Selective preservation of organic-walled dinoflagellate cysts as a tool to quantify past net primary production and bottom water oxygen concentrations

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Abstract

To understand the role of the ocean within the global carbon cycle, detailed information is required on key-processes within the marine carbon cycle; bio-production in the upper ocean, export of the produced material to the deep ocean and the storage of carbon in oceanic sediments. Quantification of these processes requires the separation of signals of net primary production and the rate of organic matter decay as reflected in fossil sediments. This study examines the large differences in degradation rates of organic-walled dinoflagellate cyst species to separate these degradation and productivity signals. For this, accumulation rates of cyst species known to be resistant (R-cysts) or sensitive (S-cysts) to aerobic degradation of 62 sites are compared to mean annual chlorophyll-*a*, sea-surface temperature, sea-surface salinity, nitrate and phosphate concentrations of the upper waters and deep-water oxygen concentrations. Furthermore, the degradation of sensitive cysts, as expressed by the degradation constant k and reaction time t, has been related to bottom water $[O_2]$. The studied sediments were taken from the Arabian Sea, north-western African Margin (North Atlantic), western-equatorial Atlantic Ocean/Caraibic, south-western African margin (South Atlantic) and Southern Ocean (Atlantic sector).

Significant relationships are observed between (a) accumulation rates of R-cysts and upper water chlorophyll-*a* concentrations, (b) accumulation rates of S-cysts and bottom water $[O_2]$ and (c) degradation rates of S-cysts (kt) and bottom water $[O_2]$.

Relationships that are extremely weak or are clearly insignificant on all confidence intervals are between (1) S-cyst accumulation rates and chlorophyll-*a* concentrations, sea-surface temperature (SST), sea-surface salinity (SSS), phosphate concentrations (P) and nitrate concentrations (N), (2) between R-cyst accumulation rates and bottom water $[O_2]$, SST, SSS, P and N, and between (3) kt and water depth. Co-variance is present between the parameters N and P, N, P and chlorophyll-*a*, oxygen and water depth. Correcting for this co-variance does not influence the significance of the relationship given above.

The possible applicability of dinoflagellate cyst degradation to estimate past net primary production and deep ocean ventilation is discussed.
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1. Introduction

The fate of organic matter (OM) in the ocean has intrigued scientists over years. Especially in the last decades the role of the ocean within the global carbon cycle has been subject of intense focus as the concern grows about the possible effects of industrial-induced atmospheric $[CO_2]$ increase on the global climate. To understand the role of the ocean, detailed information is needed on key-processes within the marine carbon cycle such as bio-production in the upper ocean, especially primary production, the export of the produced material to the deep ocean, the storage of carbon in oceanic sediments and the redistribution of carbon from the ocean to the atmosphere. The present-day marine net global production from phytoplankton has been estimated to be more or less comparable to the production of land plants (ocean about 45–50 Gt C/year, land plants about 45–68 Gt C/year; (Longhurst et al., 1995; Cao et al., 2005)). Although estimates of the above mentioned processes are thought to give more or less adequate results for the modern environments, quantification of these processes in the past is largely hampered by the difficulty to separate past bio-productivity signals from those induced by (early-) diagenetic processes. As results, separating "export productivity from diagenesis" forms a key-target of world-wide operating research programs e.g. IMAGES, JGOFS and WCRP.

Degradation of OM in surficial sediments occurs by either aerobic or anaerobic pathways. After O_2 is consumed, a series of electron acceptors are used by bacteria to decompose organic compounds in a sequence that depends on the yield of metabolic free energy (e.g. Jørgensen, 2000; Sun et al., 2002). Studies on natural diffusion-limited, oxidation phenomena, often referred to as "burn-down" events as well as laboratory experiments, reveal that early aerobic diagenesis is highly selective and that the rate of degradation with respect to the concentration of labile organic matter seems to be a typically first-order process. (e.g. Hedges and Prahl, 1993 and references therein; Cowie et al., 1995; de Lange, 1998; Prahl et al., 2003). The rate of degradation of a given concentration of labile organic matter component (G) can be expressed as $dG/dt = -kG$ where t is the reaction time and k is the first order decay constant (Hedges and Prahl, 1993). This equation can be integrated between the boundary conditions $t=0$, $G=G_0$ and $t \rightarrow \infty$ to obtain $G_t = G_0 \exp^{-kt}$. The degradation is therefore dependent on the lability of the OM expressed by the constant k, and the reaction time t.

