Seasonal flux patterns and carbon transport from low oxygen eddies at the Cape Verde Ocean Observatory: lessons learned from a time series sediment trap study (2009-2016)

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Abstract. Mesoscale eddies are abundant in the eastern tropical North Atlantic and can-act as form an oasis for 15 phytoplankton growth due to local enrichment of nutrients in an otherwise oligotrophic watersocean. It is not clear, whether these eddies can efficiently transfer organic carbon and other flux components to depth and if they are important for the marine carbon budget. Due to their transient and regionally restricted nature, measurements of eddies' contribution to bathypelagic particle flux are difficult to obtain. The rR are observations of export flux associated with low oxygen eddies have suggested efficient export from the surface to the deep ocean, indicating 20 that organic carbon flux attenuation might be low. Here we report on particle flux dynamics north of the Cape Verde Islands at the oligotrophic Cape Verde Ocean Observatory (CVOO, approx. 17°35' N/ 24°15'W). This region is a corridor for eddies and low-oxygen eddies regularly passing the position of CVOO between 2009 and 2016, while we collected biogenic and lithogenic particle flux with sediment traps moored at ca. 1 and 3 km water depth. The CVOO site is located in the preferred pathways of high productive eddies, that ultimately originate 25 from the Mauritanian upwelling region. Between 2009 and 2016, we collected biogenic and lithogenic particle flux with sediment traps moored at ca. 1 and 3 km water depth at the CVOO site. From concurrent hydrography and oxygen observations, we confirm earlier findings that high productive eddies are characterized by colder and

less saline waters and a low oxygen signal as well. Overall, we observed quite consistent seasonaline wave flux

patterns during the passages of low oxygen high productive eddies in the winters of 2010, 2012 and 2016. We 30 found flux increases in-at 3 km depth during October-November when the eddies approached CVOO and distinct flux peaks during February-March, clearly exceeding low oligotrophic background fluxes during winter 2011 and showing an enhanced particle flux seasonality. During spring, we observed a stepwise flux decrease leading to summer flux minima. The flux pattern of biogenic silicate (BSi) showeds a stronger seasonality compared to organic carbon. Additionally, the deep fluxes of total mass showed an unusually higher seasonality compared to 35 the 1 km traps. We assume that BSi and organic carbon/lithogenics had different sources within the eddies. BSirich particles may originate at the eddy boundaries where large diatom aggregates are formed due to strong shear and turbulence, resulting in gravitational settling and, additionally, in an active local downward transport. Organic carbon associated with the lithogenic material is assumed to originate from the interior of eddies or from mixed sources both constituting smaller, dust-ballasted particles. Our findings suggest that the regularly passing high

40 productive low oxygen Anticyclonic Modewater Eeddies (ACME) at CVOO repeatedly release characteristic flux signals to the bathypelagic <u>during the-winter-spring seasons</u> which were far above the oligotrophic background fluxes and sequestered higher organic carbon than expected for during oligotrophic settings. However, the reasons for a lower carbon flux attenuation below eddiesACMEs remain elusive.

1. Introduction

45 High productive mesoscale eddies, often carrying cold and less saline water masses with low oxygen concentrations, have been suggested to play an important role in the biogeochemistry and carbon cycling in the oligotrophic eastern tropical North Atlantic. The eastern tropical North Atlantic hosts one of the major Oxygen Minimum Zones (OMZ) of the world oceans (Karstensen et al. 2008; Brandt et al., 2015). The specific oxygen consumption and ventilation pattern creates two oxygen minima-in the eastern tropical North Atlantic, the shallow 50 one at about 80 m depth mostly associated with regional processes, and the deep one at about 450 m water depth (minimal oxygen about 40 µmol kg⁻¹) associated with the gyre scale ventilation (e.g. Karstensen et al. 2008, Fiedler et al., 2016; Brandt et al. 2015). Most energetic flow features in the region are the boundary current system (Mittelstaedt, 1991; Brandt et al., 2015) and, at a local scale, westwards propagating mesoscale eddies (e.g. Schütte et al., 2016a; Pietri and Karstensen, 2018). The two features are connected as the mesoscale eddies spin off 55 instabilities of the boundary current and transport water of coastal origin offshore, with elevated nutrients and high organic carbon content. The eddy origin in the Canary Current-Eastern Boundary Upwelling Ecosystem (CC-EBUE) can be traced back to certain 'hot spots' for eddy formation, one of them at Cape Vert (Senegal) where anticyclones are formed in summer and propagate westward, reaching the Cape Verde Ocean Observatory 60

(CVOO) site-about half a year later, in winter (Fig. 1; Schütte et al., 2016a; Karstensen et al., 2015). The eddies start with high nutrient load from the coastal upwelling while, en route, dynamical processes support local upwelling and high productivity (Karstensen et al., 2017; Fielder et al., 2016). The combination of high biomass, high respiration of organic matter, and the physical isolation of the eddy core water masses leads to low oxygen concentration in the eddies where even suboxic conditions ($O_2 <_1 \mu \text{mol kg}^{-1}$) have been observed at very shallow depth, just below the base of the mixed layer (Karstensen et al., 2015; Schütte et al., 2016b).

- 65 Lowest oxygen content in mesoscale eddies in the Egastern Ttropical North Atlantic have been found in Anticyclonic Modewater Eddies (ACME). These eddies can have a very isolated core related to a velocity maximum at about 70 to 100 m depth and the low oxygen content is found just below the mixed layer (Karstensen et al., 2015, 2017). In parallel, intense upwelling of nutrients into the euphotic zone have been reported and attributed to different concepts such as sub-mesoscale shear instabilities (Karstensen et al., 2017) or eddy-wind
- 70 interaction and a resulting Ekman transport divergence (McGillicuddy et al., 2007). Dedicated surveys of ACMEs revealed rather unique ecosystem responses compared with the surrounding oligotrophic region. High phytoplankton and particle concentrations, high carbon degradation and specific nitrogen cycles have been reported (Fiedler et al. 2016; Löscher et al., 2015; Grundle et al. 2017). Additionally, due to the very low oxygen availability, the diurnal migration cycle of zooplankton is for some species severely limited (e.g. Hauss et al.,
- 75 2016), while species with high oxygen tolerance, e.g. the polychaete *Poeobius*, profit from the high particle flux even in the low oxygen core of the eddies (Christiansen et al. 2018).

It has recently been shown that increasing primary production in the surface waters of different ocean basins did not show a similar increase in export flux to the deep sea (Cael et al., 2021). The authors suggested that this was due to a biological dampening of variability from primary production to deep-sea particulate organic carbon flux

- 80 (POC), most likely due to higher intensity of zooplankton grazing during productive periods. These observations were from the epi- and mesopelagic under normal oxygen conditions where grazing zooplankton plays an important role (e.g., Iversen et al., 2010). However, if oxygen content is strongly reduced to hypoxic and suboxic conditions in the sub-surface and deeper waters, degradation of organic carbon may be reduced due lower zooplankton grazing (e.g., Hauss et al. 2016). For the OMZ in the eastern tropical Atlantic, it is assumed that
- 85 organic carbon attenuation of larger particles in the water column is reduced, thereby increasing the efficiency of the biological carbon pump (Rasse and Dall'Olmo, 2019). In the OMZs of the Pacific Ocean and the Arabian Sea, low carbon flux attenuation has been suggested in suboxic waters at depths between 100 and 1000 m (Weber and Bianchi, 2020). However, the role of mesoscale eddies for carbon export and deep ocean carbon sequestration is still largely unexplored (see review of Benitez-Nelson and McGillicuddy, 2008) and therefore not reliably resolved
- 90 in global carbon cycling models (e.g. Omand et al., 2015; Shih et al., 2015).

Sediment trap flux studies in the meso- and bathypelagic associated with eddies are rare (e.g. E-Flux and EDDIES Projects: see review in Benitez-Nelson, and McGillicuddy, (2008); CVOO: Fischer et al., (2016); Romero et al., 2016)) and episodic pulses of organic matter sedimentation from eddies may be largely undersampled or even missed. Some studies show that carbon export was higher at the eddy edges and organic matter export occurred 95 partly via sedimentation of large diatom frustules and zooplankton fecal pellets (Shih et al. 2015). Other studies of organic carbon export associated with eddies did not reveal higher organic carbon fluxes compared to the surrounding oligotrophic waters (e.g., Buesseler et al., 2008). Two to three fold higher biogenic silica (BSi) fluxes compared to the oligotrophic surroundings have been observed within eddies (e.g. Maiti et al., 2008; Rii et al., 2008; Verdeny et al., 2008) have been observed within eddies. This was for instance shown for the cyclonic eddy 100 named (e.g. eddy OPAL) which was studied during the E-Flux program (Benitez-Nelson and McGillicuddy, 2008) in the North Pacific. Most of these studies, however, did not differentiate between the type of eddies investigated. Benitez-Nelson and McGillicuddy (2008) pointed out that a higher phytoplankton biomass produced within eddy blooms may not necessarily result in increasing particle export and sedimentation. Instead, micro-zooplankton grazing (e.g. by ciliates and dinoflagellates) may be stimulated, resulting in a strong upper ocean recycling and a 105 release of suspended and dissolved materials at shallow depths within eddies. Oxygen to total nitrate stoichiometry in an ACME north of Cape Verde was found to be about twice as high (16) compared with the surrounding waters (8.1) or the classical Redfield ratio (Redfield et al. 1963) and explained by local (mesoscale) upper layer nitrate recycling (Karstensen et al., 2017). The surrounding waters of the eddies are close to Redfield stoichiometry (Redfield et al., 1963) and have an Apparent Oxygen Ulilization (AOU) to nitrate ratio of 138/16 (= 8.6). However, 110 inside high productive eddies, oxygen removal by respiration was found to be about twice as high as nitrate increase through remineralization of organic matter (AOU/nitrate ratio of 16; Karstensen et al., 2017). This shift in stoichiometry was explained by different cycling pathways of oxygen and nitrate within the eddy (Karstensen et al., 2017).

