Quantitative Link Between Sedimentary Chlorin and Sea-Surface Chlorophyll-*a*

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Abstract Primary productivity in the ocean plays a major role in the global carbon cycle. To estimate its changes through geological time, different sedimentary proxies are used. However, the relative weights of the various processes driving the sedimentary accumulation of organic matter are not fully constrained or represent the flux of specific algal classes. Here, we compare sea-surface chlorophyll-*a* (SSchla) abundance estimated from remote sensing data over the last 20 years with the sedimentary concentration of its derivatives (i.e., chlorin) on a suite of 140 core-top sediments from different biogeochemical regions. We estimate with field data that only 0.33% of SSchla in tropical and subtropical regions is transferred to surface sediments in the form of chlorin. Despite the small fraction of chlorin that arrive to the sea-floor, the sedimentary spatial distribution of chlorin is driven primarily by SSchla concentration in high and moderate productivity locations (SSchla > 0.20 mg·m⁻³). Our calibration paves the way for the use of chlorin as quantitative proxies of primary productivity in paleoreconstructions and cautions on their use in low primary productivity settings.

Plain Language Summary Chlorophyll-*a* derivatives named chlorin are commonly used to reconstruct past primary productivity. However, their value has been questioned as they are posited to be controlled by diagenetic processes and often limited to draw qualitative inferences on the carbon cycle. In fact, most proxies have not been globally appraised with ocean biogeochemical data. Here, we use a combination of remote sensing and geochemical data to provide the first calibration of chlorin proxy. We estimate that 0.33% of the chlorophyll-*a* produced in surface waters is transferred to surface sediments. Despite the small fraction of chlorin that arrive to the sea-floor, we show chlorin concentration is spatially correlated with sea-surface chlorophyll-*a* in high and moderate productivity locations (SSchla > 0.20 mg·m⁻³). Our calibration paves the way for the use of chlorin as quantitative proxies of primary productivity in past periods and cautions on their use in low primary productivity settings.

1. Introduction

Chlorophyll-*a* is the essential pigment used by plants for carrying out photosynthesis. Its concentration in sea surface waters is commonly used as an indicator of phytoplankton abundance in the oceans (Davies et al., 2018). Most oceanic biogeochemical models use sea-surface chlorophyll-*a* (SSchla) concentration as the central metric of phytoplankton biomass to estimate primary productivity (PP; Behrenfeld et al., 2005). PP is the driving factor in the marine carbon cycle and regulates the flux of carbon to the deep ocean (Suess, 1980; i.e., the carbon pump). Understanding how PP varies through space, time, and across global climatic oscillations is a key objective in oceanographic and climate research, as it is a vital living link in the carbon cycle.

Remote sensing is recognized as the only feasible means to overcome spatial and temporal limitations in the estimation of PP on global scales (Z. Lee et al., 2015). Since 1997, different remote sensing sensors have been launched to estimate global SSchla concentration. The Sea-viewing Wide Field-of-view Sensor (SeaWiFS; 1997–2010), the Moderate-Resolution Imaging Spectroradiometer (MODIS; 2002–present), and the MEdium Resolution Imaging Spectrometer (MERIS; 2002–2012) are some examples. The data from these different sensors have been merged in the GlobColour project for ensuring data continuity, reducing data noise, and improving spatial and temporal coverage (http://globcolour.info). In this way, SSchla concentration can be estimated on a global scale over the last 20 years.

The estimation of SSchla concentration prior to the existence of instrumental records is uncertain. chlorophyll-*a* in the marine environment, after algae senescence and sedimentation, breaks down or transforms
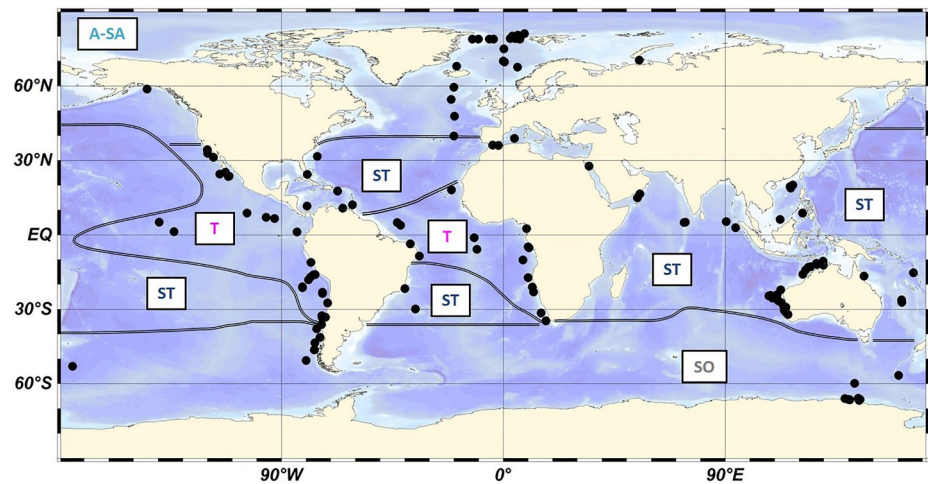
Figure 1. Core-top sediment distribution. Lines delineate distinct biogeochemical regions defined on the basis of temperature, nutrient concentration, and phytoplankton community composition (Weber et al., 2016). Abbreviations: Arctic-subarctic (A-SA), subtropics (ST), tropics (T), and Southern Ocean (SO).

into a range of degradation products mediated by biological and chemical processes (i.e., chlorin; Louda et al., 2002; Szymczak-Zyła et al., 2011). These include pheophytin-a, pyropheophytin-a, pheophorbide-a, cyclopheophorbide-a-enol, and steryl chlorin esters among others. They are diagenetically stable and can persist in sediments over millions of years (Soma et al., 2001). The measurement as the sum of these compounds (i.e., total chlorin abundance) has been used in a number of studies to infer qualitatively past PP variability in the open ocean (Harris et al., 1996; Higginson et al., 2003; Rosell-Melé et al., 1997; Summerhayes et al., 1995), coastal sites (Krajewska et al., 2020; Szymczak-Zyła et al., 2011; Szymczak-Zyła & Kowalewska, 2009), and lakes (Cuddington & Leavitt, 1999; Fietz et al., 2007; Ishiwatari et al., 2009; N. S.; Reuss et al., 2010; Rydberg et al., 2020). Thus, for its very nature and unlike any other paleo-proxies for past PP, chlorin provide a signal that it is exclusively linked to SSchla and PP. However, in common with any organic sedimentary proxy, their accumulation in sediments also depends on depositional conditions (Niggemann et al., 2007; Shankle et al., 2002) and thus, potentially complicates the interpretation of proxies to estimate past PP. The potential of such assessments has been shown for one of the commonly used PP proxies, that is, long-chain alkenone concentration in sediments (Raja & Rosell-Melé, 2021). Their global scale spatial distribution is primarily correlated with SSchla rather than diagenetic factors such as the oxygen concentration in bottom waters or water depth. In contrast to chlorin, which are produced by all phytoplankton species, long-chain alkenones are produced by few specific phytoplankton species (Schmidt et al., 2013; Volkman et al., 1980, 1995). In this study, we assess the quantitative link between sedimentary chlorin and SSchla as the first step in assessing the transfer of primary production into the sedimentary record. We compared sedimentary chlorin concentrations spatial variability in a core-top sediment compilation from different biogeochemical regions with SSchla (Figure 1). We also assess the effect of depositional factors (oxygen concentration in bottom waters, sedimentation rate, and water depth) on the spatial accumulation of chlorin in the upper (~2 cm) of modern sediments.