Recently Versteegh and Zonneveld (2002) suggested a method to separate the production and preservation signals as archived in fossil sediments, by using this difference in lability of OM components in relation to aerobic degradation. Their studies of post-depositional aerobic OM degradation at natural oxidation fronts in Late Quaternary sediments of the Madaira Abyssal Plain f-turbidite (140 ka BP), the mid-Holocene Eastern Mediterranean Sapropel S1 and the modern Arabian Sea Oxygen Minimum Zone and surrounding sediments, show that the ranking of different OM components, with respect to their degree of degradation, is similar in all studied regions and time intervals. End-members on this scale of lability are groups of organic-walled dinoflagellate cyst species (Zonneveld et al., 1997, 2001). Versteegh and Zonneveld (2002) concluded that concentrations of components resistant against degradation within (fossil) sediments are a reflection of the initial export production (with export production being the amount of material exported from the photic zone prior to degradation) of the component whereas the final concentrations of more labile components are the result of their export production and the aerobic degradation process within the water column and the sediments. Variability in accumulation rates of resistant components can therefore be used as proxy to reconstruct past component production by assuming minimal degradation within the water column. The rate of (post-depositional) decay (kt) can be calculated using the stable ranking of the components with respect to their lability.

Here we aim to develop this method further and discuss if this method can be used to quantify past productivity and the rate of degradal overprint. For this, we concentrate on organic-walled dinoflagellate cyst species forming the end members of the "lability ranking". Dinoflagellates are a diverse group of eukaryotic, primarily unicellular organisms having two distinctive flagella giving the organisms a (species-) characteristic spiral motion. Many planktonic dinoflagellates show dial vertical migration as results of endogenous rhythms and their geotactic and phototactic preferences (e.g. Anderson and Stolzenbach, 1985; Lieberman et al., 1994; Kamykowski et al., 1998) by which they can move several meters through the water column. Although species dependent, their migration ability is limited to several meters only, as result of their small size (the majority of species have sizes between 10–60 μm). Together with diatoms and coccolithophorids, dinoflagellates constitute the majority of the marine eukaryotic phytoplankton and are, therefore, important primary producers. Fossilisable organic-walled dinoflagellate cysts are thought to be formed during the sexual life-cycle of dinoflagellates. During cyst formation they
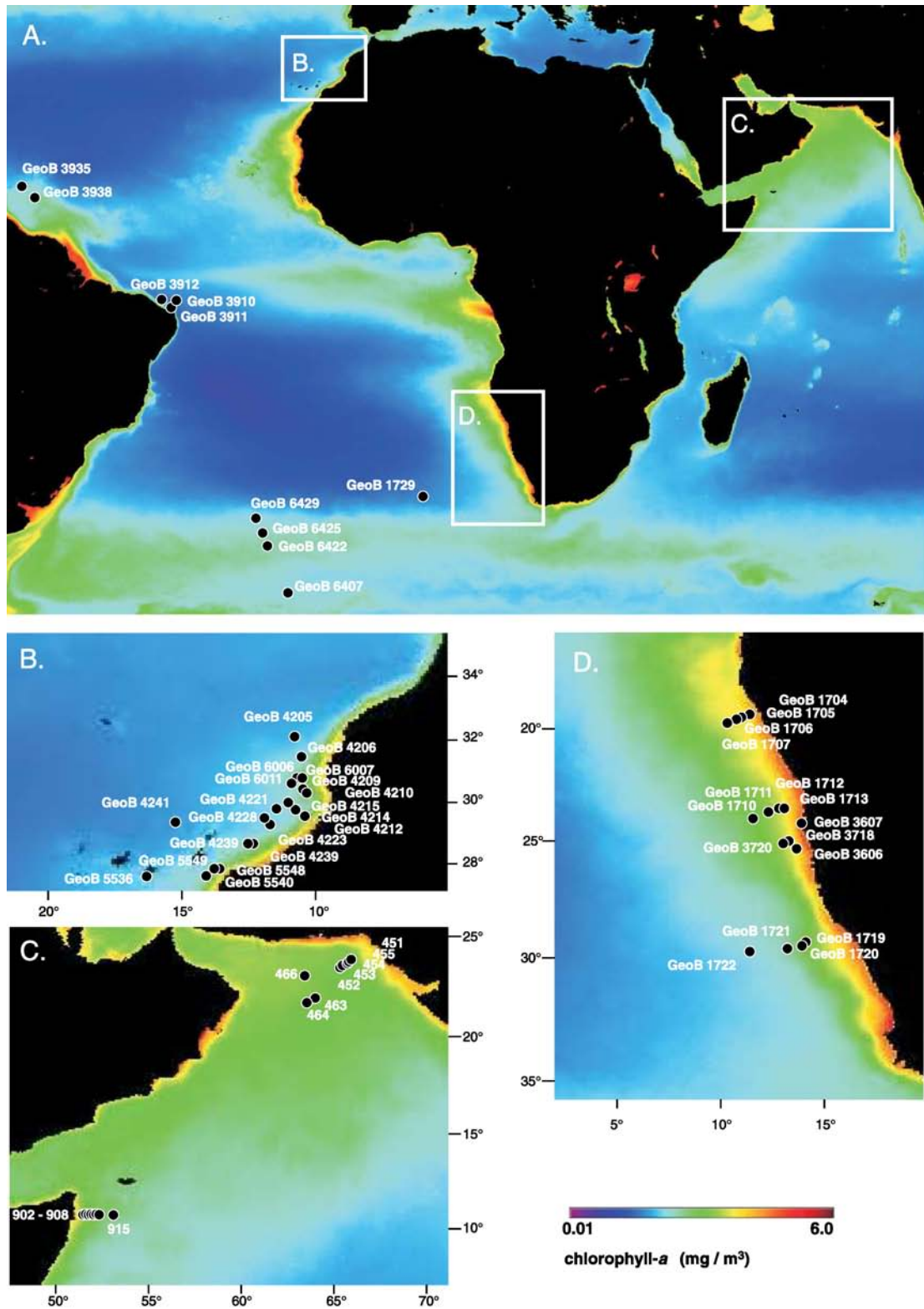
Fig. 1. Maps of the Atlantic Ocean and Indian Ocean showing mean annual chlorophyll-*a* concentrations of surface waters and sample positions of surface sediment samples. (A) Overview map of the studied regions, (B) Detailed map of the NW African margin (C) Detailed map of the Arabian Sea, (D) Detailed map of the studied region off SW Africa.