Site CVOO is north of Sao Vicente (Cape Verde <u>Islands</u>, approx. 17°35'N/ 24°15'W), located within one of the eddy corridors from the west African coast at ca. 15-20°N (Schütte et al. 2016a, Fig. 1), is ideal to investigate particle fluxes and deep carbon sequestration in response to the passage of cyclonic and anticyclonic eddies with specific hydrography and oxygen characteristics in the epi- and mesopelagic. from different types of eddies characterized by variable oxygen conditions in the epi- and mesopelagic. A great advantage are continuous <u>Given previous</u> oceanographic studies and surveys at this site (e.g. Karstensen et al., 2015; Löscher et al., 2015; Schütte et al., 2016a, Pietri and Karstensen, 2018) as well as paired with synchronous time-series measurements of hydrography and oxygen concentrations in the epi- and mesopelagic, the passages of different types of eddies can

be reconstructed from the time series data, particularly for high productive/low oxygen eddies.-which aid in the

identification of the passing of low oxygen eddies. A detailed description of the biogeochemical responses in terms of export flux during winter 2010 in response of from an ACME passage with a hypoxic-anoxic core was provided
 by Fischer et al. (2016a). This study discussed the impact of such an hypoxic/-anoxic eddyies on bulk export flux, stable nitrogen isotopes, major planktonic groups (diatoms, coccolithophores, planktonic foraminifera) and biomarkers from traps at ca. 1300 and 3400 m depth. The most striking observation was a 2-3two to three--fold higher organic carbon flux in-collected by the 1 km trap compared to the surrounding oligotrophic waters and a high seasonality (Berger und Wefer, 1990). Additionally, we found a massive increase of organic matter flux with increasing depth, which was interpreted bypointing to particle flux focusing (Fischer et al., (2016), to particle flux focusing in the deeper water column.

The aim of theirs present study is to investigate the transfer of biogenic and lithogenic particles (Saharan dust) in association with eddy passages from different types of eddies to sequestration depths at about 1 and 3 km water depth and to compare against oligotrophic background conditions. We use a multi-year sediment trap record (2009-2016, with interruptions; Fig. 1; Table 1) of particle fluxes at the oligotrophic site CVOO. Our emphasis is on the fall-winter flux peaks when different high productive/low oxygen eddies pass through the study site and we compare these fluxes maxima to oligotrophic, low-seasonality conditions. Data discussed are partly based on earlier investigations from deployments CVOO-3 and 4 (2009-2012; Fischer et al., 2016, Romero et al., 2016). Here Wwe also use the deeper trap flux data to unravel organic carbon transfer to the deep CVOO site within

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2. Materials and Methods

2.1. Cape Verde Ocean Observatory (CVOO)

passing eddies and extend the flux record to 2016.

The study site CVOO in the eastern tropical North Atlantic (approx. 17°35'N/ 24°15'W; Fig. 1) is located about 800 km off the <u>west</u> African coast and about 80 km north of the island of São Vicente, Cape Verde (Fig. 1a). It consists of a steel wire mooring of approx. 3600 m length, first deployed in 2006 and maintained continuously since then. The mooring is equipped with several temperature and salinity sensors at multiple depth, water current profiler and single point current meters (also in conjunction with the sediment traps), and Aanderaa AADI optodes (Type 3830) oxygen sensors, typically at about 50 and 180 m depth. The optode calibration was refined over the years but followed essentially two strategies – a laboratory calibration with zero and saturated oxygen concentrations and a calibration against reference points acquired by mounting the logger to a CTD rosette and

comparing the logger readings with calibrated (Winkler titration) CTD oxygen readings (see e.g., Hahn et al. 2014). For the deployment period 2015 to 2016 a programming error for the logger occurred and only a record of two weeks was acquired. However, the temperature and salinity sensors were operational and were used to estimate mesoscale eddy occurrence, at least in case of the ACMEs, which are characterized by low salinity and cold waters

- 155 compared to the surrounding waters. Time series of oxygen and salinity discussed here were acquired in the depth range between 30 to 100 m. The oxygen record stems from one single sensor mounted between nominal 43 to 55 m water depth. For the deployment period 2015 to 2016, a programming error occurred and the oxygen record is only two weeks long. Salinity was recorded with at least three, but up to six sensors, depending on the respective deployment period. As found in earlier studies (Karstensen et al., 2015; 2017, Schütte et al., 2016a), high
- 160 productive and well isolated eddies of coastal origin correlate with low salinity events, and eventually may be paired with low oxygen concentrations. We defined occurrences of such eddies at CVOO when minimal salinity (35.0 to 35.6 ‰) and low oxygen (< 5 to 110 µM) records were encountered and compared these events with the flux observations.</p>

Except for the periods when mesoscale eddies cross the CVOO site, the currents are generally sluggish as expected

- for a site in the OMZ region. Fischer et al. (2016) reported ca. 2-6 cm s⁻¹ for about 600 m depth and around 2 cm s⁻¹ for the deep water column. As a consequence, the mooring, which has it head buoy at about 40 m depth, was mostly in an upright position<u>and catchment was unaffected by mooring tilt. At site CVOO, pressure sensors indicate a maximal deflection angle of ca. 12° in the upper ca. 1300 m of the water column, which is in the normal range measured. This might affect trapping efficiency (e.g., Buesseler et al., 2007) but it is difficult to quantify these changes as the mooring line oscillates around the upright position, depending on local current directions and intensities including tidal currents. A detailed description is given by Fischer et al. (2016). Oceanography and
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- biogeochemistry of the area around CVOO including the passages of different types of eddies is outlined elsewhere (Karstensen et al. 2015, 2017, Schütte et al. 2016a).

2.2. Sediment trap collections

- 175 Particle fluxes were collected with cone-shaped and large-aperture sediment traps (0.5 m²; Kiel type, Kremling et al., 1996) in ca. 1300 m (hereafter word to as 1 km) and in ca. 3000-3500 m water depths (hereafter word referred to as 3 km; Table 1), respectively. We used samples collected on roughly monthly intervals (Table 1). The traps were equipped with 20 cups, which were poisoned with HgCl₂ before and after deployment by addition of 1 mL of a saturated HgCl₂ solution in distilled water at 20°C per 100 ml. Pure NaCl was used to increase the density of
- 180 <u>the water added toin</u> the cups prior to the deployments (final salinity was 40_‰). Large swimmers were removed

manually and/or by filtering carefully through a 1 mm sieve. All fluxes therefore refer to the major size fraction of $<_1$ mm. Samples were wet-split in the home laboratory using a rotating McLANE wet splitter and freeze-dried. Additional methods information is given elsewhere (Fischer and Wefer, 1991).

Deep ocean sediment traps usually collect material from a rather large catchment area, typically around 100 km in
 diameter or wider, depending on particle settling rates and ocean currents (Siegel and Deuser, 1997). As ocean currents are generally in a western and southwestern direction, we used a catchment area for environmental data (MODIS chlorophyll, SST, surface wind speed and dry dust deposition rate) from GIOVANNI (https://giovanni.gsfc.nasa.gov/giovanni/#service= TmAvMp&starttime=&endtime=) for the surface ocean located to the northeastNE of CVOO (17°30-18°30. N / 23-24° W; Fig. 1a). We made different tests with the size of the study box (e.g., one or two degrees) and the location (above the trap, to the west or northwest) but we did not observe significant changes of the seasonality of the environmental parameters compared to the one-degree box to the northeast. Calculated mean seasonal and annual fluxes allow a better comparison among seasons and

years to identify interannual variability. Seasons are defined using the dates of opening and closure of the sampling cups closest to the start of the astronomical seasons (March 21, June 21, September 23, December 21). To illustrate

and quantify the seasonal variability of particle fluxes, we applied the Seasonality Index (SI) from Berger and Wefer (1990). This seasonality index is defined in terms of the number of months which yield one half of the total production/flux (= production/flux half-time) over an annual cycle. The Seasonality Index is then six minus the production/flux half-time in months. A seasonality index of zero (= 6-6) therefore means no seasonality at all or a constant flux pattern which is typical for oligotrophic settings (Berger and Wefer, 1990). In contrast, a seasonality index of five (= 6-1) indicates a very high seasonality (or a highly peaked flux pattern) with 50 % of the total flux occurring within one month only; this is, for instance, observed in high latitude oceans like the Southern Ocean (Berger and Wefer, 1990).

2.3. Sample <u>a</u>Analysis of <u>settling Pp</u>articles

Samples were analyzed using freeze-dried and homogenized material of 1/5 wet splits. The collected material was weighed for total mass and analyzed for organic carbon, total nitrogen, <u>calcium</u> carbonate and biogenic silica. Particulate organic carbon, total nitrogen and calcium carbonate were measured by combustion with a Vario EL III Elemental Analyzer in the CN mode. <u>Total Cc</u>arbonate was determined by subtracting organic carbon from total carbon, where the latter was measured by combustion without pre-treatment with 2N HCl. Biogenic opal was determined with a sequential 1M NaOH leaching <u>method-technique</u> according to Müller and Schneider (1993).

210 This method does not account for the variable water content of biogenic opal but corrects it for Si derived from

clay minerals. Leaching duration depends on the course of the continuous leaching curve and recordings were terminated when a linear dissolution course is reached which usually occurs after around $\frac{1}{2}$ to one hour. The precision of the overall method based on replicate analyses is between ± 0.2 and ± 0.4 %. Lithogenic fluxes were calculated from total mass flux by subtracting the flux of carbonate, biogenic opal and two times the flux of organic carbon (Hedges et al. 2002) to approximate organic matter. As there is no river input into the study area, we assume

that all non-biogenic (= lithogenic) material was supplied via aeolian transport to site CVOO.

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2.4. Diatom fluxes at CVOO (upper traps)

We used 1/125 splits of the original samples for quantification of diatom flux. Samples were rinsed with distilled water and prepared for diatom analysis as previously published (see details in Romero et al., 2016; 2017; 2020).
Identification and counts of diatom taxa at the species level were done at x1000 magnifications using a Zeiss®Axioscop with phase-contrast illumination (MARUM, University Bremen, Bremen). Counts were carried out on permanent slides of acid cleaned material (Mountex® mounting medium). Depending on valve abundances in each slide, several traverses were examined. Total amount of counted valves per slide ranged between 300 and 600. Two cover slips per sample were scanned in this way. Diatom counts of replicate slides indicate that the analytical error of concentration estimates is 12 %. The counting procedure and definition of counting units for diatoms follows Schrader and Gersonde (1978).

