separate corer deployments is significantly higher in the +Fe region than the –Fe region (Supplementary Table 3). Significant sediment focussing and winnowing occurs in this region and thus data are expressed as $^{230}Th_{xs}$ corrected preserved fluxes (equivalent to the preserved vertical rain rate at the seafloor). A 2-fold increase in the $^{230}Th_{xs}$ corrected, preserved, core-top, organic carbon accumulation was observed in the +Fe region relative to the –Fe region (Table 1). This is consistent with published data from a suite of export production proxies that imply enhanced phytoplankton growth, export and burial throughout the Holocene at this site[24].

Our analyses thus indicate that shallow, seasonally integrated export, annually integrated deep-water POC flux and core-top organic carbon accumulation were all enhanced 2-3-fold due to the Fe fertilised bloom (Table 1). Consequently we can confirm Martin's hypothesis[5] that relief of iron deficiency enhances carbon sequestration into the deep ocean (here >3000m) and sediment. Results from CROZEX thus support increased atmospheric Fe deposition[1] as a mechanism for the inferred increase in organic carbon flux in the SubAntarctic during the Last Glacial Maximum (LGM)[24, 25].

The ratio of carbon exported below some depth to iron added at the surface, (C:Fe) is termed the export or (if below the depth of winter mixing) sequestration efficiency[6, 8]. Our ^{234}Th derived estimates of the seasonal enhanced (+Fe less -Fe) POC flux at 100 m (670 mmol m^{-2}) and additional Fe supply (0.039 mmol m^{-2}) lead to C:Fe (at 100 m) of 17200 (mol:mol) (range 5400-60400, Table 1). This value for the shallow export efficiency from CROZEX was somewhat higher than comparable values from Fe addition experiments (6600 for SOFEX[12], 1200 for SERIES[7]).

Interpolating with a Martin curve[26] to a winter mixed layer depth of 150 - 200 m[18], we further calculated a seasonal C:Fe sequestration efficiency of 11500-8600 (Table 1), compared to previous estimates of 500-3300[7, 12] and the KEOPS[8] seasonal estimate of 668000. Given the different methods used to estimate both additional Fe supply and carbon export between studies[3, 7, 8, 12], the reasons for the wide range of export efficiencies are unclear. However, we note that the KEOPS result depends on a combination of an 8-fold lower estimate for seasonal Fe supply and a 10-fold higher estimate for carbon export (Supplementary Table 1). It is possible that iron supply was higher to the KEOPS bloom prior to the late summer observation period on which the seasonal Fe supply was based, from either enhanced vertical supply before surface water stratification in spring coupled with luxury Fe uptake[27] or from horizontal input of lithogenic material from nearby islands[28, 29].

The results from CROZEX indicate that natural Fe fertilisation enhanced new production[17] and near surface export at 100m by 2-3 fold (Table 1). Moreover we present the first evidence that carbon fluxes at 3000 m and the sediment were similarly 2-3 times higher beneath the natural fertilised region than for a nearby HNLC region with similar end-of-winter macronutrient concentrations. Carbon sequestered past 200 m was only 50% of that exported past 100 m. Although the CROZEX estimate of carbon sequestration for a given iron supply was 20 times that of SERIES[7], it still falls 15-50 times short of geo-engineering estimates[6], casting further doubt on the claims that artificial addition of iron to the ocean can enhance carbon sequestration enough to significantly mitigate the effects of climate change.

Methods Summary

Chlorophyll was determined using remote sensing techniques referenced to *in situ* data. Iron concentrations in the bloom were estimated using a simple model including horizontal and vertical advection and atmospheric deposition. Organic carbon and opal export rates were determined using ^{234}Th deficits and ^{234}Th/opal and organic C

ratios from large particles. Biogenic silica was determined by spectrophotometric analysis of silicate levels in digested filtered samples. Sediment traps were McClane traps. Core data were derived from analysis of multiple gravity and Mega-core derived samples.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Information Data are held at the British Oceanographic Data Centre (www.BODC.ac.uk). Reprints and permissions information are available at npg.nature.com/reprintsandpermissions. Correspondence should be addressed to R.J.S. (rics@noc.soton.ac.uk).