Table 1
List of samples with information about the sample position, water depth/sedimentation rates at the sample sites and stratigraphy

Sample	Latitude	Longitude	Depth [m]	SR	Stratigraphy after
GeoB 4205	32.182	−11.648	272	1.83	Kuhlmann et al. (2004)
GeoB 4206	31.498	−11.015	1855	4.67	Kuhlmann et al. (2004)
GeoB 4209	30.357	−11.083	2150	4.17	Kuhlmann et al. (2004)
GeoB 4211	30.193	−10.821	1173	3.83	Kuhlmann et al. (2004)
GeoB 4212	29.603	−10.95	1256	4.42	Kuhlmann et al. (2004)
GeoB 4214	29.781	−11.198	1788	3.08	Kuhlmann et al. (2004)
GeoB 4215	30.036	−11.553	2106	3.00	Kuhlmann et al. (2004)
GeoB 4221	29.775	−12.338	1826	3.08	Kuhlmann et al. (2004)
GeoB 4223	29.018	−12.467	777	11.17	Kuhlmann et al. (2004)
GeoB 4228	29.47	−12.99	1633	6.67	Kuhlmann et al. (2004)
GeoB 4237	28.493	−13.18	800	6.50	Kuhlmann et al. (2004)
GeoB 4239	28.493	−13.18	881	10.75	Kuhlmann et al. (2004)
GeoB 4241	29.167	−15.453	3610	3.08	Kuhlmann et al. (2004)
GeoB 5536	27.537	−16.135	3456	6.50	Kuhlmann et al. (2004)
GeoB 5540	27.535	−14.175	2035	9.92	Kuhlmann et al. (2004)
GeoB 5548	27.992	−13.518	1162	8.83	Kuhlmann et al. (2004)
GeoB 5549	27.978	−13.695	1454	11.25	Kuhlmann et al. (2004)
GeoB 6006	30.868	−10.63	1282	5.92	Kuhlmann et al. (2004)
GeoB 6007	30.852	−10.267	899	86.75	Kuhlmann et al. (2004)
GeoB 6011	30.315	−10.288	993	6.83	Kuhlmann et al. (2004)
ARZE 451	23.41	66.02	495	25.50	van der Weijden et al. (1999)
ARZE 452	22.56	65.28	2001	5.00	van der Weijden et al. (1999)
ARZE 453	23.14	65.44	1555	8.10	van der Weijden et al. (1999)
ARZE 455	23.33	65.57	998	10.10	van der Weijden et al. (1999)
ARZE 463	22.33	64.03	970	16.00	van der Weijden et al. (1999)
ARZE 464	22.15	63.35	1511	15.00	van der Weijden et al. (1999)
ARZE 466	23.36	63.48	1960	6.40	van der Weijden et al. (1999)
ARZE 902	10.46	51.34	459	8.10	Ivanova (2000)
ARZE 903	10.46	51.39	789	48.00	Ivanova (2000)

Table 1 (continued)