The resulting counts yielded abundance of individual diatom taxa as well as daily fluxes of valves per m-2 d-1 (DF), calculated according to Sancetta and Calvert (1988), as follows:

DF = [N] x [A/a] x [V] x [Split] / [days] x [D]

where, [N] number of valves, in an area [a], as a fraction of the total area of a petri dish [A] and the dilution volume [V] in ml. This value is multiplied by the sample split [Split], representing the fraction of total material in the trap, and then divided by the number of [days] of sample deployment and the sediment trap collection area [D].

3. Results

3.1. Seasonal and interannual environmental variability in the CVOO eddy box

- Sea Surface Temperatures (SSTs) in the box northeast of CVOO (Fig. 1) showed a seasonal cycle and varied between about 20.5 and 27.5°C with lowest values occurring induring winter and spring (Fig 2a). Highest SSTs occurred during late summer/early fall, where after SSTs decreased rapidly until the turn of the year. Satellite-derived chlorophyll biomass (Fig. 2b) increased with decreasing SSTs and was highest during winter and spring. Modelled dust dry deposition peaked <u>during</u> winter and occurred ca. 1-2 months prior to the chlorophyll maxima (Fig. 2c). The years 2010 and 2011 showed higher SSTs, lower chlorophyll and reduced dust deposition compared to 2012-2016 (Fig. 2). Chlorophyll content was very low and remained below the mean value <u>during</u> winter 2011 and 2010 (oligotrophic conditions, Fig. 1b). During winter 2010, a high chlorophyll eddy approached the trap site CVOO (Fig. 1b, Fischer et al., 2016). During the following winter seasons from 2012 to 2016, chlorophyll was
 - above the mean values (Fig. 1b).

245 3.2. Oxygen and salinity time series at CVOO

The oxygen (Fig. 3a) and salinity (Fig. 3b) time series from 2010 to 2016 recorded between 30 and 9100 m depth showed different scales of variability. Note that the time series are aligned with the CVOO 3-7 sediment trap particle sampling inat ca. 1 and 3 km depth (Fig. 4; Table 1). For both, oxygen (one instrument only) and salinity (23 to 36 instruments), a seasonal cycle can be seen was observed with highest oxygen and salinity during summer. 250 Lowest oxygen values concentrations weare found during February 2010, December 2013 and August 2015₄, and maybe in January 2016 and to some extent in January 2016, all associated with low salinity signals (Fig. 3b). Low salinities indicate the presence of boundary current waters of South Atlantic Central Water (SACW) origin and awere most likely linked to the presence of coherent and isolated eddies from the Mauritanian-Senegalese coast (Schütte et al., 2016a; Fiedler et al., 2016). The most severe and longest oxygen drawdown, with lowest values 255 concentrations reaching almost anoxic conditions, were observed for the entire February 2010, largely overlapping with the collection period of one sampling cup of the CVOO-3 sediment traps (cup #3, Fischer et al., 2016). However, low salinity events were also obtained for January 2011, February to April 2012, August-September 2013, and April to June 2015, which indicate the presence of isolated eddies of coastal origin. Unfortunately, oxygen data were not available for the winter season in 2016 but the relationship to the salinity values (Fig. 3b) 260 suggest that a low oxygen ACME was passing in winter 2016 as well. Note that because of the complexity in underlying drivers, water mass characteristics and intermittency of eddy occurrences in space and time, we do not expect a robust correlation between low oxygen and low salinity with a flux event at the CVOO site. However, we make use of both, low salinities (ca. 35.6 to 35 %) and low oxygen (ca. < 5 to 110 μ M) as an indicator for the potential passage of eddies. To compare to the flux events during winter, we show these eddy events with a duration

265 of at least one month and longer as bars in Figures 4 and 5. Note that the events need to be considered carefully as eddies may only pass the mooring site with their periphery. A single oxygen sensor may miss the main signal of the eddy, hence, not resolving it properly.

3.3. Time-series of sediment trap particle fluxes

270 Total mass flux was highest during winter at both traps in 1 km and 3 km and reached >100 mg m⁻² d⁻¹ (Fig. 4). Fluxes started to decrease during spring (except 2011) and reached a minimum during summer. Mass fluxes increased from late summer until fall, sometimes constituting a maximum during fall (e.g. in 2011, lower traps, Fig. 4b). The only winter-spring flux pattern with values below 50 mg m⁻² d⁻¹ was observed during 2011, observed at both trap depths. Between summer 2010 and spring 2011, total mass fluxes remained below 25 mg m⁻² d⁻¹ with low seasonal variability. Mean total mass fluxes for the whole time-series were 51 ± 18 and 62 ± 49 mg m⁻² d⁻¹ for 1 275 km and 3 km, respectively (Fig. 4). However, this overall increase in flux with increasing depths was mainly due to riven by the exceptional high mass fluxes to 3 km during 2010 (Fischer et al., 2016). Between 2015 and 2016, total particle fluxes into the upper CVOO-6 trap were above the overall mean of \sim 51 mg m⁻² d⁻¹, however, the trap malfunctioned and the export flux for the whole complete deployment period was collected into one cup (Fig. 4). Particle fluxes mostly decreased with increasing depth. During the CVOO-3 deployment (2009-2011), peak mass 280 fluxes at both 1 km and 3 km were highly correlated ($R^2=0.69$, N=16, p-value <_0.05). The pattern showed no temporal shifts of flux maxima during winter 2010, the same period collected the flux maxima despite a vertical distance of 2 km between the two traps. This suggests that the material settled faster than 100 m d⁻¹ (Fischer et al., 2016). During the deployment CVOO-4 (2011-2012), however, the mass flux peak during winter 2012 was delayed 285 by one cup (26.5 days) when comparing the upper and lower traps (Fig. 4) and flux correlations between the two trap depths were weaker, though still statistically significant (R²=0.54; N=16; p-value <_0.05). In 2016 (CVOO-7), particle settling velocities $<100 \text{ m} \text{ d}^{-1}$ were estimated from February to March due to the temporal shift in mass flux maxima by one cup (28 days, Fig. 4). Nevertheless, overall correlations between the upper and lower mass fluxes (CVOO-7) were high ($R^2=0.81$, N=13) and statistically significant (p-value < 0.05).

290 3.4. Diatom fluxes and <u>community</u> composition of the assemblage

We here combine new with former diatom data only for the upper traps at the CVOO. In an earlier study, Romero et al. (2016) published and discussed diatom fluxes from the mooring deployments CVOO-3 and CVOO-4 (Dec

2009-Oct 2012). Here, we add CVOO-7 (Sept 2015-Aug 2016, upper traps; Table 1). Marine diatoms delivered most of the BSi flux. Silicoflagellates, radiolarians, the dinoflagellate *Actiniscus pentasterias* and land-derived
295 freshwater diatoms and phytoliths were sporadically present. The total diatom flux ranged from 6.2 x 10⁵ to 2.3 x 10³ valves m⁻² d⁻¹ between December 2009 and August 2016 (average = 9.4 x 10⁴ valves ±1.2 x 10⁵). Diatom maxima (>9.4 x 10⁴ valves m⁻² d⁻¹) mainly occurred <u>during</u> winter and fall (Fig. 5c); minor peaks occur <u>during the middle of spring 2010, middle spring and late summer 2011. Except for this later maximum, summer generally showsed mostly the lowest diatom fluxes.
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300 The marine diatom community was composed of 118 marine species. The average relative contribution of main diatom species or group of species over the whole trap experiment interval was: *Bogorovia* cf. *spp.Bogorovia* spp. (12.11_%), *Nitzschia interruptestriata* (11.64_%), *Nitzschia bicapitata* (7.26_%), *Nitzschia capuluspalae* (5.15_%), *Thalassionema nitzschioides* var. *parva* (5.00%) (sum of the average relative contribution of these five species = 41.2_%). Accompanying taxa were resting spores (RS) of *Chaetoceros spp.* (3.51_%), *Azpeitia tabularis* (3.49_%),

Fragilariopsis doliolus (3.19_%), Thalassiosira subtilis (2.10_%), and Roperia tesselata (1.90_%).

3.5. Composition of settling particles and flux relationships between upper and lower traps

The overall composition of sinking materials-_in the upper traps was 2.1-5.9 % of BSi, 3.1-5.7 % organic carbon, 48-68 % of total carbonate and 16-36 % of lithogenic material. Lower traps collections contributed 3.1-6.4 % of BSi, 3.2-5.7 % of organic carbon, 44-58 % of carbonate and 29-40 % of lithogenic material to total mass flux, based on annual means. Excluding the extreme winter ACME-2010 (Fischer et al., 2016), we observe decreasing percentages of BSi and organic carbon with increasing depth and more or less stable contributions of carbonate and lithogenic materials to total flux. Winter C:N ratios were between 8.9 and 10.0 for the upper traps and between 7.1 and 10.4 for the lower traps (excluding the year 2010, Table 3), respectively, thus being in the range of partly degraded phytodetritus collected in the deep ocean (Schneider et al., 2003). However, during the ACME 2010, winter C:N ratios were 13.8 for the upper and 15.5 for the lower traps, respectively (Table 3).
Figure 6 shows the changes of total mass fluxes (numbers) and its composition during winter for the upper traps to reveal the potential flux output of the eddies passing during the winters 2010, 2011, 2012 and 2016 at CVOO. Winter flux compositions varied among years and oceanographic conditions (Fig. 6). Only organic carbon content remainsed rather constant, despite different total mass and organic carbon fluxes during winter (Fig. 6, Table 3).

320 remainsed rather constant, despite different total mass and organic carbon fluxes during winter (Fig. 6, Table 3). Under oligotrophic conditions in winter 2011 (Figs. 1b, 2), lithogenic and BSi contributions were low, whereas the percentage of carbonate was high at both trap depths. Particle flux compositions <u>during</u> winters 2010, 2012 and 2016 during low-oxygen ACME passages (Fig. 3) showed comparable values for the upper trap collections (Fig. 6). Lithogenic content was generally high (around <u>one third</u>^{1/3} of the total flux), except-<u>during under</u> oligotrophic conditions <u>during winter 2011</u> (Fig. 6); <u>during this season, the contribution of lithogenic materials</u> was unusually low (5.4%) for this region while carbonate amounted to 80 % (Fig. 6). Winters 2012 and 2016 showed almost similar total fluxes (98 and 96 mg m⁻² d⁻¹, respectively) and flux constituents.