2. Methods

2.1. Chlorin Abundances

We compiled a suite of 140 core-top sediments, generally corresponding to the upper 2 cm of the sediment core (Figure 1, Table S1 in Supporting Information S2). Approximately 45% of the samples were retrieved using a box corer or multicorer. The compilation is dominated by samples along continental margins, since they represent the most intensively studied regions. However, sample sites span a wide range of chlorin concentrations distributed in diverse biogeochemical regions based on temperature, nutrient concentration, and phytoplankton community composition as defined in Weber et al. (2016) (Figure 1). The defined regions also represent different particle export fluxes to the deep ocean (DeVries & Weber, 2017). In addition, over 80% of the compiled surface

sediments are in sites with a water column deeper than 1,000 m. Consequently, the compilation is mainly representative of the water column of the open ocean.

Total chlorin in sediments (ca. 1 g) were extracted using 10 mL of acetone (HPLC grade, LiChrosolv) in a MARS5 microwave accelerated extraction system (CEM Corporation). During extraction, the mixture was stirred continuously with a magnetic bar, while temperature was increased from ambient to 70°C over 5 min and left at this temperature for a further 5 min. After extraction, samples were left to cool down at room temperature, and the supernatants were decanted into glass tubes and centrifuged. Extracts were then concentrated to 0.5 mL under vacuum and filtered through anhydrous Na_2SO_4 columns. To quantify total chlorin abundance, we used the method described in (Higginson et al., 2003). Briefly, we used a high-performance chromatographic system operated in the off-column mode (i.e., by-passing the chromatography column), with a quaternary pump, automatic sampler, photodiode array detector (Surveyor, Thermo Finnigan), and fluorescence detector (FL3000; Thermo Finnigan). Absorbance was measured at 665 nm, while for the fluorescence measurement we used the 407 and 662 nm bands as the excitation and emission wavelengths, respectively. In order to take into account the effect of the matrix in the quantification analysis, a control sediment sample, characterized with pheophorbide-a standard (Sigma-aldrich), was processed in every batch of samples (14 samples). The reproducibility of our measurements brings a relative standard deviation of 4%.

Our total chlorin concentration data were combined with those from sites around Australia published in (Radke et al., 2017). These yielded results with a range of concentration variability equivalent to those generated for the present study (Figure S1 in Supporting Information S1).

Chlorin fluxes to surface sediments were estimated as follows. We first calculated the amount of chlorin that are accumulated in the surface sediment every year for each location by dividing chlorin concentration by the estimated age of each core-top sediment (i.e., how many years represent every of our surface sediment samples). For this, we used the global burial map published in Dunne et al. (2012) and assumed that the upper centimeters are representative of the burial fluxes. Then, we estimated the amount of SSchla produced per year in each location by dividing the total amount of SSchla produced since data became available (i.e., the sum of monthly SSchla since September 1997 to December 2017) by 20 years of available data. Next, we divided the amount of chlorin buried per year by the amount of SSchla produced per year for each location and multiplied the obtained value by 100. Finally, we calculated the average of all locations.

2.2. Uncertainties in the Sedimentary Data

For all samples used in the study, we had no control on handling and storage conditions before samples arrived at our laboratory. The chlorophyll signal is preserved in frozen sediments over long timescales (N. Reuss & Conley, 2005; Rydberg et al., 2020). In less favorable storage conditions, arguably, a decrease of sedimentary chlorin concentration might be expected but the evidence is inconclusive and a sediment matrix effect might protect pigments from degradation during storage (N. Reuss & Conley, 2005). Consistent with this notion, we did not observe a decrease in chlorin concentration in comparison to the year of retrieval of the sediment from the seafloor. In contrast, chlorin concentration range is roughly constant over the years of collection (Figure S2 in Supporting Information S1). Thus, we argue that despite chlorophyllic pigment composition might change over time, the total concentration of chlorin is not significantly altered.

The goal of the study was to analyze modern pigment inputs to seafloor sediments, and thus we considered only the bottom ocean surficial sediments. For this reason, we prioritized the analysis of sediments obtained using box corers and multicorers that are devices specially designed to retrieve with a minimum of disturbance to the sediment surface during coring. To expand the size of the sediment compilation, we eventually also included sediments obtained using other coring devices. To assess the variability induced by using different types of corers, we classified the samples in two groups (Figure S2 in Supporting Information S1), and compared their sedimentary chlorin mean concentrations. As every group counts with more than 30 observations, we did a z-test. We defined the null hypothesis, Ho: $\mu = \mu o$, and the alternate hypothesis, H1: $\mu \neq \mu o$. The z-statistic obtained was z-calc = 0.58, while a two-tail z-tab is equal to 1.96. Hence, zcalc < ztab, from which it is derived that the means of the values from the two types of corers are statistically indistinguishable. Therefore, the type of coring device does not influence significantly the concentration values in our compilation.