Sample	Latitude	Longitude	Depth [m]	SR	Stratigraphy after
ARZE 904	10.47	51.46	1194	40.00	Ivanova (2000)
ARZE 905	10.54	51.56	1567	29.00	Ivanova (2000)
ARZE 906	10.48	52.07	2020	20.00	Ivanova (2000)
ARZE 907	10.48	52.14	2807	14.00	Ivanova (2000)
ARZE 908	10.46	52.54	3572	8.00	Ivanova (2000)
ARZE 915	10.41	53.31	4035	5.00	Ivanova (2000)
GeoB 1704	−19.4	11.62	395	3.60	Mollenhauer (2002)
GeoB 1705	−19.5	11.38	647	13.10	Mollenhauer (2002)
GeoB 1706	−19.57	11.18	980	9.00	Mollenhauer (2002)
GeoB 1707	−19.7	10.65	1234	9.40	Mollenhauer (2002)
GeoB 1710	−23.43	11.68	2995	5.30	Mollenhauer (2002)
GeoB 1711	−23.32	12.37	1975	10.00	Mollenhauer (2002)
GeoB 1712	−23.25	12.8	1004	8.00	Mollenhauer (2002)
GeoB 1713	−23.22	13.02	600	7.70	Mollenhauer (2002)
GeoB 1719	−28.93	14.17	1023	6.50	Mollenhauer (2002)
GeoB 1720	−29	13.83	2011	4.00	Mollenhauer (2002)
GeoB 1721	−29.18	13.08	3079	2.90	Mollenhauer (2002)
GeoB 1722	−29.45	11.75	3971	1.90	Mollenhauer (2002)
GeoB 1729	−28.9	1	4401	1.45	Thießen (1993)
GeoB 3606	−25.46	13.08	1793	7.38	Mollenhauer (2002)
GeoB 3607	−23.88	14.33	97	60.00	Mollenhauer (2002)
GeoB 3718	−24.9	13.17	1313	7.70	Mollenhauer (2002)
GeoB 3720	−25.07	12.67	2517	10.50	Mollenhauer (2002)
GeoB 3910	−4.245	−36.347	2359	3.56	Mollenhauer (2002)
GeoB 3911	−4.613	−36.635	825	14.29	Mollenhauer (2002)
GeoB 3912	−3.665	−37.718	773	3.45	Mollenhauer (2002)
GeoB 3935	12.613	−59.388	1556	2.63	Mollenhauer (2002)
GeoB 3938	12.257	−58.33	1972	1.32	Mollenhauer (2002)
GeoB 6407	−42.05	−19.5	3354	1.76	Franke et al. (2004)
GeoB 6422	−35.71	−22.44	3972	1.77	Franke et al. (2004)
GeoB 6425	−33.83	−23.59	4352	1.05	Franke et al. (2004)
GeoB 6429	−31.95	−24.25	4335	2.00	Schmieder (2004)

lose their flagellae after which they sink through the water column most probably as part of faecal pellets, aggregates and/or marine snow (Mudie, 1996). Field studies reveal that maximal cyst formation occurs during, or just after periods of maximal vegetative cell division (e.g. Ishikawa and Taniguchi, 1996; Montresor et al., 1998; Kremp and Heiskanen, 1999; Godhe et al., 2001; Matsuoka, 2001). The cyst species that have been classified as resistant against aerobic decay by Versteegh and Zonneveld (2002; R-cysts) are all able to photosynthesize although most, if not all of them are thought to be mixotrophic (Schnepf and Elbrächter, 1992). It is assumed that their vegetative production is positively influenced by enhanced availability of nutrients and/or trace elements when other biologic and a-biotic factors remain constant. Cysts that are known to be extremely sensitive for aerobic decay (S-cysts) are found, or thought, to be heterotrophic. Their vegetative growth is likely to be enhanced when more pray is available when other factors being equal. To investigate if the cyst production of both groups of dinoflagellate cysts can be related to the net primary production or other environmental parameters we correlated cyst accumulation rates of S-cysts and R-cysts with mean annual chlorophyll-*a* concentrations, mean annual Sea-Surface Temperature (SST), mean annual Sea-Surface Salinity (SSS), mean annual nitrate concentrations (N) and mean annual phosphate concentrations (P) of the upper waters at the sampling sites (Fig. 1).

To investigate if the rates of decay of S-cysts might be useful to reconstruct ventilation of the deep ocean, we correlated their accumulation rates as well as the degradation of the sensitive cysts expressed by their "*kt*"-values with bottom water oxygen conditions at the above mentioned sites.