Flux components of both trap depths showed no correlation during winter 2011 under oligotrophic conditions (Table 2). However, winter 2010 showed a high correlation coefficient (above 99 % confidence -level-) between organic carbon and lithogenic fluxes at both trap depths (Table 2), while none of the other flux components correlated. In contrast, a relatively high R² between organic carbon and lithogenic fluxes was observed during winter 2012 for the upper trap, indicating differences between both ACMEs in 2010 and 2012. DuringIn winter 2012, the correlations between organic carbon and BSi, carbonate and lithogenic fluxes become weaker with increasing depth.

335 3.6. Seasonal patterns of biogenic and lithogenic fluxes

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The seasonal flux pattern for BSi, organic carbon, total carbonate and the lithogenic components are given in Fig. 7 on a Julian day scale. The flux signals from 2010 showed a high seasonality with discrete peaks from January to February (Fig. 7). The deep-flux peak at 3 km from February to March 2010 was even more clear-pronounced due to flux focusing (Fischer et al. 2016). The yYear 2012 revealed high fluxes from January to March in the upper 340 trap with a step-like decrease during spring (Fig. 7a). The deeper traps showed higher individual peaks for BSi, organic carbon, total carbonate and the lithogenic fluxes (Fig. 7). When low oxygen eddies approached, particle fluxes increased stepwise starting during fall to values of ca. 100 mg m⁻² d⁻¹ (deep traps, Figs. 4, 7), where after they declined during the turn of the year, and increased again to form a significant eddy-induced flux peak during late winter to early spring (Fig. 7). Total carbonate flux is a mixture of different primary and secondary producers, i.e. planktonic foraminifera, coccolithophores, pteropods and calcareous dinoflagellates. However, the exact 345 composition of the flux components in different environments is largely unknown and difficult to assess quantitatively (e.g., Guerreiro et al., 2021). This is in part reflected by the different seasonality compared to the other components during the strongest anoxic event observed during February 2010 (Figs. 3, 4), where the total carbonate fluxes (mostly foraminifera, Fischer et al., 2016) showed a minimum (Fig. 7). Furthermore, the 350 carbonate record in the shallow trap during 2010 revealed a completely different seasonality compared to the other flux components with a peak during late spring (June 2010, Fig. 7). During the other years and seasons, carbonate flux patterns are comparable to the other flux components (Fig. 7).

4. Discussion

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Biogeochemical responses in terms of organic carbon fluxes from different types of eddies in oligotrophic oceans are difficult to quantify (e.g., Fischer et al., 2016). In particular, the transfer mechanisms and processes of organic carbon sequestration associated with eddies are still a matter of controversial debate (e.g., Benitez-Nelson and McGillicuddy, 2008). Here, we focus the discussion on the flux patterns and seasonality of total fluxes and compositions of exported materials associated with the passages of different eddy types north of the Cape Verde Archipelago at site CVOO (Fig. 1a)-, We and further examine organic carbon flux attenuation in the water column 360 between ca. 1 and 3 km water depth at CVOO in relation to the oxygen availability at epi- and mesopelagic depth within passing eddies.

4.1. Flux patterns and seasonality associated with low oxygen eddies vs. oligotrophic background sedimentation at site CVOO

- Site CVOO is located within a corridor for mesoscale cyclonic (CE) or anticyclonic eddies (including ACME), originated eastward off the west African coast (Fig. 1). Schütte et al. (2016b) found a large variability in oxygen 365 consumption between different types of eddies (CE, ACE, ACME) and surface chlorophyll. They allocated this to (1) differences in the initial conditions in coastal waters where eddies originated, and (2) the degree of isolation as well as the external forcing (e.g. wind, dust/iron input) occurring en route to site CVOO. As a consequence, one might expect a high variability in the release of particles, seasonality and flux magnitudes derived from different
- 370 eddies, all of which are also significantly affected by zooplankton communities (e.g. Hauss et al., 2016; Goldthwait and Steinberg, 2008).

The seasonal flux patterns influenced by low oxygen eddies that reach CVOO during late fall and winter look quite rather consistent (Fig. 7). Total flux often reached values above 100 mg m⁻² d⁻¹ (Figs. 4, 8a, b) and clearly exceeded the typical fluxes characteristic for oligotrophic settings of ca. 50 mg m⁻² d⁻¹ (e.g., Bory et al., 2001_{rs} Fischer et al.,

- 375 2010; Korte et al., 2017 (site M3)) and showed a low to moderate seasonality (Berger and Wefer, 1990). Mean mass fluxes with standard deviations (1 SD) at the oligotrophic site BATS was 31.1±19.0 to 1500 m and 35.2±16.9 mg m⁻² d^{-1} to 3200 m based on long-term recordings (Conte et al., 2001), substantially lower than the fluxes measured during low oxygen eddy passages at CVOO. However, fluxes from BATS are close to the CVOO record during winter 2011 (Figs. 4, 8a) when oligotrophic conditions prevailed at site CVOO. Fluxes of BSi and organic 380 carbon at CVOO were very low during winter 2011 (Fig. 7), matching low chlorophyll values (Figs. 1b, 2). The
 - entire flux record (Figs. 4, 8), however, suggests that the oligotrophic conditions during winter 2011 is an

exceptionwere exceptional and the occurrence of low oxygen eddies delivering higher particle fluxes mainly during winter is the regular situation at CVOO. This observation supports statements of an existing eddy corridor occurring north of the Cape Verdes and that mesoscale eddies seem to be created rather regularly at the coast 385 around summer and reach site CVOO during late fall to winter (e.g. Karstensen et al., 2015; Schütte et al., 2016a). Elevated winter fluxes in winter at CVOO delivered by the different eddies awere not generally correlated to a particular environmental parameters at CVOO (Fig. 2). In winter 2010, fFor example, during winter 2010, SSTs remained relatively high, while chlorophyll and dust deposition were low (Fig. 2); but however, the resulted output of the ACME in terms of fluxes was high (Fig. 4, 7). Comparably high fluxes were recorded for the winter ACMEs 390 in 2012 and 2016 (Fig. 4, 7); however, under different environmental conditions (low SSTs, high chlorophyll and dust depositions) (Figs. 1b, 2). Typical oligotrophic fluxes with low seasonality were observed during winter 2011 under environmental forcing similar to that of the extreme winter 2010-ACME. During winter 2011, however, the oxygen drawdown was less severe than during the other winter seasons (Fig. 3), albeit-but salinity was low, suggesting the presence of a coastal eddy (ACME) around CVOO (Tables 2, 3). The most severe and longest 395 oxygen drawdown (reaching almost anoxia), combined with a low salinity-low, wereas observed for the entire February 2010 (Fig. 3), largely overlapping with the collection period of one sampling cup of the CVOO-3 sediment traps (cup #3, Fischer et al., 2016). This resulted in clear distinct peaks in-of all fluxes (except total carbonate flux (Fig. 7)-during this time interval and a significant increase of fluxes with depth (Fischer et al., 2016), suggesting that an eddy passed directly over the mooring site CVOO. Overall, only winter organic carbon 400 fluxes to the upper traps tend showed a tendency to increase with satellite chlorophyll (Table 3), but this relationship is statistically not significant ($\frac{-R^2=0.69}{N=4}$; N=4; p-value = 0.168). On the other hand, satellite chlorophyll peaks during winter-spring largely followed maxima in dust deposition rate (Fig. 2), whereby no statistically significant relationship between both satellite-derived environmental parameters is seen. This could indicate that dust may act as some kind of fertilizer (e.g. of nitrogen or phosphate) in the oligotrophic Northeastern Atlantic 405 suggested by Fomba et al. (2014) and Guerreiro et al. (2021).

The interpretation of total carbonate fluxes and its seasonality is complex, largely due to the unknown groups of carbonate-secreting primary and secondary producers contributing to total carbonate. Generally, planktonic foraminifera and coccolithophores constitute the major part in the Atlantic Ocean while pteropods are less important (e.g., Guerreiro et al., 2021). However, to quantitatively assess coccolithophore-carbonate, counts, size and mass of individual coccoliths of different species (e.g. Guerreiro et al., 2021), performed on very small splits (in the order of 1/1000 or even less) are needed. This method leads to relative large errors in the calculation of carbonate. In a recent coccolithophore-carbonate flux study conducted in the tropical Atlantic, coccolithophores accounted for ca. 15 and 23 % of the carbonate mass (minimum values, ca. 1 km traps) in the oligotrophic and

mesotrophic settings (Guerreiro et al., 2021). This range of percentages may apply to the oligotrophic site CVOO

- 415 as well and it would mean that planktonic foraminifera account for about one half of the total carbonate flux. The time-consuming counting data of coccoliths were not performed for the complete CVOO 3-7 time series and total carbonate fluxes are therefore not discussed in detail. In the study on the CVOO-3 deployment (2009-2010), however, Fischer et al. (2016) counted coccoliths, planktonic foraminifera and pteropods and estimated carbonate fluxes of these groups. It turned out that pteropods accounted for ca. 4-8 % and foraminifera between ca. 32 and 52 % of the total carbonate fluxes (1290 m trap) during winter 2010 and the passage of the suboxic ACME (Fischer
- et al., 2016; Karstensen et al., 2015). Unpublished upper trap carbonate fluxes contributed by coccolithophores ranged between ca. 12 and 38 % during the ACME passage. The data indicate a sequence of contribution by the carbonate producers at CVOO during winter 2010 from planktonic foraminifera, accounting roughly about one half of the carbonate production/flux, followed by slightly lower contributions by coccolithophores, and with lowest contributions by pteropods.
 - The deep flux pattern of all components showed more distinct peaks and a higher seasonality (SI = ca. 2.4) during the passages of low oxygen eddies than to in the shallower traps (SI = ca. 2.0; Figs. 7, 8). Usually, the upper traps in the open ocean record a higher seasonality (Berger and Wefer, 1990; Conte et al., 2001), which is due to a smaller catchment area and a shorter vertical distance for the settling material between production in surface waters
- and particle transfer to 1 km compared to the deeper traps. In contrast, seasonality is generally lower in the deep traps (3-4 km, e.g., Conte et al., 2001) due to a larger particle catchment area (Siegel and Deuser, 1997), longer particle descent time, and a higher impact-contribution of particles from lateral advection (McCave, 1984).
 However, thisThe typical pattern of a decreasing seasonality with increasing depth iwas not observed at CVOO (e.g. Fig. 7). This is most probably-likely due to the occurrence of eddies with their different particle transport, a potential subduction of particles at frontal systems (e.g. Boyd et al., 2019) and flux focusing within funnel like structures during the winter ACME 2010 (Fischer et al., 2016). The latter authors interpreted the two to three-fold
- increase of winter biogenic and lithogenic flux components between ca. 1 and 3 km water depth (and a perfect match of upper and lower lithogenic fluxes, $R^2=0.97$, N=17, p-value < 0.05) as a concentration mechanism of particles in funnel-like structures (Zhang et al., 2014; Waite et al., 2016), associated with the direct passage of the
- 440 low oxygen ACME over the trap location (see also 4.3). The BSi flux pattern of eddies in the upper traps derived from eddies showed a higher seasonality compared to organic carbon and lithogenic fluxes (Fig. 7), the two latter showing a significant correlation (Table 2). This suggests that BSi (mostly from diatoms) and organic carbon together with the non-biogenic components may have had different particle sources within the respective eddies. Diatoms are mostly produced at the eddy edges (Shih et al., 2015) due to vertical nutrient supply (Karstensen et al.)
- al., 2015), where a strong shear<u>, high turbulence</u> and high particle concentrations could result in the formation of