Table 1 Seasonally integrated carbon fluxes at naturally iron fertilized and HNLC sites and the sequestration ratio C:Fe

	Carbon mmol $m^{-2}y^{-1}$		C:Fe ratio[e]
Site	+Fe (fertilized)	-Fe (HNLC)	mol:mol
^{234}Th via Si[a] at 100 m	960	290	17190
range	(626 - 1252)	(166 - 415)	(5420 - 60360)
Deep flux[b] at 3000 m	25.0	7.1	
best estimate[c]	28.9	11.6	440
range[c]	(25.0-34.2)	(7.1-17.4)	(195 - 1506)
Core top[d]	9.3 ± 0.5	4.5 ± 0.4	123
Interpolated flux at 150 m[f]	642	194	11487
Interpolated flux at 200 m[f]	483	146	8641

a Summarized from Supplementary Table 2

b From Fig. 2

c Summarized from Supplementary Information

d Summarized from Supplementary Table 3

e Calculated from the differences between +Fe and -Fe carbon fluxes divided by winter period Fe supply (0.018 - 0.039 mmol m^{-2})

f Calculated from 100 m values using a Martin curve $F(z) = F(100\ m) \times (z/100)^b$, where b = -0.99 to fit the 3000 m carbon flux values

Figure legends

Figure 1. Chl *a* images of Crozet region. a Chl *a* in October for the whole of the Southern Ocean showing location of Crozet. **b** Merged SeaWiFS/MODIS chl *a* image for the 8-day peak bloom period 23-30 October 2004 Solid and dashed lines show circulation[13] with SubAntarctic Front (SAF, the northern boundary of the Antarctic Circumpolar Current) and Agulhas Return Current (ARC) bold. Main sampling (+) and coring (•) sites are labelled. Thin white lines are the 2000 m depth contour, with the main Crozet Islands (Île de la Possession, Île de l'Est) seen at 46.5°S, 52°E.

Figure 2. Time series of chl *a* and particulate organic carbon (POC). a, Chl *a*, obtained for each 8-day merged SeaWiFS/MODIS image by averaging all non-cloud pixels in a 45 km radius circle about each mooring site. Error bars (for M10 only) give the standard deviation of the mean of these pixels. **b**, POC (solid line) obtained from deep sediment traps at each site (Methods). Arrowheads mark mooring deployment and recovery. The traps could not be deployed until after the start of export from the 2004-5 bloom, so the export rate into the first cup has been extrapolated (Supplementary Information) using a range of sinking rates after the peak of chl *a* to give minimum, mean and maximum (dashed) seasonal integrals of total export.

Methods

Chlorophyll a (Figures 1 and 2) was determined from NASA's merged SeaWiFS/MODIS products, adjusted to match *in situ* data[18].

Iron concentrations in the bloom region[14] were estimated by considering lateral advection of DFe from the islands into the surrounding water, vertical mixing of Fe from beneath the seasonal thermocline and atmospheric deposition. Total dissolved iron concentrations (DFe <0.2 µm fraction) were determined using flow injection catalytic spectrophotometric detection. Horizontal Fe flux was estimated from

samples of DFe collected along a series of stations extending seawards from the northern coast of Île de la Possession and by using the terrestrially derived short-lived radium isotopes ^{223}Ra and ^{224}Ra to estimate horizontal mixing coefficients at the same stations[30]. Horizontal gradients in these species were combined with estimates of the plateau circumference to estimate total DFe release from the plateau over the 100 day winter period when the mixed layer depth is such that the surface ocean is in contact with plateau sediments. Vertical Fe flux was diagnosed from analysis of ^{228}Ra and DFe profiles. Finally, the estimated atmospheric (wet and dry) Fe flux was based on Ca and Si concentrations in aerosols and DFe measurements in rain samples by ICP-OES. The flux of DFe to surface waters was extrapolated to and integrated over the winter period. Values are consistent with atmospheric dust transport models.

Organic carbon and opal export rates were estimated by multiplying the observed 0-100 m deficit of the short-lived natural radioisotope ^{234}Th by the ^{234}Th/POC or ^{234}Th/Opal ratio in large volume samples of large particulate material (>53 µm) collected using a Standalone Pumping System deployed approximately 20 m below the mixed layer[22].

Biogenic silica (BSi) measurements were made on 1-L seawater samples filtered onto 0.4 mm polycarbonate filters, stored at -20°C, digested in 0.2 mol sodium hydroxide and neutralized with 0.1 mol hydrochloric acid[31, 32] and analyzed using a Skalar Sanplus autoanalyser. Opal accumulation was estimated by integrating values in the upper 100m.