We avoided the use of sedimentation rates in Equations 1–7, which are limited by number in the current database and susceptible to errors caused by uncertainties in age models. Thus, regional lateral supply and bottom ocean dynamics might affect the vertical link between the surface water and sea floor. Hence, to provide a first-order information on the effect of sedimentation rates in our sedimentary data, we compared the chlorin mass accumulation rate (MARchlorin) against chlorin concentration in Figure S3 in Supporting Information S1. MARchlorin were estimated by multiplying chlorin concentration by the sedimentation rate and dry bulk density. In the absence of these data for each sample site, we extracted sedimentation rates from two global maps (Dunne et al., 2012; Jahnke, 1996) and discussed in Cartapanis et al. (2016). However, sedimentation rates could only be extracted for 71% of the sites. Dry bulk densities were assumed to be 0.9 g·cm^{-3}, as it corresponds to the mean dry bulk density for marine sediments in the global sediment core database published in Cartapanis et al. (2016), which has been created by retrieving available data from online data repositories. Variations in lithology and porosity are sources of uncertainty in our calculations. But, presumably these variations are not substantial in logarithmic ranges. The correlation between MARchlorin and chlorin concentrations is high as attested by their coefficient of determination of $R^2 = 0.93$ and $R^2 = 0.85$, depending on the sources of sedimentation rates (Dunne et al., 2012; Jahnke, 1996). Consequently, overall for our compilation, the differences in using MARchlorin and chlorin concentrations when compared to values of SSchla concentration are not likely to lead to significantly different results. To maximize the size of data points in our compilation, we used chlorin concentrations rather than MARchlorin.

$$[Chlorin] = 9.23 \cdot ln \sum [SSchla] - 30.22 \tag{1}$$

$$[Chlorin] = 4.75 \cdot ln \sum [SSchla] - 16.16 \tag{2}$$

$$[Chlorin] = 2.40 \cdot ln \sum [SSchla] - 7.64 \tag{3}$$

$$[Chlorin] = 5.71 \cdot ln \sum [SSchla] - 20.07 \tag{4}$$

$$[Chlorin] = 0.03 \cdot \sum [SSchla] + 1.35 \tag{5}$$

$$[Chlorin] = 3.65 \cdot ln \sum [SSchla] - 12.28 \tag{6}$$

$$[Chlorin] = 0.79 \cdot ln \sum [SSchla] - 2.14 \tag{7}$$

$$[Chlorin] = 4.01 \cdot ln\overline{x}[SSchla] + 8.25 \tag{8}$$

$$[Chlorin] = 3.69 \cdot ln\overline{x}[SSchla] + 6.41 \tag{9}$$

$$[Chlorin] = 3.25 \cdot ln\overline{x}[SSchla] + 5.39 \tag{10}$$

2.3. SSchla Concentrations

SSchla concentrations (mg·m^{-3}) were obtained from the Globcolour Project. GlobColour data (http://globcolour.info) used in this study have been developed, validated, and distributed by ACRI-ST, France. CHL1 ocean color L3 is a merged product from different sensors that were in operation from 1997 to present: SeaWiFS (1997–2010), MERIS (2002–2012), MODIS (2002–2017), and VIIRS (2012–2017). The algorithms used to obtain the CHL1 product were OC4v5 for SeaWiFS, OC4Me for MERIS, and OC3v5 for MODIS and VIIRS (O'Reilly et al., 2000). The spatial resolution of CHL1 product is 1/24° (4.63 km at the equator). Monthly SSchla concentrations were extracted for each location from the merged global-scale matrix (nxm), where $n = 2160$ vector with values from 90 to −90 (steps = 0.041667) was created for latitudes and $m = 4,320$ vector with values from −180 to 180 (steps = 0.041667) was created for longitudes. A search was then conducted for the nearest value in those vectors that coincided with the sample locations (latitude and longitude), to deliver the chlorophyll-a concentration values of the matrix that correspond to every location. Each matrix contains monthly data, thus, we obtained chlorophyll-a concentration for every location and for every month over the last 20 years.
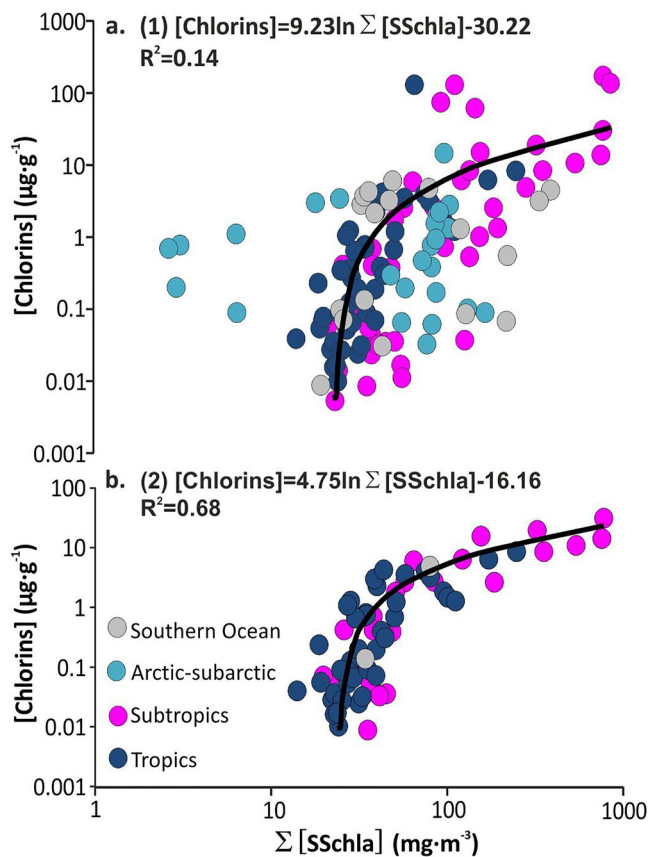
Figure 2. Correlations between sedimentary chlorin concentration and the sum of sea-surface chlorophyll-*a* (SSchla) concentration from 1997 to 2017. (a) includes the whole compilation and (b) includes regions presenting RMS log errors lower than 31% between remote sensing and in situ SSchla. Samples are classified by biogeochemical regions as defined in Figure 1.

To obtain SSchla concentration for the last 20 years, we added the concentrations from September 1997 to December 2017, for every location.

Averaged values of SSchla were also estimated to evaluate the impact of SSchla seasonal variability on our correlations. We calculated the annual SSchla by averaging SSchla values of all months since September 1997 to December 2017. We also estimated the season maxima SSchla and the month maxima SSchla by only considering the most productive season or month of each year, respectively.

2.4. Uncertainties in the Remote Sensing Data

One of the principal sources of scatter in the remote sensing data might be the poor accuracy of remote sensing SSchla concentration products in some specific oceanic regions, where the complexity of the optical and biological properties is significant. Potential contributors to SSchla uncertainty are contrails in the atmosphere, cloud shadows, aerosols, and exceptional plankton blooms such as red tides or macro-algae blooms, strong wind with white caps, Sun glint, shallow water with bottom reflection, proximity to land, or very high concentrations of water constituents among others (IOCCG, 2019). Potential contributions to uncertainty are intended to be subtracted during the atmospheric correction (Gordon & Wang, 1994; IOCCG, 2010). In general, the atmospheric correction algorithms for global ocean-color data processing are considered successful (IOCCG, 2010). However, atmospheric correction is still one of the most challenging problems that hampers accurate retrievals of optical properties and biogeochemical concentrations in some regions (IOCCG, 2010, 2019; Zheng & DiGiacomo, 2017). Besides, algorithm OC4 (O'Reilly et al., 2000), the most used algorithm for SSchla estimations, is particularly subject to uncertainties derived from variations between ocean basins as it aims at covering the global open ocean (IOCCG, 2019).