large and fast settling diatom aggregates (e.g., Kiørboe, 2001). At these frontal zones, a concentration threshold for diatoms to encounter each other and form aggregates may be reached (Jackson and Kjøørboe, 2008). Most of the Dominant diatoms at CVOO possess small valves (ca. 10-15µm) but produced high numbers (Fig. 5c) which could not sink individually sink at higher enough rates to form the observed sharp flux peaks-_(Fig. 7). Larger diatom aggregates, presumably formed at the eddy edges, may sink passively (biological gravitational pump, Boyd et al., 2019), although their sinking could be accelerated by active subduction at frontal structures (eddy subduction pump, Boyd et al., 2019) to form a-distinct flux signals to in the 1 km traps and below. However, grazing and transfer of biogenic matter via fecal pellets to the bathypelagic may have occurred as well, even under low oxygen concentrations. Preliminary microscopic analysis and fecal pellet counts of cups # 1-5 of the deployment CVOO-3 (upper trap) revealed a higher contribution from zooplankton fecal pellets during the period when the low oxygen eddy (ACME) was passing over the trap position during February 2010 compared to non-eddy conditions. This was quite surprising but needs further confirmation and studies at site CVOO before reliable conclusions can be drawn.

4.2. Diatom sedimentation at CVOO affected by eddies

- 460 The predominant occurrence of highest diatom flux maxima <u>dur</u>ing winter and fall (Fig. 5) temporally matches<u>d</u> the passage of ACMEs over site CVOO. This seasonal pattern suggests that mesoscale edd<u>yies</u> impact diatom productivity through two primary processes, namely, (1) pulsed nutrient injections into the sunlit layer, and/or (2) horizontal advection of phytoplankton (Gaube et al., 2014). Since ACMEs north of the Cape Verde Archipelago are a hotspot of primary productivity (Hauss et al., 2016) with elevated chlorophyll concentrations (Karstensen et al., 2015; Schütte et al., 2016a), and high content of nitrate, phosphate, and silicate in the mixed layer (Fiedler et al., 2016; Karstensen et al., 2017), we favor the scenario of nutrient injection. This promotes diatom productivity under regular, open-ocean oligotrophic conditions and translates into substantially increased productivity in surface waters of the ACME when passing through the CVOO site (Romero et al., 2016).
- The seasonal dependence of diatom production on the ACME-associated nutrient delivery resultsed in a strong seasonality of <u>diatom</u> flux occurrence: independent of the year, between ca. 45 and 65 % of the total yearly diatom flux at the CVOO site wasere captured in intervals shorter than 70 days, leading to a strong seasonality. During episodes of nutrient injections, small diatoms <u>may have</u> reproduced fast and valves <u>potentially</u> sank quickly after the formation of large diatom aggregates <u>or the production of fecal pellets(see chapter above)</u>, possibly diminishing the chance of being grazed <u>intensively e.g.</u>, by meso-zooplankton (Smetacek, 1985). Earlier observations in the
- 475 low oxygen Cape Verde ACME in winter 2010 showed that meso-zooplankton populations were reduced due to

suboxia within ACMEs crossing site CVOO <u>during winter 2010</u> (Fischer et al., 2016) and, hence, grazing pressure was <u>probably likely</u> reduced (Karstensen et al., 2015; Hauss et al., 2016). <u>The decline of diatom maxima by mid-January 2016</u> The decline of the diatom maxima was likely due to the decrease nutrient <u>depletion</u> availability (mainly dissolved silica) after the ACME moves further west (Fiedler et al., 2016). The diatom flux returned to values typical of the low latitude pelagic areas of the oligotrophic northeastern Atlantic Ocean (Mittelstaedt, 1991;

on their efficiency in nutrient uptake (Smetacek, 1985). Although the overall seasonality of total diatom and BSi

Oschlies and Garçon, 1998; Romero et al., 1999) <u>dur</u>ing early spring and summer. The obvious success of the small-sized diatoms (valve size range = $10-15 \mu$ m) during ACME passages possibly lays in their fast growth rates under high-turbulence conditions and the advantage conferred by the small cell size

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- fluxes broadly matched (winter until mid-spring, Fig. 5), the comparison of major peaks between both parameters showed some leads/lags. This is most evident <u>during</u> winter 2016, when the highest diatom peak occurred between mid-December 2015 and mid-January 2016, while BSi had two peaks: the first between mid-November and mid-December 2015, and the second <u>during</u> March 2016. The temporal difference in the occurrence of peaks of diatoms (microscope counts) and BSi fluxes (chemical analysis) could be related to the temporal contribution of species.
- The late 2015/early 2016 diatom peak was dominated by species with predominantly valves smaller than 12 μm in diameter/length, such as *T. nitzschioides* var. *parva*, *N. bicapitata*, *N. capuluspalae* and RS *Chaetoceros*, while diatom with valves larger than 15 μm dominated before and after the main 2016 diatom peak. The presence of benthic diatom species (*Delphineis surirella*, *Neodelphineis indica* and *Pseudotriceratium punctatum*) in the upper trap cups (ca. 1 km) was rather low (ca. 5 % of total diatoms) and is attributed to shallow water coastal origin. These species are assumed to be transported from the west African coast to CVOO within eddies (Karstensen et al., 2015). The same benthic species have also been found offshore Cape Blanc (Mauritania) at the sediment trap mooring sites CBeu (Romero et al., 2020) and CBmeso (Romero et al., 2021). Their occurrence in the sediment trap samples in the hemipelagic points to lateral transport within the eddy from the inner shelf (< 50 m) of the African coast to CVOO. Taking all oceanographic, biogeochemical and biological observations
- 500 <u>together, an origin of benthic diatom groups from the southward lying Cape Verde Plateau to CVOO seems rather</u> unlikely.

4.3. Carbon flux attenuation and transport within eddies and under oligotrophic conditions

Studies from OMZ in the Eastern Tropical Atlantic showed that organic carbon flux attenuation of large particles is reduced, thereby increasing the efficiency of the biological carbon pump (Rasse and Dall'Olmo, 2019). However, small particles seem to react differently and show a normal-_to-_higher attenuation_inside the OMZ

compared to the outside where enough oxygen is available (Rasse and Dall'Olmo, 2019). During Tthe winter 2010-ACME, show that organic carbon fluxes increased by more than two-fold with <u>increasing</u> depth due to flux focusing (Fischer et al., 2016; Table 2, Figs. 7, 9). In addition, other biogenic flux components such as BSi but also the lithogenic material increased strongly with increasing depth by a factor of ca. two to three-fold

- 510 simultaneously. Fischer et al. (2016) interpreted this observation as a concentration mechanism of particles in a funnel-like structure associated with the direct passage of the ACME over the trap location. Waite et al. (2016) named this the 'wine class effect'. Other authors described funnel-like eddy structures from oceanographic observations (e.g., Zhang et al., 2014; Waite et al., 2016). However, the downward transport of larger marine snow particles which may occur in spiral-like trajectories within eddies is unknown from direct observations.
- 515 During oligotrophic conditions <u>as observed for in</u> winter and spring 2011, however, organic carbon fluxes show<u>ed</u> a comparable slope to the Martin curve (open-ocean composite) or the log-line (Fig. 9). <u>IDuringn</u> winters 2012 and 2016, when <u>other</u> ACMEs reached site CVOO, the deep ocean fluxes clearly exceeded the projected values from the Martin curve (Fig. 9). Low oxygen values in the epipelagic during the ACME 2012 (Schütte et al., 2016a) might have reduced organic carbon degradation (Fischer et al., 2016). This decreased degradation in the epipelagic,
- 520 however, would also have caused higher flux to the upper traps <u>deployed atin</u> 1 km-. This leads to the question of the potential factors, which act to reduce organic carbon degradation in the bathypelagic. According to Iversen and Ploug (2010), particle settling rates are critical for carbon flux attenuation and are primarily influenced by ballast content, composition and density of the settling particles (Ploug et al., 2008). A highly ballasted particle stock within eddies, most probably due to high dust dry deposition <u>during</u> winter in this region (Gama et al., 2015), could
- 525 contribute to lower carbon flux attenuation during eddy passages, also in the deeper water column. On the other hand, an active downward transport of particles at frontal systems, i.e. at the boundaries of these structures, should be considered ('eddy subduction pump', Boyd et al., 2019), thus reducing carbon degradation and leading to higher carbon fluxes above the predicted values (Martin et al., 1987).

Estimated carbon fluxes at 100 m (flux below the photic zone) from the deep traps were between ca. 5.5 and 19.5
mg C m⁻² (winter means), including the oligotrophic background scenario of winter 2011 (ca. 12 mg C m⁻² d⁻¹; Fig. 9). The highest value of 19.5 mg C m⁻² d⁻¹ in during winter 2012 iwas about one order of magnitude lower compared to organic carbon fluxes of 190-230 mg m⁻² d⁻¹ at 100 m derived from oxygen consumption rates during March 2014 at site CVOO (Fiedler et al., 2016). This discrepancy may be due to a strong variability in productivity and export flux between the different eddies (2012 and 2014) or caused by short-term seasonal changes of the oxygen consumption rates. At the nearby oligotrophic sediment trap site NASG in the North Atlantic subtropical gyre, a POC export flux of ca. 15 mg m⁻² d⁻¹ at 100 m was obtained, decreasing severely in the mesopelagic to almost zero at ca. 1 km water depth (Marsay et al., 2015). In the CVOO recordings, organic carbon fluxes during

winter 2011 were 1.12 and 0.45 mg m⁻² d⁻¹ to the 1 km trap during oligotrophic conditions, which resembles findings from site NASG (Marsay et al., 2015). During the other years, winter organic carbon fluxes at ca. 1 km were significantly higher at CVOO (3.5-5 mg C m⁻² d⁻¹, Table 3, Fig. 9) compared to typical oligotrophic settings in the NE Atlantic Ocean.