2. Materials and methods

Surface sediments derived from 62 surface sediment samples from well-dated multi-cores from the western-equatorial Atlantic Ocean, the northwest African margin (North Atlantic Ocean), southwest African margin (South Atlantic Ocean), the Southern Ocean (Atlantic sector) and the Arabian Sea, have been collected from boxcores and multicores during several cruises of the RV METEOR and RV Tyro (Fig. 1, Table 1). Sediment samples have been processed using standard palynological techniques according to the aliquot method described by Marret and Zonneveld (2003). Accumulation rates are calculated by multiplying the numbers of cyst per gram dry sediment by the dry bulk density and the sedimentation rates at the sample sites. Sedimenta-

tion rates have been estimated based on linear interpolation between the AMS dates of the studied multi cores (Table 1). Accumulation rates of both R-cysts and S-cysts (Table 2) have been compared to chlorophyll-*a*, SST, SSS, N and P concentrations of the upper waters at the sampling sites and bottom water oxygen concentrations. Chlorophyll-*a* values have been extracted from the SEAWIFS satellite images that depict mean annual chlorophyll data compiled from 30 October, 1978–1 June, 2005 using the program NCSA JHV 2.7. Bottom water [O_2], SST, SSS, N and P have been derived from the NOAA, 1998 dataset (Table A1).

The degradation of S-cysts expressed by "*kt*" has been calculated assuming a first order decay process $kt = \ln(X_i/X_f)$ with X_f = final cyst concentration (cysts/cm^2/ky) and X_i = initial cyst concentration (cysts/cm^2/ky). We assume that in regions with minimal aerobic degradation in bottom waters, such as OMZ's, the accumulation rates (AR) of R- and S-cysts reflect their initial export productivity rates. Material from the surface samples of the OMZ's of the Arabian Sea and the Namibian shelf (SW Atlantic Ocean) as well as Western Arabian Sea sediment traps indicate that AR of R- and S-cysts is related to the equation: AR S-cysts = 68 × AR R-cyst (Table A1, Zonneveld and Brummer, 2000). Based on