Thus, we focused our study on SSchla data located in well-performing remote sensing regions. We applied the threshold established in Gregg and Casey (2004), where basins associated with lower RMS log errors than the global mean (31%) are considered well-performed regions. This value is within the range of 30%–35% threshold values proposed in the remote sensing literature, including the Global Climate Observing System (GCOS) and the Ocean Colour Climate Change Initiative (OC-CCI), as the desired error benchmark for open ocean waters or optically clear waters. Consequently, we have not included in our final analysis (see Figure 2b) SSchla data from the North Atlantic (Gregg & Casey, 2004; Mendonça et al., 2010; Stramska et al., 2003), the Antarctic (Gregg & Casey, 2004; Moore et al., 1999), and the California current for high SSchla concentration (>1 mg·m^{-3}; Kahru et al., 2014); nor from the western South American margin, as the SSchla error estimate of this region has not been thoroughly studied. Although data for the equatorial Atlantic present an RMS log error of 48%, it lowers to 23% when removing samples located offshore of the north-eastern coast of South America (Gregg & Casey, 2004). Thus, as our samples are not located in this region, we included samples from the equatorial Atlantic in the regression analysis.

SSchla estimates correspond to 20 years of remote sensing observations, meanwhile sedimentary data for most of the samples (>85%) correspond to about 155 years, based on the average of sedimentation rates of our locations (13 cm·ka^{-1}).

3. Results

3.1. Correlation Between SSchla and Sedimentary Chlorin

Comparison between sedimentary chlorin and SSchla concentrations estimated over the last 20 years is shown in Figure 2. We represented data on a logarithmic scale based on the natural distribution of ocean chlorophyll, which is lognormal (Campbell, 1995). High scatter is observed in the relationship between chlorin and SSchla, especially for some regions such as the North Atlantic (Figure 2a). However, for this analysis, we took into account that the remote sensing SSchla estimates using global standard algorithms can have a wide range of error values and specific regional biases (Dutkiewicz et al., 2018; Global Climate Observing System, 2011; IOCCG, 2009). Hence, to minimize uncertainty in the regression analysis, we applied the methodology used in Raja and Rosell-Melé (2021) and briefly discussed in the Methods.

Data finally plotted in Figure 2b span several oceanic biogeochemical regions (Weber et al., 2016) and show that the spatial variability in sedimentary chlorin concentration is related to changes in SSchla, following a logarithmic trend with an RMS log error of 26% and a coefficient of determination (R^2) of 0.68.
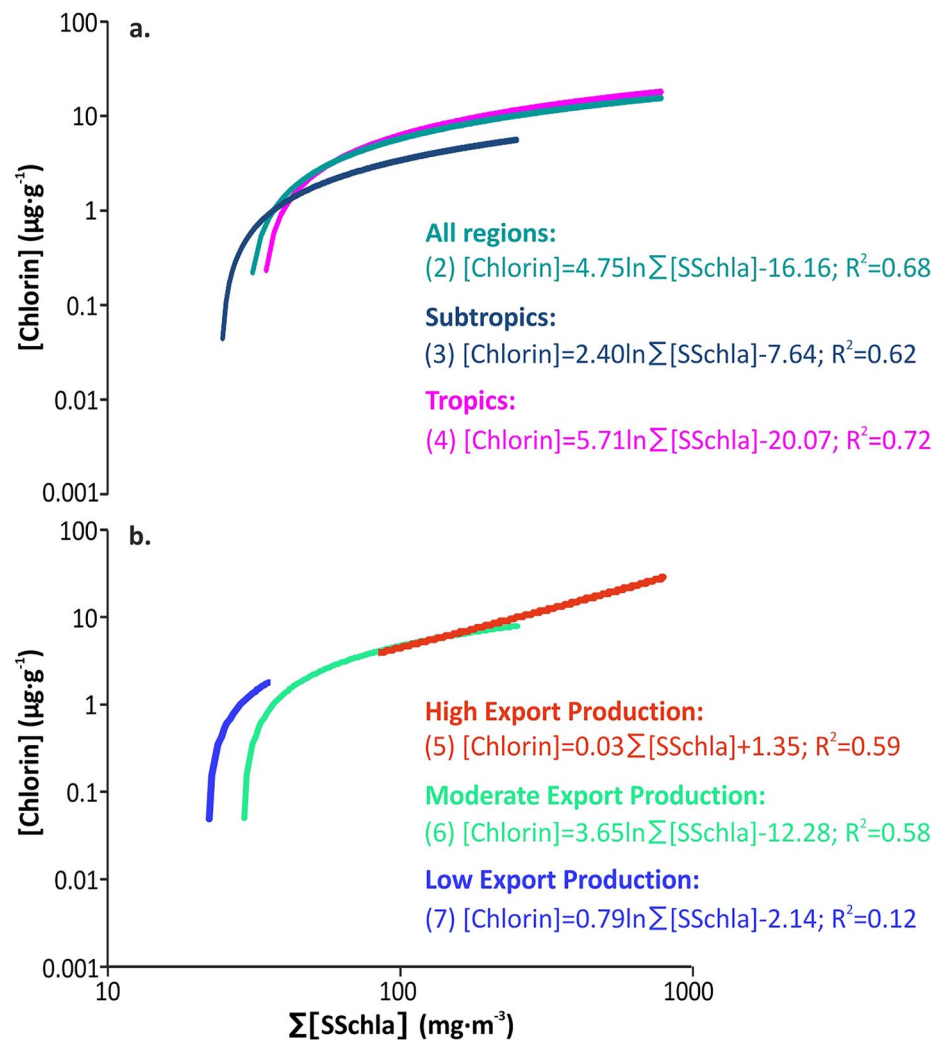
To investigate the influence of regional variability in the flux of chlorophyll-*a* from surface to sedimentary chlorin in our correlation, we undertook two different approaches. In our first approach, we divided the global ocean in the different regions defined in Weber et al. (2016), which is based on factors influencing transfer efficiency, such as phytoplankton community, nutrient concentration, and temperature (Figure 1). The defined regions are as follows: the tropics, the subtropics, the arctic-subarctic and the Southern Ocean. However, due to the lack of enough data, we did not appraise all the biogeographic regions. As can be seen in Figure 3a, we did not find significant differences in the correlation between the two regions appraised, the tropics, and the subtropics, and the RMS log error ranges from 19% to 29% (Table 1). In our second approach, we classified the samples according to the global annual export production map published in Laws et al. (2011). Briefly, export production in the latter study was calculated from monthly ef ratios and net primary productivity for the global ocean, where ef-ratio refers to the ratio of new or export production to total photosynthetic production in their steady-state model. We defined 3 different regions, which correspond to high (100–1000 gC·m^{-2}), moderate (10–100 gC·m^{-2}), and low (0–10 gC·m^{-2}) export production (Figure 4). Our study reveals different trends for the evaluated regions (Figures 3b and Table 1). Samples from high export production locations show a good linear correlation between SSchla and chlorin concentrations, with a coefficient of determination of $R^2 = 0.59$ and RMS log error of 32%. In contrast, we found a poor correlation for samples in low export production locations as attested by its coefficient of determination $R^2 = 0.12$. A moderate export production region includes samples that correspond to the different patterns described above, showing a logarithmic trend as a result ($R^2 = 0.58$ and RMS log error = 37%).