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Altogether, carbon fluxes during eddy passages (Fig. 7) seem to indicate that attenuation-<u>i_wa</u>s reduced between ca. 1 and 3 km water depth (Fig. 9). This cannot be linked to the OMZ, which occur between ca. 75 and 400 m water depth (Schütte et al., 2016a). The increased fluxes compared to the background situations (low biomass

- 545 combined with less severe oxygen drawdown; Figs. 1b, 2, 3) may be due to a combination of higher production due to local eddy upwelling, higher aggregate formation due to the concentration of small diatoms at the eddy boundaries (Shih et al., 2015), and low oxygen concentrations, limiting degradation of the organic matter in the upper water column, i.e. allowing more organic matter to sink to the deep ocean. Whether the latter is due to reduced zooplankton grazing or less microbial degradation or both needs further exploration of particle formation
- and fluxes, and degradation in the epi- and mesopelagic.
 Except during the extreme winter ACME 2010, the molar C:N ratios were between ca. 9 and 10, falling in the range for degraded marine phytoplankton detritus (<u>Conte et al., 2001;</u> Schneider et al., 2003; Fischer et al., 2010) (Table 3). Only <u>during winter 2016</u>, a mean <u>C:N</u> value of 7.1 points to rather fresh material sinking to the 3 km trap (Table 3). Under oligotrophic conditions <u>during</u> winter 2011, C:N ratios were <u>slightly</u> higher (10-10.4) than
- during the eddies in 2012 (8.7-8.9) and 2016 (7-9). This could point to a higher degradation due to zooplankton grazing <u>during</u> winter 2011. <u>Other potential causes for these elevated C:N rations might be a more distant source</u> (lateral advection) and, thus, an older age of particles combined with a higher degradation of particles reaching the trap during winter 2011.

However, during the extreme winter 2010-ACME in 2010, Fischer et al. (2016) obtained mean winter-C:N ratios

of 13.5 and 15.7 at 1 and 3 km depth, respectively, which is far above the classical Redfield Ratio (Redfield et al., 1963) and typical sediment trap values for degraded phytodetritus in the bathypelagic (Schneider et al., 2003; Martin et al., 1987; Conte et al., 2001). The high values suggest that-the sedimentation of highly degraded zooplankton fecal pellets or very slowly settling organic matter. However, estimated settling rates of particles during the low oxygen ACME during winter 2010 contradicts this scenario (Fischer et al., 2016). The C:N ratios during the ACME-2010 (CVOO-3, both depths) provided a best fit with a non-linear function, whereas the 2012 data (CVOO-4, both depths) showed a normal linear relationship with a high correlation coefficient (Fig. 10). Investigating the composition of organic matter during the winter ACME-2010, Fischer et al. (2016) argued that the <u>unusually</u> high C:N ratios may be best explained by nitrate limitation in the surface layer of the eddy. Nitrogen limitation and recycling within low oxygen ACMEs are also considered (Karstensen et al., 2017; Löscher et al.,

570 2015). Due to flux focusing, C:N ratios increased with depth to 15.7. Individual collection cups provided C:N ratios around even as high as 25 (deep traps; Fischer et al., 2016). Based on the organic carbon composition, we conclude that the conditions prevailing in the surface layer of the eddies <u>during</u> 2010, 2012 and 2016 were different, despite the fact they were characterized as ACMEs (Schütte et al., 2016a) (Table 2). Indeed, the oxygen anomaly <u>dur</u>ing winter 2010 was lower and of longer duration (the entire February 2010 approaching zero <u>oxygen</u>)

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5 compared to 2012 (Fig. 3; Schütte et al., 2016a), thus suggesting different biogeochemical conditions. However, a relationship between fluxes (e.g. of organic carbon) and the oxygen drawdown and duration of low oxygen conditions due to eddy passages over site CVOO <u>is-can</u>not <u>be</u> observed.

5. Conclusions and Outlook

580 A multi-year monitoring of the biogeochemical particle fluxes of passing eddies north of the Cape Verde Islands (site CVOO, oligotrophic setting) revealed the following major findings. - <u>dD</u>uring eddy passages <u>during</u> the winters of 2010, 2012 and 2016, particle fluxes showed a consistent sinusoidaleasonal flux pattern with increasing fluxes in fall, a decrease at the turn of the year and maxima around February-March.- The flux of BSi showed a stronger seasonal pattern with distinct peaks compared to organic carbon and the lithogenic component. In 585 addition, BSi flux patterns at 3 km depth revealed a higher seasonality compared to the BSi flux collected at 1 km depth level which was interpreted to be due to passages of low oxygen eddies..., <u>T</u>the diatom assemblage during winter eddy passages in winter was dominated by small species and the diatom flux was not related to the organic carbon or BSi fluxes. Such small species were presumably transported downwards within large fast settling diatom aggregates or fecal pellets, - wWe speculate that BSi and Corg/lithogenics originate from different sources within 590 the eddies and are transported differently to depth. Large BSi-rich ballasted aggregates with-containing diatoms may be formed at the eddy boundaries where high shear and turbulence occurs and may be actively transported downwards (via the 'eddy subduction pump', Boyd et al., 2019) at the eddy boundaries to constitute distinct flux peaks at depth., deep ocean eCarbon flux attenuation between ca. 1 and 3 km at CVOO appears to be reduced limited during low oxygen eddy passages when compared to the Martin eCurve (open-ocean composite). This may 595 be due to a combination of a reduced microbial degradation of organic carbon and/or lower zooplankton grazing under low oxygen availability within the eddies, - wWe suggest that high productive and low oxygen eddies (ACMEs) at site CVOO sequester more carbon (except in winter 2011) compared to oligotrophic conditions combined with less severe OMZ in the epi- and mesopelagic of the eastern North Atlantic.

Thise study presents particle fluxes over a ca. 7-seven year long period from the oligotrophic site CVOO 600 characterized by a regular passage of low-oxygen eddies containing elevated phytoplankton biomass. This resultsed in significantly higher organic carbon fluxes than during oligotrophic conditions at CVOO (during winter 2011) or in the North Atlantic Subtropical Gyre (e.g., sites EUMELI-oligo, NASG or BATS). Theis study supports other findings, suggesting a positive effect of low-oxygen eddy structures or OMZ on organic carbon export and sequestration (e.g., Weber und Bianchi, 2020). However, it remains unclear why Given that similar eddies (e.g. 605 ACMEs) with comparable oxygen/salinity conditions release different flux signals and compositions at bathypelagic depths suggests that productivity is intermittent, may be triggered by vertical nutrient flux into the euphotic zone. One reason Sampling with a single mooring could be another reason for the discrepancies because could be that the eddies approaching site CVOO can directly moved over the mooring site (i.e. flux focusing during winter ACME-2010, Fischer et al., 2016) or could have touched affected CVOO only marginally. Deep ocean sediment traps collect particles from a relative large surface area (100 km² or more; Siegel and Deuser, 1997), 610 therefore we might the traps record flux signals from more remote areas. In contrast, oxygen and salinity weare directly measured with sensors at the CVOO sitemooring line and, thus, a comparison of both time series (sediment

traps and sensors) maywill be limited.

Surface water conditions such as satellite measured chlorophyll did not show a statistical significant relationship
 to the fluxes, e.g. of organic carbon. Carbon degradation between ca. 1 and 3 km during eddy passages appears to be smaller than predicted although the reasons remain unclear so far. Organic carbon attenuation may be less due to a shorter residence time of the settling particles (Iversen and Ploug, 2010) within the low oxygen eddies when microbial degradation and zooplankton grazing was reduced. A combination of the biological gravitational pump with the eddy subduction pump (Boyd et al., 2019), leading to high particle settling velocities may have led to a higher efficiency of the biological pump within the ACMEs in winters 2010, 2012 and 2016.

Data availability. Data are available at <u>www.pangaea.de</u> (data were already submitted, doi will be given upon exception of the manuscript, Fischer, 2021). <u>https://doi.pangaea.de/10.1594/PANGAEA.931052</u>

625 *Author contributions*. G<u>.</u>F and O<u>.</u>E<u>.</u>R wrote the manuscript. A.-K and J.C. devised the study at CVOO (GEOMAR) and provided the oxygen and the oceanographic data. M.I.<u>_and</u> N.M. <u>and K.-H. B.</u> contributed to interpretation and discussion of results. M.K. and G.R. prepared the sediment traps and performed the sample analysis.

630 *Competing interests.* The authors declare that they have no conflict of interest.

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645 *Review statement.*

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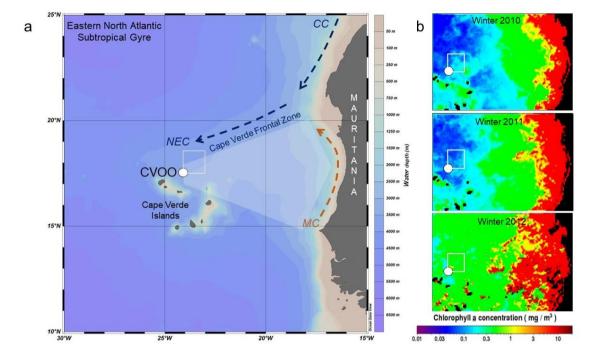


Fig. 1. (a) Location of the CVOO site in the eastern tropical North Atlantic with the major currents systems of the Canary Current (CC), the North Equatorial Current (NEC) and the Mauritanian Current (MC) (ODV map: Schlitzer, Reiner, Ocean Data View, odv.awi.de, 2021). Note the corridor of eddy passages from the African coast to CVOO schematically indicated as a light polygon. A white box with the environmental data from GIOVANNI is shown NE of CVOO. (b) Winter MODIS satellite chlorophyll (DJFM) between the African coast and the Cape
Verde Islands (site CVOO = white dot) for winters 2010, 2011 and 2012 (2016 is comparable to 2012, not shown) showing the increasing extensions of the high chlorophyll area (> 1 mg m⁻³) from the coast to the open ocean, approaching site CVOO.