Table 2
List of cyst-species included within the S-cyst and R-cyst groups

| R-cysts:	S-cysts:
Dalella chathamensis	*Brigantidinium* spp.
Impagidinium aculeatum	Cysts of *Diplopelta parva*
Impagidinium pallidum	Cysts of *Diplopelta symmetrica*
Impagidinium paradoxum	Cysts of *Protoperidinium avellanum*
Impagidinium patulum	Cysts of *Protoperidinium americanum*
Impagidinium plicatum	Cysts of *Protoperidinium monospinum*
Impagidinium sphaericum	Cysts of *Protoperidinium nudum*
Impagidinium strialatum	Cysts of *Protoperidinium stellatum*
Impagidinium variaseptum	*Echinidinium aculeatum*
Impagidinium velorum	*Echinidinium granulatum*
Impagidinium spp.	*Echinidinium transparantum*
Nematosphaeropsis labyrinthus	*Echinidinium delicatum*
Operculodinium israelianum	*Echinidinium* spp.
Pentapharsodinium dalei	*Lejeunecysta oliva*
Polysphaeridium zoharyi	*Lejeunecysta Sabrina*
	Quinquecuspis concreta
	Selenopemphix Antarctica
	Selenopemphix nephroides
	Selenopemphix quanta
	Stelladinium robustum
	Trinovantedinium applanatum
	Votadinium calvum
	Votadinium spinosum
	Xandarodinium xanthum
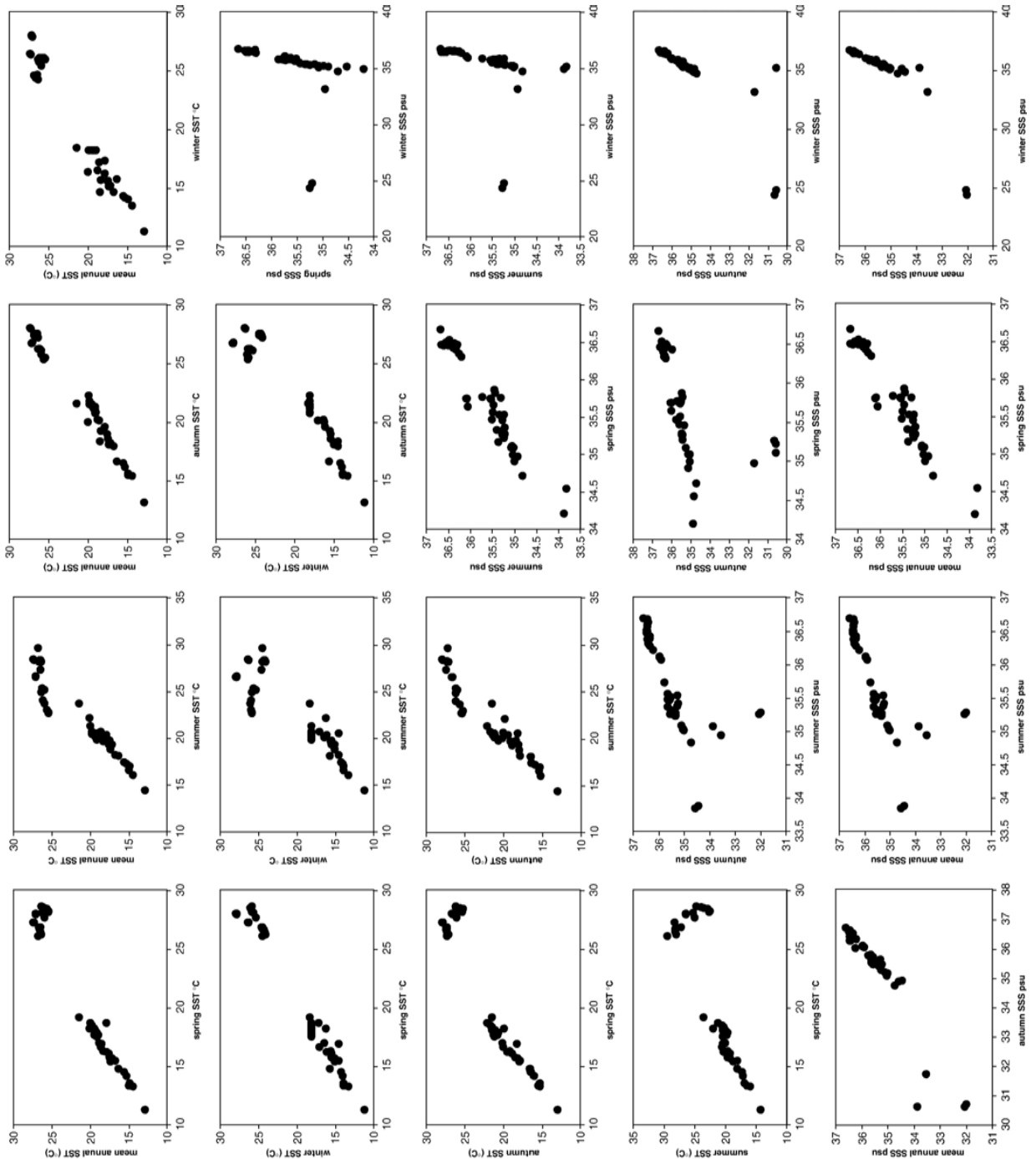
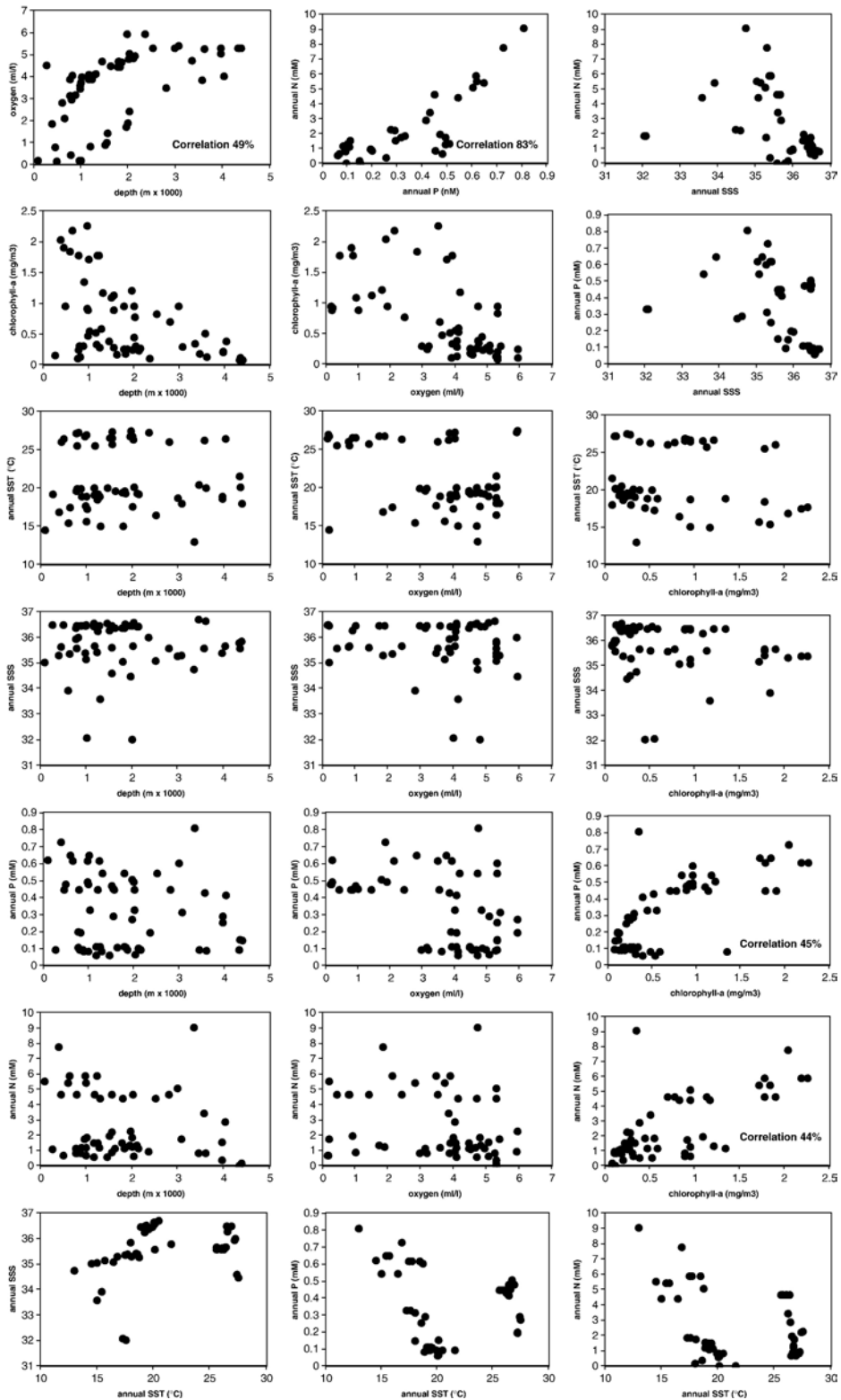Fig. 2. Draftman's plots of the seasonal variables of SST and SSS.