Sediment traps were McLane 21-cup time-series arrays deployed on bottom tethered moorings. Sampling bottles were filled with buffered preservative solution according to JGOFS protocols. Upon recovery samples were filtered through a 1 mm Nitex mesh. Swimmers were carefully removed from the <1 mm fraction. The >1 mm size fraction was comprised exclusively of large swimmers. Some cups were contaminated by fish (*Notolepis coatsi*) feeding on the sinking material. All fish debris was picked

out by hand. All chemical analysis was performed on the <1 mm fraction after it had been freeze-dried and homogenised. Following acidification with hydrochloric acid, particulate organic carbon and nitrogen were measured using a Carlo-Erba NA-1500 elemental analyser following standardisation with acetanilide.

Core top accumulation rates. A Mega-corer was used to obtain sediment cores with an undisturbed sediment-water interface and gravity core deployments were used to sample deeper sediments. Samples from the surface mixed layer (0-10 cm below surface) were dried, ground and subjected to the same methodology as described for the sediment trap material for POC and PON at NOCS and NIGL. U-series isotopes were determined by isotope dilution multi-collector ICP-MS at the Department of Earth Sciences, University of Oxford. ^{230}Th-normalised preserved organic carbon fluxes were estimated from the sediment composition and the ^{230}Th normalised sediment accumulation rate (measured ^{238}U/^{232}Th activity ratio of detrital end member is 0.9. These data supplement published data[24] also tabulated for comparison.