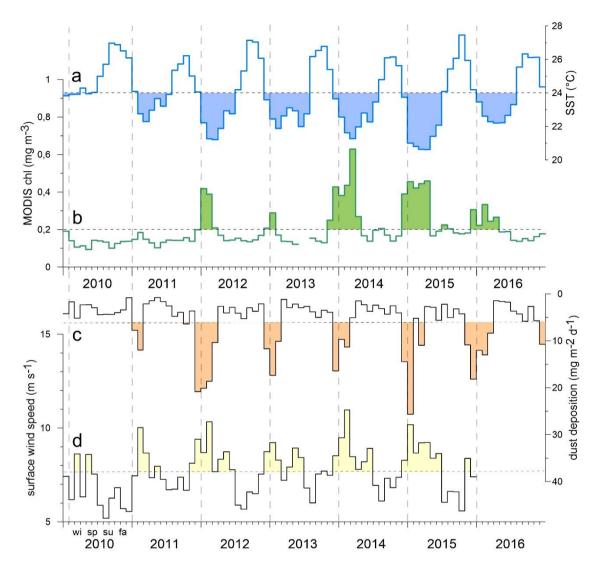


Fig. 2. Monthly SSTs (a), chlorophyll (b), modelled (MERRA) dry dust deposition (c) and surface wind speed (d) recorded in the study box northeast (17.5-18.5° N / 23-24° W) of CVOO between 2010 and 2016 (satellite-derived, from GIOVANNI, https://giovanni.gsfc.nasa.gov/giovanni/#service=TmAvMp&starttime=&endtime=). Note that during the extreme ACME <u>during</u> winter 2010, chlorophyll, surface wind and dust deposition were all low, combined with relatively high SSTs. Thereafter, surface biomass, winds and dust increased during winter and early spring. Horizontal dashed lines indicate mean values, peaks above or below are marked as filled bars. Vertical dashed lines mark years, wi sp su fa indicate the seasons <u>(winter, spring, summer, fall)</u>-

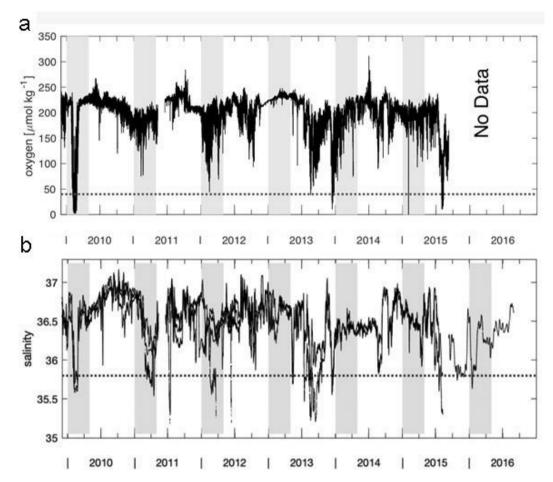


Fig. 3. CVOO time series of 12h low_pass oxygen (a, μmol kg⁻¹) and salinity (b, in PSS-78). Dotted lines are considered thresholds that indicate the passage of low oxygen eddies. Well isolated eddies of coastal origin are assumed to correlate with low salinity events, and eventually may be paired with low oxygen concentrations. However, a statistically significant relationship between oxygen (based on one sensor) and salinity (based on four to six sensors, see chapters 2.1 and 3.2) is not found. Grey shaded areas indicate the periods January to April for reference. For instrument depths see text_a.

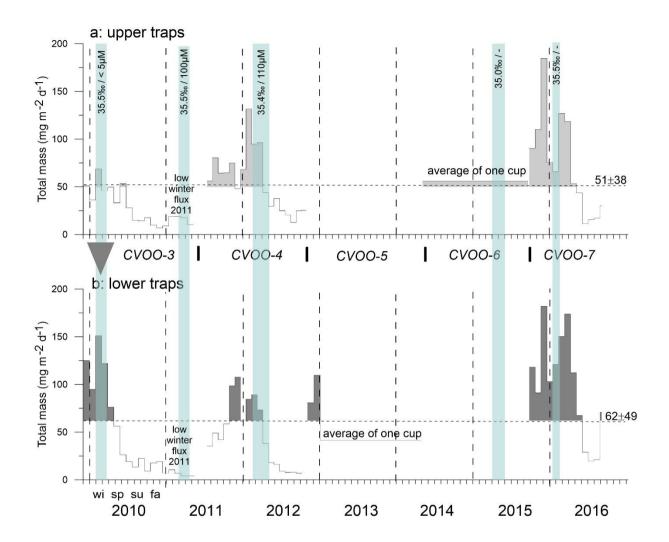


Fig. 4. Total mass fluxes between 2009 and 2016 for the upper (a) and the lower traps (b) and low oxygen/low salinity events during winter of a duration of one month and longer (vertical blue bars, with salinity and oxygen concentrations). Means with SD (horizontal stippled lines) were only slightly above typical oligotrophic flux values (ca. 50 mg m⁻² d⁻¹; Bory et al., 2001: Fischer et al., 2010; Korte et al., 2017). Peak fluxes (above the means) are grey-shaded to indicate maxima <u>dur</u>ing late fall and winter. <u>Black triangleArrow</u> indicates <u>'</u>flux focusing' during the winter ACME 2010 (Fischer et al., 2016). Note the low (= oligotrophic) fluxes <u>during</u> winter 2011 far below the means. Horizontal dashed lines indicate mean fluxes, vertical lines separate years, wi sp su fa indicate the seasons.

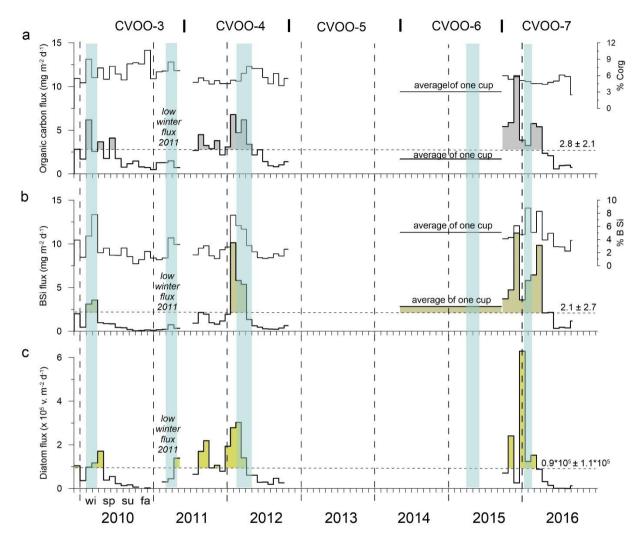


Fig. 5. Organic carbon (a), BSi (b) and diatom fluxes (c) of the upper traps at site CVOO-. <u>The relative contribution</u> (%) of organic carbon and BSi to total flux is given as well. Blue bars indicate the passage low oxygen/low salinity eddies in winter with a duration of one month and longer (see text). Flux peaks are highlighted (grey, olive and green) when above the mean values (horizontal dashed lines). Note that the peaks of diatom valves (largely composed of small species) only partly matched the BSi fluxes. Vertical dashed lines separate years, wi sp su fa indicate seasons.

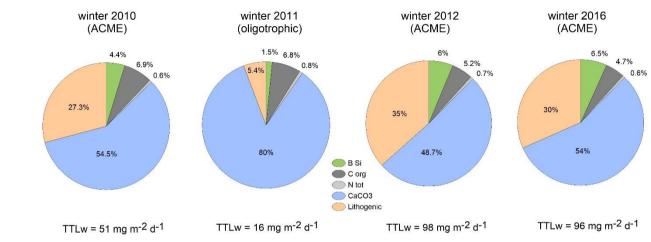
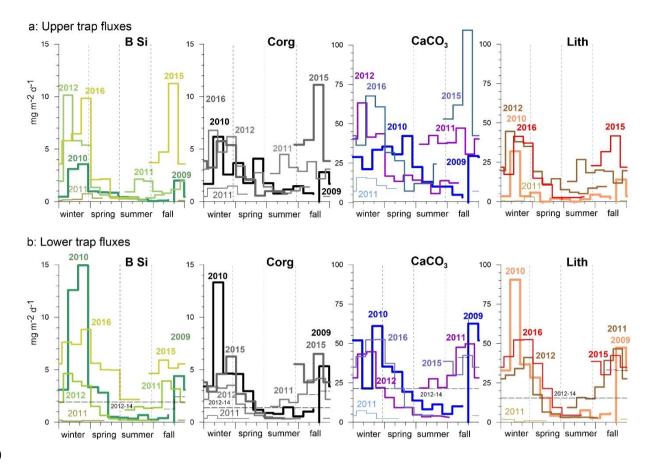




Fig. 6. Flux compositions <u>during</u> winter (% of total winter mass flux = TTL_w) <u>derived</u> from the upper traps during the low-oxygen ACME 2010 (Fischer et al., 2016), the low flux (oligotrophic) conditions <u>during</u> winter 2011 (<u>with</u> <u>low lithogenic and high carbonate contents</u>) and during the following ACMEs in winter 2012 and 2016 (high and almost equal total fluxes <u>and composition</u>). Lithogenic components constitute approx. <u>1/3one third</u> of the total flux, except during oligotrophic conditions <u>during</u> winter 2011. Note that organic carbon content is almost constant among the winter seasons despite variable total fluxes.



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Fig. 7. Upper (a) and lower trap (b) seasonal flux patterns of BSi, organic carbon, <u>carbonate</u> and<u>and</u>_lithogenics <u>fluxes</u> on a Julian day scale. In 2013, only one sampling cup was available which collected all the material (Table 1). Note the overall higher seasonality recorded in the lower traps (<u>Bb</u>) and for BSi in both trap depth levels. During the oligotrophic winter-spring 2011, fluxes remained <u>very</u>-low compared to the other years, revealing almost no seasonality.