Fig. 3. Draftman's plot of the analysed variables.

Table 3
Correlation matrix of the environmental variables depicting the rate of co-variance

Correlation matrix								A.	B.
Oxygen (ml/l)	1							51%	51%
Chlorophyll-a (mg/m^3)	−0.4087	1						19%	3%
Annual SST (°C)	−0.3886	−0.2064	1					7%	0%
Annual SSS (psu)	−0.1498	0.0204	0.1289	1				1%	0%
Annual P mM	−0.3309	0.4478	−0.0446	−0.0754	1			14%	2%
Annual N mM	−0.1712	0.4406	−0.2808	−0.0341	0.8292	1		5%	1%
Depth (m)	0.4951	−0.3637	−0.0134	−0.2431	−0.1462	−0.1951	1	19%	1%
	Ox ml.l	Chloroph	Ann SST	Ann SSS	Ann P	Ann N	Depth (m)		

Amount of variance in the dataset explained by the environmental variables. A. without co-variance correction, B. with co-variance correction.

this relationship initial concentrations of S-cysts can be calculated by multiplying the AR of R-cysts in the surface sediments by 68 and by using the above mentioned first order decay function to determine the degradation; kt. kt values of the studied samples have been compared to mean annual bottom water oxygen values.

Sample GeoB 1711 has been excluded from the analyses since accumulation rates of the cysts appeared a factor 10 higher than the surrounding samples. ARZE 454 showed a remarkable difference in association as samples in its close vicinity and is excluded as well. Since both sites are not characterised by exceptional sedimentation regimes or deviant environmental conditions in the water column we ascribe these discrepancies to "errors" during the counting process.

Accumulation rates of R-cysts, S-cysts and kt have been compared with oxygen concentrations of bottom waters, and upper water mean annual chlorophyll-a, SST, SSS, N and P concentrations using the mutlivariate

Fig. 4. Relationship between accumulation rates of S-cysts and bottom water [O$_2$].

ordination methods Redundancy Analysis (RDA) using the CANOCO for Windows software package (Jongman et al., 1987; ter Braak and Smilauer, 1998). Seasonal values of SST and SSS at the investigated sites strongly co-vary to each other (Fig. 2). As a result seasonal differences can be considered as of minor importance and annual values have been included within our analyses. As seasonal data of P and N concentrations are available for a few sites only, we have included annual data. N and P values co-vary strongly (Fig 3, Table 3). Slight co-variation between chlorophyll-a and N, P and between oxygen and water depth occurs. For this co-variance is corrected in the RDA analysis.

The preformed analyses are based on the assumption of a linear response of the species in relation to environmental variables. A detrended correspondance analysis carried out before the analysis confirmed such a linear response model.

3. Results

Accumulation rates of S-cysts (x) show an exponential decrease with oxygen concentrations (y) in bottom waters that is significant on all significance levels (Fig. 4, Table 4) according to the equation:

$$Y = 4.3374 \ e^{-0.00001x} \text{ with } R^2 = 0.73 \qquad (1)$$

R-cyst accumulation rates and bottom water oxygen concentrations show a insignificant correlation ($R^2 = 0.23$; Fig. 5, Table 4).