To study the influence of temporal SSchla concentration variability (i.e., seasonality) in our data set, we looked into the correlation between the seasonal variation index (SVI; Lutz et al., 2007), as an indicator of temporal variability and sedimentary chlorin concentration. We determined the SVI for every location by calculating the SSchla average of every month for the whole period of remote sensing available data, and then the average and the standard deviation of the calculated averages. Both SVI and sedimentary chlorin abundances were logarithmically transformed before statistical analysis for obtaining a normal distribution. We obtained a p-value of 0.004 (for a confidence level of 95%), which indicates that there is a significant correlation between SVI and sedimentary chlorin concentration, but the R^2 obtained for this correlation is of 0.12.

To further evaluate the extent of seasonality of SSchla in our study, we also compared the correlation between sedimentary chlorin concentration and the SSchla, (a) annual, (b) the seasonal maxima, and (c) the monthly maxima, averaged over the last 20 years. As it is shown in Figure 5, there are no significant differences between any of the correlations. The coefficients of determination range from 0.58 to 0.63 and the RMS log errors between 33% and 43% (Table 1).

3.2. Depositional Factors in the Transfer of Chlorophyll-*a* to Surface Sediments

To study the influence of depositional factors in altering the spatial variability of chlorophyll-*a* transfer from surface waters to surface sediments, we correlated water depth, sedimentation rate, and oxygen concentration in bottom waters, with the SSchla-chlorin ratio, as a measurement of chlorophyll-*a* transfer efficiency (Figure 6).

All regions:
(2) $[\text{Chlorin}] = 4.75\ln\sum[\text{SSchla}] - 16.16$; $R^2 = 0.68$

Subtropics:
(3) $[\text{Chlorin}] = 2.40\ln\sum[\text{SSchla}] - 7.64$; $R^2 = 0.62$

Tropics:
(4) $[\text{Chlorin}] = 5.71\ln\sum[\text{SSchla}] - 20.07$; $R^2 = 0.72$

High Export Production:
(5) $[\text{Chlorin}] = 0.03\sum[\text{SSchla}] + 1.35$; $R^2 = 0.59$

Moderate Export Production:
(6) $[\text{Chlorin}] = 3.65\ln\sum[\text{SSchla}] - 12.28$; $R^2 = 0.58$

Low Export Production:
(7) $[\text{Chlorin}] = 0.79\ln\sum[\text{SSchla}] - 2.14$; $R^2 = 0.12$

Figure 3. Regional correlations between sedimentary chlorin concentration and the sum of sea-surface chlorophyll-*a* (SSchla) concentration from 1997 to 2017. Different colors for lines and text indicate the evaluated biogeochemical defined in (a) Figure 1 and (b) Figure 4.

Table 1
Equations Coefficients and Errors

Equation	A	B	R^2	Standard error	RMS log error (%)	n
1[a]	9.23 ± 1.96	-30.22 ± 8.13	0.14	±23.26	109	140
2[a]	4.75 ± 0.39	-16.16 ± 1.58	0.68	±2.85	25	70
3[a]	2.40 ± 0.30	-7.64 ± 1.10	0.62	±1.12	19	42
4[a]	5.71 ± 0.73	-20.07 ± 3.25	0.72	±4.04	29	26
5[b]	0.03 ± 0.0088	1.35 ± 4.13	0.59	±6.51	32	8
6[a]	3.65 ± 0.47	-12.28 ± 1.80	0.58	±1.87	22	46
7[a]	0.79 ± 0.60	-2.14 ± 2.05	0.12	±0.73	37	15
8[c]	4.01 ± 0.38	8.25 ± 0.66	0.63	±3.10	33	70
9[c]	3.69 ± 0.35	6.41 ± 0.53	0.62	±3.12	36	70
10[c]	3.25 ± 0.34	5.39 ± 0.49	0.58	±3.28	43	70

[a]$[\text{Chlorin}] = a\cdot\ln\sum[\text{SSchla}] + b$. [b]$[\text{Chlorin}] = a\cdot\sum[\text{SSchla}] + b$. [c]$[\text{Chlorin}] = a\cdot\ln\bar{x}\,[\text{SSchla}] + b$.
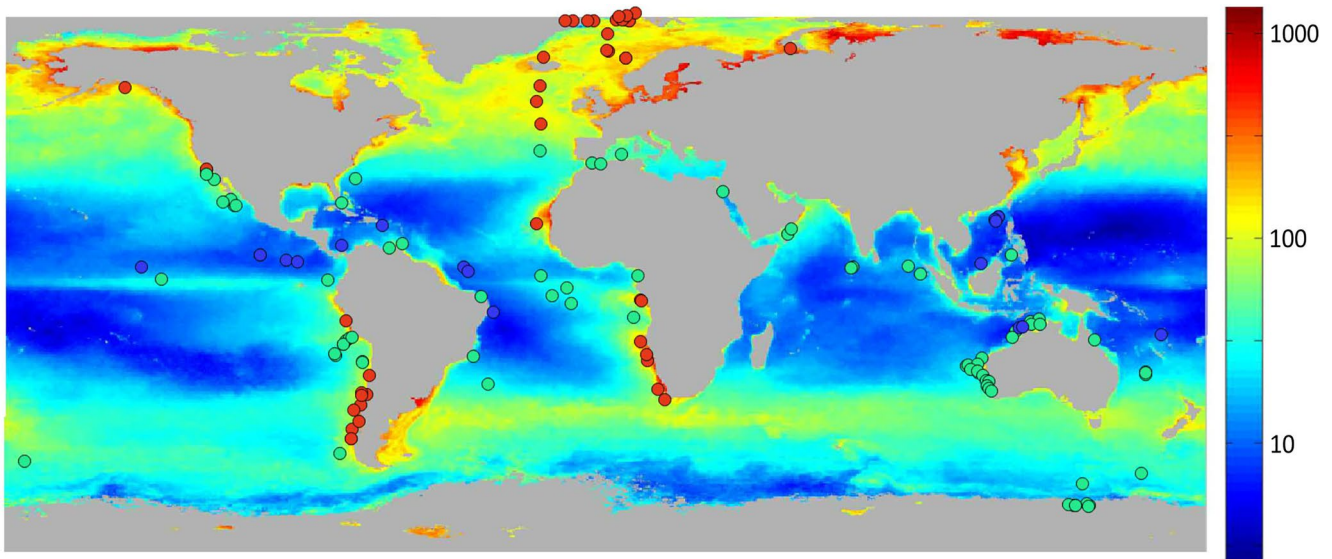
Figure 4. Core-top sediment classification based on global annual export production (Laws et al., 2011). Red, green, and blue dots correspond to samples in high (100–1000 gC·m^{-2}), moderate (10–100 gC·m^{-2}), and low (0–10 gC·m^{-2}) export production regions, respectively.