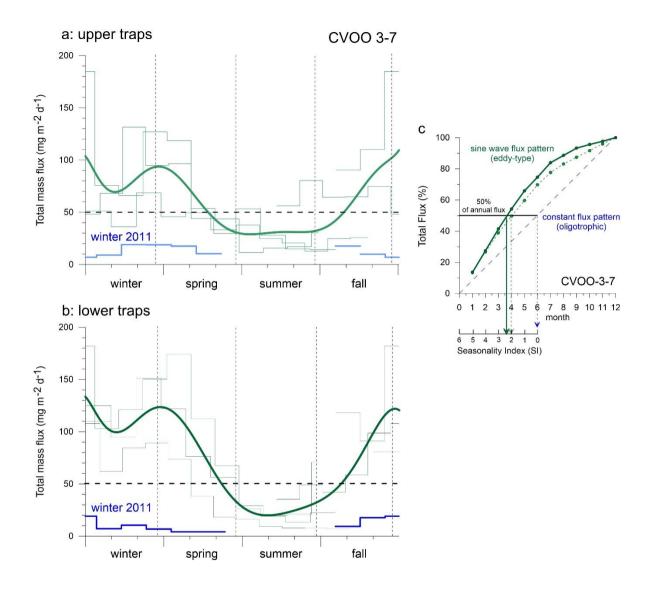
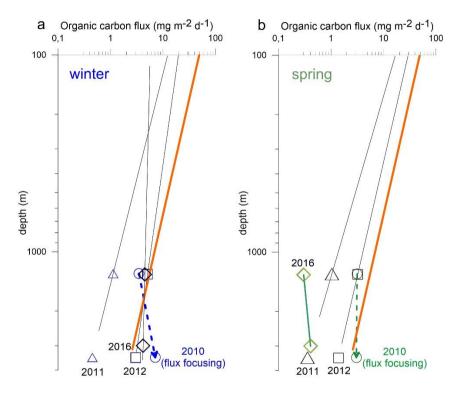


Fig. 8. Seasonal total flux patterns for the upper (a) and lower traps (b) characteristic for different types of eddies
(light and dark green (9-order polynomial fit) vs oligotrophic conditions <u>during</u> winter 2011 (blue: oligotrophic background with more or less constant flux/productivity pattern and low seasonality (SI-Index of 0-1 in c) at CVOO. <u>Grey shadedStippled horizontal line</u>: typical oligotrophic background fluxes (ca. 50 mg m⁻² d⁻¹) in the North Atlantic Gyre (see text). (c) Sum of total particle fluxes and Seasonality Index (<u>SI</u>, Berger and Wefer, 1990) for the upper (stippled light green) and lower traps (dark green) taken from the means in a/b. <u>The SI is defined as six minus the production half-time in months (Berger and Wefer, 1990)</u>. Note the overall higher seasonality (=

sine wave production) in the lower (SI = ca. 2.4 (= 6-3.6)) compared to the upper traps (SI = ca. 2.0 (= 6-4)) during eddy passages (2010, 2012, 2016). For comparison, a constant flux pattern, typical for oligotrophic settings is shown schematically in b.



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Fig. 9. Carbon flux attenuation (log-log plot) in the water column <u>dur</u>ing winter (a) and spring (b) for 2010 (extreme low oxygen ACME), 2011 (oligotrophic situation), 2012 and 2016 (ACME). Attenuation according to Martin et al. (1987; with b=-0.858, orange line) is shown. Note a reduced carbon flux attenuation than predicted by the Martin eCurve <u>dur</u>ing the winters 2010, 2012 and 2016, when low-oxygen/low salinity eddies passed. During the extreme winter ACME 2010, deep ocean fluxes increased strongly with depth (also in spring) due to flux focusing (arrows, Fischer et al., 2016). Fluxes more typical for oligotrophic conditions and carbon flux attenuation occurred in winter and spring 2011.

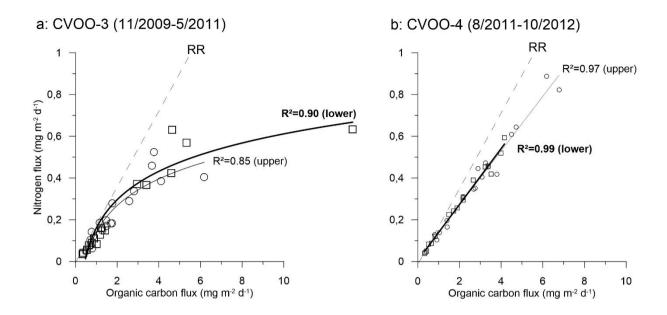


Fig. 10. Different C:N flux relationships (best fits) during the 2010 and 2012 ACME passages <u>dur</u>ing fall-winter (2011 oligotrophic fluxes are included in a); RR=Redfield Ratio (Redfield et al. 1963). Note the non-linear changes during the extreme 2010-ACME (a), pointing to nitrogen limitation and, for comparison, the linear relationship later in 2012 (b).

TAB	LES
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Trap deployment	Location		Trap depth	Start	End	Days sampled	Number of samples	Remarks/References	
	LAT N	LONG W	m			d	x days		
CV00-3	ca. 17°35.	ca. 24°15.	1290	2009-12-01	2011-05-11	522	18 x 29 d	Fischer et al. (2016);	
								Romero et al. (2016)	
			3439	2009-12-01	2011-05-11	555.5	17 x 29d;	Fischer et al. (2016)	
							1 x 62.5		
CVOO-4	ca. 17°35.	ca. 24°15.	1300	2011-07-12	2012-10-24	471	17 x 26.5;	Romero et al. (2016)	
							1 x 20.5		
			3449	2011-07-12	2012-10-24	450.5	17 x 26.5		
CVOO-5	ca. 17°35.	ca. 24°15.	2993	2012-12-01	2014-04-24	539	2 x 30.5;	3 samples only	
							1 x 478d		
CVOO-6	ca. 17°35.	ca. 24°15.	1304	2014-05-01	2015-09-07	500	1 x 500d	1 sample only	
CVOO-7	ca. 17°35.	ca. 24°15.	1304	2015-09-20	2016-08-29	344	12 x 28;		
							1 x 8d		
			3002	2015-09-20	2015-09-20	344	12 x 28;		
							1 x 8d		

Table 1. Data of sampling with sediment particle traps at site CVOO.

Corg		N=	B Si	CaCO ₃	lithogenic	structure
<u>flux</u>			<u>flux</u>	<u>flux</u>	<u>flux</u>	salinity/oxyge
$(mg m^{-2} d^{-1})$			(mg m ⁻² d ⁻¹)	<u>(mg m⁻² d⁻¹)</u>	$(mg m^{-2} d^{-1})$	<u>‰ / µM</u>
winter 2010	upper	4	0.31	-0.72	0.92	ACME (<u>35.6 / 5)</u> S an
	lower	4	0.22	-0.83	0.99	$\left(\frac{33.073}{\Theta_2}\right)^{-1}$
winter 2011	upper	4	0.42	0.48	0.22	ACME
	lower	3	0.17	0.70	0.20	(<u>35.5 / 100</u> and O ₂)
winter 2012	upper	4	0.77	0.53	0.78	ACME (<u>35.4 / 110</u> 8
	lower	4	0.74	0.04	0.50	$\frac{(33.47-110)}{\text{and } O_2}$
winter 2016	upper	4	0.37	0.99	0.99	ACME (<u>35.5 /</u> S , no
	lower	4	0.66	0.76	0.51	O ₂)

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Table 2. Flux relationships with correlation coefficients (R²) between organic carbon and BSi, CaCO3 and lithogenic material for the winter ACMEs 2010, 2012 and 2016 and under oligotrophic conditions in 2011. Values at the 99 % c-onfidence l-evel are in bold-and were found only during the ACME in winter 2010. The case of the 950 structure is estimated from the salinity (S) and oxygen (O₂) upper water column recordings from the CVOO site (Fig. 3). With respect to <u>T</u>the slopes of the <u>flux</u> relationships <u>from the</u> -ACME 2012 and 2016 largely match. <u>ACME = Anticyclonic Modewater Eddy.</u>

	Season	Trap	days in	Chl-a	Salinity/oxygen	eddy	References (eddy)	FLUXES					RATIOS	
	WINTER		winter	MODIS	(eddy)	type		B Si	Corg	Ntot	CaCO ₃	Lith	C:N	Corg:Lith
				mg m ⁻³	<u>‰/µM</u>			mg m ⁻² d ⁻¹	molar					
	winter 2010	upper	89	0.15	35.6/<5	ACME	Karstensen et al. 2015	2.25	3.49	0.30	27.60	13.83	13.7	0.25
							Fischer et al. 2016							
		lower	89				Schütte et al. 2016a	9.25	7.13	0.54	45.32	54.04	15.5	0.13
	winter 2011	upper	90	0.15	<u>35.5 / 100</u>	ACME	Karstensen et al. 2015	0.24	1.12	0.13	13.09	0.88	10.0	1.27
		lower	90				Fischer et al. 2016	0.13	0.45	0.05	5.46	1.25	10.4	0.36
							Schütte et al. 2016a							
	winter 2012	upper	94	0.30	35.4/110	ACME	Romero et al. 2016	5.88	5.07	0.66	47.66	34.22	8.9	0.15
		lower	94				Schütte et al. 2016a	3.47	3.02	0.41	36.13	32.18	8.7	0.09
	winter 2013	upper		0.20	±.	CE	Schütte et al. 2016a	-	-	-	-	-	-	-
		lower	90					1.99	1.57	0.21	27.10	17.57	8.9	0.09
	winter 2014	upper		0.47	=		Schütte et al. 2016a	-	-	-	-	-	-	-
		lower	90					1.93	1.38	0.18	22.01	15.43	9.0	0.09
	winter 2015	upper	90	0.43	<u>-</u>	ACME	Schütte et al. 2016a	2.84	1.70	0.21	34.95	14.67	9.37	0.12
		lower						-	-	-	-	-	-	-
	winter 2016	upper	90	0.28	<u>35.5 / -</u>	ACME	-	6.18	4.51	0.58	51.33	28.99	9.08	0.16
		lower	91					10.05	4.18	0.69	71.13	45.23	7.06	0.09

Table 3. Biogeochemical characterization of the different eddies passing CVOO <u>during</u> the winter seasons between 2010 and 2016 with respect to deep ocean fluxes and compositions. Flux characteristics are also shown for winter 2011 with oligotrophic background conditions. ACME_=_Anticyclonic Modewater Eddy, CE_=_Cyclonic Eddy.