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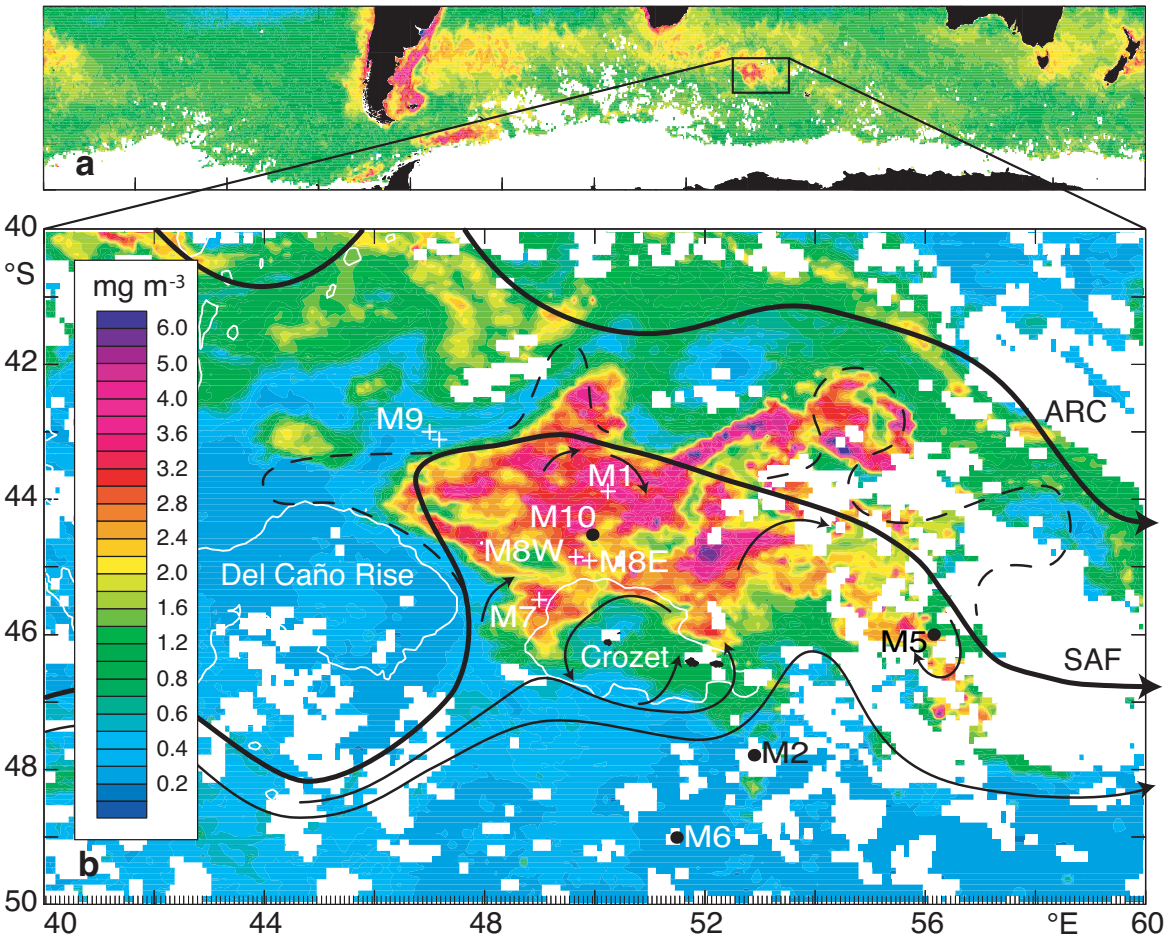
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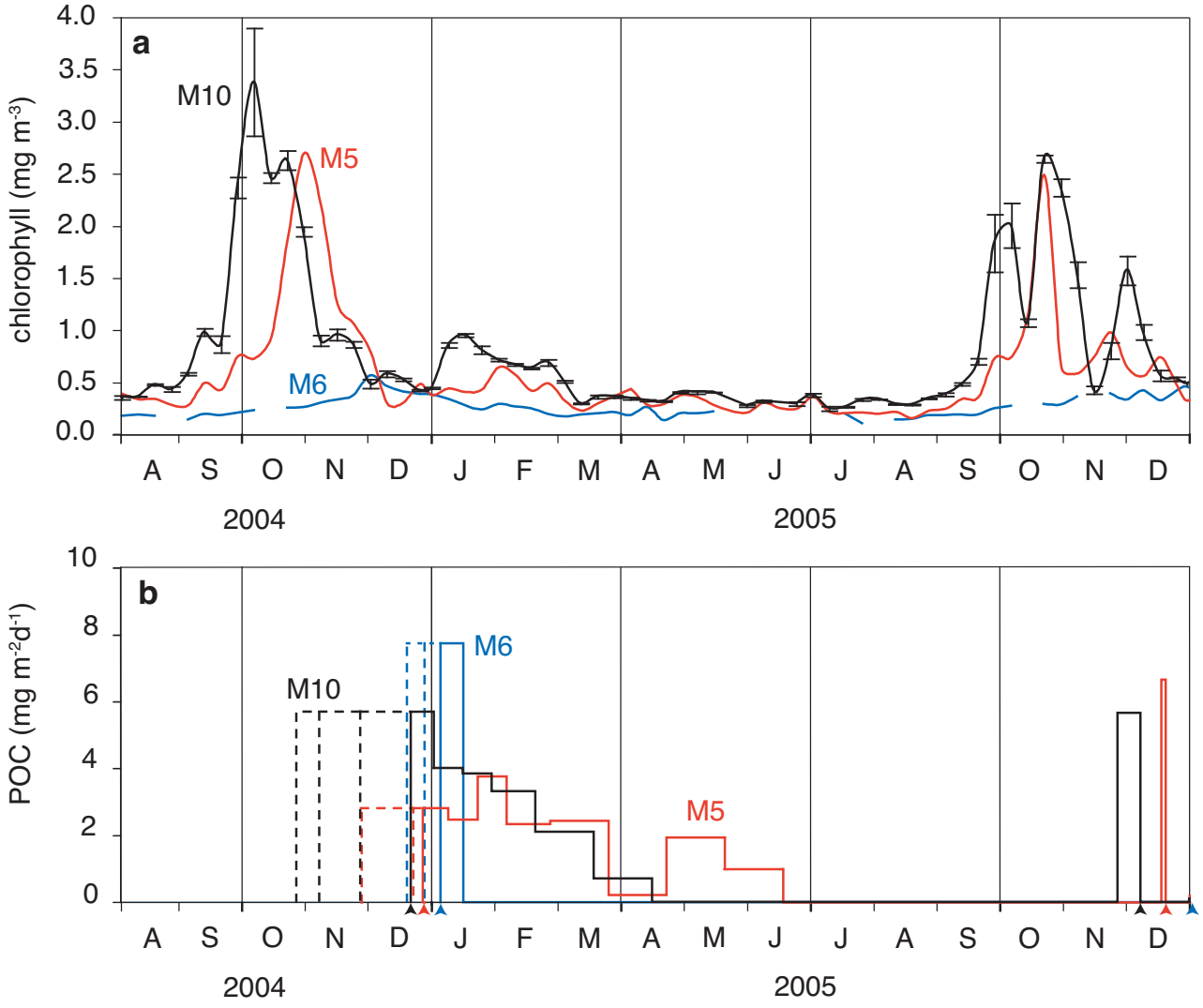
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M6
M5
POC (mg m-2d-1)
10
8
6
4
2
0
A S O N D J F M A M J J A S O N D
2004
2005