Sedimentation rates were extracted from the map published in Dunne et al. (2012) and oxygen concentrations in bottom waters from NOAA database (World Ocean Atlas, 2013 version 2: volume fraction of oxygen in sea water, annual 1.00°). Comparisons between sedimentary chlorin and depositional factors are shown in Figure S4 in Supporting Information S1.

The obtained p-values (with a confidence level of 95%) for the correlation between SSchla-chlorin ratio and oxygen, sedimentation rate, and water depth were 0.21, 0.60, and 0.03, respectively. These results indicate that there is no significant correlation between SSchla-chlorin ratio and neither oxygen nor sedimentation rates, but it is significant against water depth. The R^2 obtained for the latter correlation was, however, of 0.05. Future investigations on deeper sediments would further elucidate the diagenetic effects of these depositional factors on chlorin accumulation.
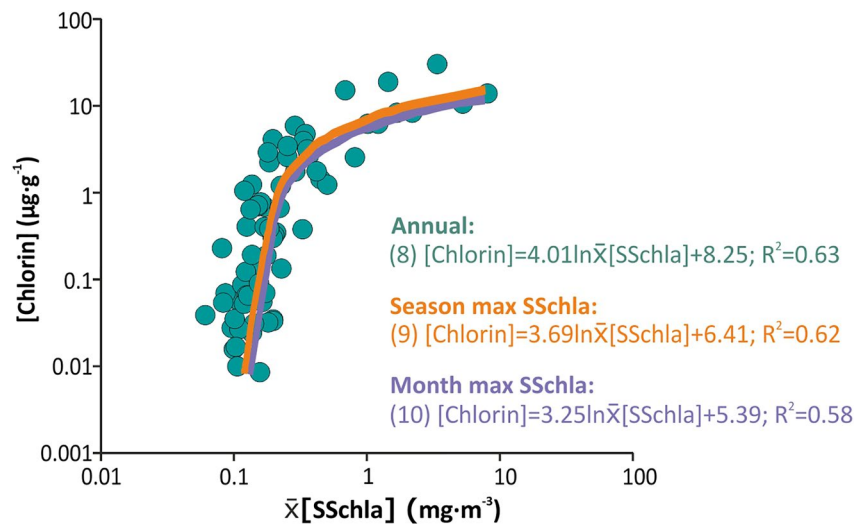
Figure 5. Correlation between sedimentary chlorin concentration and the average of sea-surface chlorophyll-*a* concentration (SSchla) from 1997 to 2017. Different colors for lines and text indicate: *(i)* annual SSchla: average of all months (green dots), *(ii)* seasonal maxima average SSchla: the most productive season (orange line), and *(iii)* monthly maxima average SSchla: the most productive month (purple line).
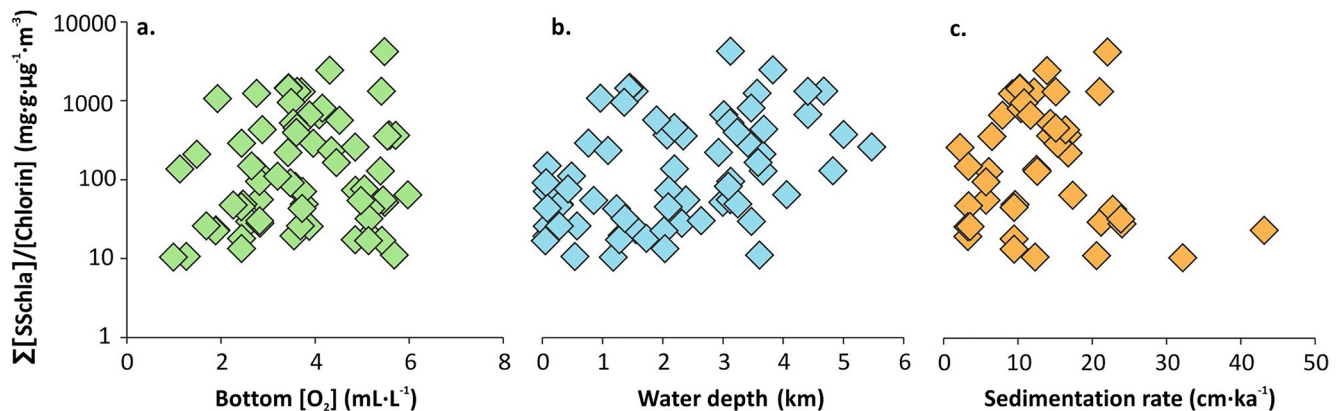
Figure 6. Correlations between the ratio of the sum of sea-surface chlorophyll-*a* concentration from 1997 to 2017 and chlorin concentration with depositional factors: (a) Bottom oxygen concentration, (b) Water depth, and (c) Sedimentation rate.

4. Discussion

4.1. Chlorin as a Quantitative Proxy for Past PP

Only a small fraction of the organic matter produced in the ocean surface is eventually buried in the sediments. For instance, global models estimate that 47.91 PgC·yr^{-1} are produced in ocean surface waters (Muller-Karger et al., 2005) while only 6 PgC·yr^{-1} (Siegel et al., 2014) are exported out from the photic zone. Furthermore, the amount of organic matter that reaches the sea floor is estimated to be 0.93 PgC·yr^{-1} and around 0.15 PgC·yr^{-1} eventually accumulates in the sediment (Muller-Karger et al., 2005).

We estimate that 0.33% of the chlorophyll-*a* produced in surface waters is accumulated in the upper 2 cm of the surface sediment in the form of chlorin. The accumulation of chlorin in sediments is only a small fraction of the SSchla produced in surface waters. Nevertheless, our results suggest that surface ocean algal biomass, a productivity metric, is the dominant factor in controlling the spatial distribution of sedimentary chlorin concentration in moderate and high productivity regions (SSchla >0.20 mg·m^{-3}; Figure 2b). Moreover, Equation 2 allows the quantification of past SSchla concentration from sedimentary chlorin concentration upper than 1 µg·g^{-1}, and therefore offers a means for estimating quantitatively past PP. This result is similar to that observed between the sedimentary concentration of alkenones and SSchla (Raja & Rosell-Melé, 2021). We note, however, that the sedimentary alkenone versus SSchla relationship is lineal, while the one in Figure 2b is better described by a logarithmic relationship.

The occurrence of a logarithmic relationship between SSchla and sedimentary chlorin marks an apparent threshold around 1 µg·g^{-1}, which has important implications in the interpretation of paleoceanographic archives. In paleoclimatic reconstruction studies, sedimentary chlorin are assumed to correlate with SSchla for any chlorin concentration (Harris et al., 1996; Higginson et al., 2003; Rosell-Melé et al., 1997; Summerhayes et al., 1995). However, according to the calibration in Figure 2b, this assumption might lead to an under- or overestimation of past PP changes in low productivity regions (SSchla <0.20 mg·m^{-3}, see Figure S5 in Supporting Information S1), where our data show poor correlation between chlorin and SSchla.

For instance, in studies carried out in the Benguela and the Canary current (Harris et al., 1996; Petrick et al., 2015; Summerhayes et al., 1995), chlorin concentration was higher than 1 µg·g^{-1} in both glacial and Holocene periods. In these settings, a linear relationship can be assumed between SSchla and chlorin as their range in the records corresponds to the part of the relationship above the threshold around 1 µg·g^{-1}. In fact, chlorin and organic carbon proxies in these studies were found to estimate similar productivity changes between climatic periods. However, chlorin data in some records span across the putative 1 µg·g^{-1} threshold (C.J. Schubert et al., 1998). In these cases, small under- or overestimations in PP might be derived from chlorin proxy if assuming a good correlation between chlorin and SSchla for low chlorin concentration (<1 µg·g^{-1}).

For instance, average chlorin concentration was estimated to be 0.7 µg·g^{-1} during the Holocene and 1.36 µg·g^{-1} in the glacial section from data in the latter study (Figure S6 in Supporting Information S1). Consequently, chlorin

concentration was estimated to be 1.94 lower in the Holocene than in the glacial (1.36 µg·g^{-1}/0.7 µg·g^{-1}). But, total organic carbon (TOC) shows a decrease of 1.16 between these periods (0.52 µg·g^{-1}/0.45 µg·g^{-1}). Thus, the implicit assumption that chlorin are correlated to SSchla might only apply to regions with high and moderate productivity. Presumably, the poor correlation found in low productivity regions might be caused by diagenetic processes affecting chlorin abundance through the water column and the water-sediment interface (e.g., remineralization; Junium et al., 2015; Kashiyama et al., 2012; C.; Lee et al., 2000). Further research using sediment traps might help to elucidate the biogeochemical processes that influence chlorin pathways from production to sedimentation.

4.2. Role of Depositional Factors in the Spatial Distribution of Sedimentary Chlorin

Depositional factors play an important role in the vertical flux and accumulation of organic matter in sediments, and it is often argued that local changes in preservation conditions may be a significant driver of the downcore variability of organic matter and its components (Niggemann et al., 2007; Shankle et al., 2002). For instance, organic matter deposition in shallow waters, as opposed to deeper ones, will reduce its degradation by reducing time exposure to oxygen and organisms through the water column (Hartnett et al., 1998). Similarly, high sedimentation rates move organic matter more rapidly down through the diagenetically active zone (i.e., the sediment-water interface), reducing time exposure to oxygen and benthic organisms. Besides, lower oxygen concentration in the water-sediment interface also diminishes organic matter degradation (Canfield, 1994). A number of reports have shown that indeed chloropigments are susceptible to degradation in the water column and water-sediment interface (C. Lee et al., 2000; Niggemann et al., 2007; Szymczak-Zyła et al., 2011). In addition, we have discussed that only a small fraction of SSchla, 0.33, is likely to be accumulated in surface sediments.

It may appear thus unexpected that SSchla, and thus a metric related to productivity, is the primary driver of the spatial variability (as opposed to the vertical flux) of two classes of phytoplankton biomarkers (e.g., chlorin and alkenones) in the surface sediments of our compilations. We would like to emphasize that by primary driver we do not imply that productivity or rather SSchla is the only variable explaining the sedimentary values of the appraised biomarkers, but rather most of the variability in our compilation. Thus, the regression coefficient (R^2) of the regression in Figure 2b is 0.68 for chlorin versus SSchla, while for alkenones, we obtained a value of 0.60 (Raja & Rosell-Melé, 2021), which does not explain of course 100% of the spatial variability of our data. Nevertheless, in relation to the spatial variability of our data, we did not obtain a significant correlation between sedimentary chlorin and variables related to depositional conditions. For instance, in Figure 6, the obtained p-values and R^2 between SSchla-chlorin ratio and bottom oxygen concentration (p-value = 0.21), sedimentation rates (p-value = 0.60), and water depth ($R^2 = 0.05$) suggest that depositional and burial processes do not greatly affect the spatial variability of chlorophyll-a accumulation in surface sediments. These results can be interpreted as evidence of the minor role of depositional factors in the spatial distribution of sedimentary chlorin. Consequently, relevant factors controlling the vertical flux of organic matter are not likely to explain most of the spatial variability of chlorin contents. However, the combined role of various depositional processes in controlling chlorin concentration still needs to be assessed.

4.3. Spatial and Seasonal Variability on SSchla Transfer to Surface Sediments

There is some uncertainty in the literature regarding the spatial variability of the export efficiency of organic matter to the deep ocean. A number of authors have argued that the export efficiency of surface biomass to the deep ocean depends on the latitude or biogeographical regions due to differences in biogeochemical properties, such as phytoplankton community and ballast biominerals (Armstrong et al., 2002; Honjo et al., 2008). In contrast, other studies indicate that there are no significant latitudinal trends in export efficiency (Martin et al., 1987; Suess, 1980) or that with depth the spatial variability in export efficiency decreases (Lutz et al., 2002; Jahnke, 1996).

In relation to our chlorin/SSchla data, our comparison between the tropics and the subtropics does not show significant differences (Figure 3a). We suggest that our data can be interpreted as indicating that there are no significant regional differences in the transfer efficiency of SSchla to surface sediments between the tropics and the subtropics. Hence, chemical, physical, and biological processes that take place through the deep-water

column and in the water-sediment interface could play a key role in spatially homogenizing the transfer efficiency of SSchla to surface sediments.

Another approach to study global organic matter export to the deep ocean is to estimate export production from empirical correlations of in situ measurements of vertical carbon fluxes, with properties that can be derived from remote sensing (Brewin et al., 2021). One of the first techniques was proposed by Laws et al. (2000). In this approach, the ratio of export production to primary production is approximated based on empirical relationships with sea-surface temperature. Since then, other satellite-based empirical algorithms have been developed (Dunne et al., 2005; Henson et al., 2011; Laws et al., 2011; Siegel et al., 2014).

Our study on the effect of global organic matter export in our correlations between SSchla and chlorin concentrations shows different trends for the defined regions (high, moderate, and low export production; Figure 3b). The good linear correlation obtained for the high export production region can be explained by the fact that this region only includes sediments with chlorin concentration higher than 2.5 $\mu g \cdot g^{-1}$, which corresponds to values upper than the 1 $\mu g \cdot g^{-1}$ threshold established from Equation 2. Consequently, the dominant factor in controlling the spatial distribution of sedimentary chlorin concentration in this region is SSchla. In contrast, the low export production region presents a poor correlation. In the latter region, more than 85% of the data correspond to sediments with lower chlorin concentration than 1 $\mu g \cdot g^{-1}$. Hence, finding a poor correlation for this region is also in agreement with the results derived from the global equation, which points out that SSchla is not the primary factor controlling the accumulation of chlorin in core-top sediments at low chlorin concentrations (<1 $\mu g \cdot g^{-1}$). The logarithmic trend presented by the moderate production region might be due to the inclusion of sediments with higher (65% of the samples) and lower chlorin concentrations than 1 $\mu g \cdot g^{-1}$.

Therefore, SSchla can be quantified from sedimentary chlorin in high export production locations using the linear Equation 5, which has the potential to estimate quantitatively past PP in those regions. Despite the good correlation obtained in Equation 6, we suggest that similar concerns to those previously raised on the use of Equation 2 should be considered. Namely, caution its use on estimating SSchla from sediments with lower chlorin concentration than 1 $\mu g \cdot g^{-1}$.

Besides biogeochemical region conditions, short-term temporal variability of SSchla concentration might also potentially alter chlorin export from sea-surface to sediments and thus, sedimentary chlorin concentration. Thus, more episodic PP regions are believed to export a greater amount of particulate organic matter than regions that show lower seasonal variability (Berger & Wefer, 1990; Dunne et al., 2005). Our results indicate a minor role of SSchla temporal variability in altering sedimentary chlorin concentration ($R^2 = 0.12$) and suggest that the transfer efficiency from sea-surface to core-top sediments is not significantly higher during episodes of higher PP (i.e., phytoplankton blooms) in comparison with the rest of the year (Figure 5). Hence, although seasonality might lead to changes in export fluxes, this variability is not the predominant cause of the spatial variations in sedimentary chlorin concentration, and has no significant effect in the correlation between SSchla and sedimentary chlorin concentrations for the samples evaluated in this study.

4.4. TOC vs Chlorin

TOC is widely used as a proxy for past PP as it represents the single largest constituent of organic matter that provides the most direct proxy for productivity (Bunzel et al., 2017; Moreno et al., 2004; Nieto-Moreno et al., 2011; Pedersen, 1983; Schoepfer et al., 2015; Carsten J.; Schubert et al., 2001; Summerhayes et al., 1995; Xu et al., 2017). However, global scale data sets do not show a dominant relationship between TOC in surface sediments and PP, and paleoproductivity equations have a large associated uncertainty yielding order of magnitude estimates (Felix, 2014; Schoepfer et al., 2015). In fact, the relationship between both variables is often explained by multivariate regressions that include primary productivity, water depth, and sedimentation rate (Felix, 2014). The apparently simpler relationship we have obtained between chlorin and SSchla appears at odds with previous studies investigating the relationship between sedimentary organic matter and productivity. Moreover, one of the challenges of conducting these types of assessments is on the choice of PP data as biogeochemical models diverge in their estimates of this metric (Z. Lee et al., 2015). We chose instead to use SSchla for the spatial analysis of sedimentary chlorin on which models usually rely to estimate PP.

The appraisal of the correlation between TOC and chlorin discussed in this paper is not optimal since we only obtained TOC values in 43% of the samples (Text S1 in Supporting Information S1, Table S1 in Supporting

Information S2). With these data, we do not observe a clear correlation between TOC and sedimentary chlorin (Figure S7 in Supporting Information S1), and albeit some relationship can be argued for with a subset of the data, we think that further work must be undertaken to further clarify the issue. Arguably, a lack of correlation between TOC and chlorin might be expected because TOC includes a range of organic substances with their own chemical reactivity and preservation rates (Zonneveld et al., 2010). In contrast, chlorin are a class of compounds with relatively analogous reactivities that exclusively derive from chlorophyll-*a*. In fact, we postulate that different compound classes may yield their own unique relationship with SSchla, if any, as inferred from the different correlations obtained between SSchla with chlorin and alkenones (Raja & Rosell-Melé, 2021).

5. Conclusions

SSchla abundance is the primary driver explaining the spatial distribution of sedimentary chlorin concentration higher than 1 µg·g^{-1} in tropical and subtropical regions, rather than depositional factors. Thus, this study provides the first spatial-based calibration for oceans that show the potential use of sedimentary chlorin to quantify sea-surface chlorophyll-*a*, which ultimately can be used to quantify PP in paleoreconstructions. However, we did not find a strong correlation between sedimentary chlorin and SSchla in oligotrophic waters, which challenges previous assumptions on the use of chlorin at any locations. Only around 0.33% of chlorophyll-*a* is eventually transferred to surface sediments in the form of chlorin at low latitudes. Moreover, these results also provide past SSchla and chlorin values, against which it is possible to validate and improve ocean biogeochemical models and their estimates of PP and organic carbon sedimentary burial.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

GlobColour data (http://globcolour.info) used in this study have been developed, validated, and distributed by ACRI-ST, France. All data generated from this study are freely downloadable at https://ddd.uab.cat/record/257609.

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