Accumulation rates of R-cysts show a significant linear relationship with chlorophyll-a concentrations in the upper water column (Fig. 6, Table 4) according to the equation:

R-cysts (r) — chlorophyll-a (y):

$$Y = 0.0002r + 0.2271 \text{ with } R^2 = 0.70 \qquad (2)$$

Site GeoB 3607 is located at the edge of an active upwelling cell along the Namibian coast (Fig. 1) and is
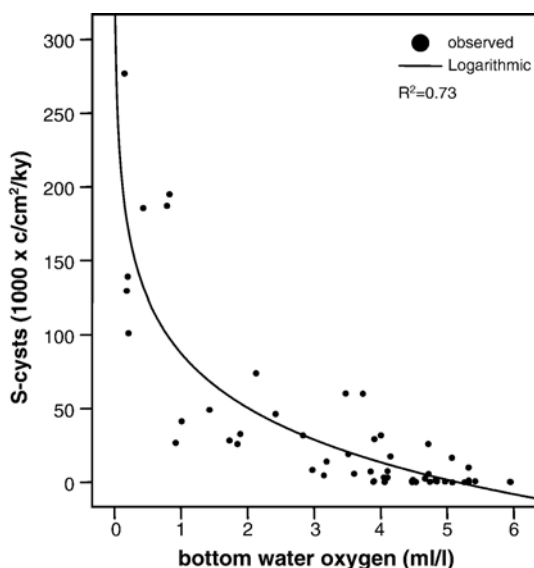
Table 4

Regression table of the factors compared. Dependent variables: S-cyst ($1000 \times$ cysts/cm^2/ky), R-cyst ($1000 \times$ cysts/cm^2/ky), kt (cysts/cm^2/ky)

Regression variables	Model	R	R square	df regr.	df res.	F
S-cysts (c/cm^2/ky)−[O$_2$]	Logarithmic	0.85	0.73	1	55	145.53
S-cysts (c/cm^2/ky)−Chlorophyll (ml/l)	Linear	0.59	0.35	1	57	30.36
S-cysts (c/cm^2/ky)−SST (°C)	Linear	0.26	0.07	1	58	4.35
S-cysts (c/cm^2/ky)−SSS (psu)	Linear	0.04	0.002	1	57	0.11
S-cysts (c/cm^2/ky)−P (mM)	Linear	0.37	0.13	1	58	9
S-cysts (c/cm^2/ky)−N (mM)	Linear	0.23	0.05	1	58	3.14
R-cysts (c/cm^2/ky)−[O$_2$]	Linear	0.48	0.23	1	54	16.17
R-cysts (c/cm^2/ky)−Chlorophyll (ml/l)	Linear	0.84	0.7	1	56	128.98
R-cysts (c/cm^2/ky)−SST (°C)	Linear	0.0048	0.00002	1	57	0.0013
R-cysts (c/cm^2/ky)−SSS (psu)	Linear	0.31	0.1	1	56	6.13
R-cysts (c/cm^2/ky)−P (mM)	Linear	0.62	0.38	1	57	35.58
R-cysts (c/cm^2/ky)−N (mM)	Linear	0.56	0.31	1	57	25.42
kt (c/cm^2/ky)−[O$_2$]	Non-linear least square	0.92	0.85	3	54	655.8
kt (c/cm^2/ky)−water depth (m)	Linear	0.64	0.42	1	58	41.26
kt (c/cm^2/ky)−sedimentation rate (cm)	Linear	0.75	0.56	1	58	74.96

Independent variables: [O$_2$], chlorophyll-a, SST, SSS, [P], [N], water depth and sedimentation rate. df regr.=degrees of freedom of regression, df res.=degrees of freedom of residual. The F-value is the measurement of the distance between individual distributions. As F goes up, P goes down (i.e., more confidence for a difference between the two means).

characterised by extreme high chlorophyll-a values that are a factor 100 higher than the other studied samples. This sample has been excluded from the establishment of Eq. (2).

Although by visual examination a positive relationship between accumulation rates of S-cyst with chlorophyll-a concentrations seems to be present, this trend is extremely weak and not significant (Fig. 7, Table 4).

kt values show a clear relationship with [O$_2$] according to the equation (Fig. 8A, Table 4):

$$[O_2] = 5.184/1 + e^{-1.131(kt-1.98)} \text{ with } R^2 = 0.73$$

When samples GeoB 5540 (NW African margin) and GeoB 1704 (SW African margin) are excluded from the dataset a relationship between oxygen concentration and
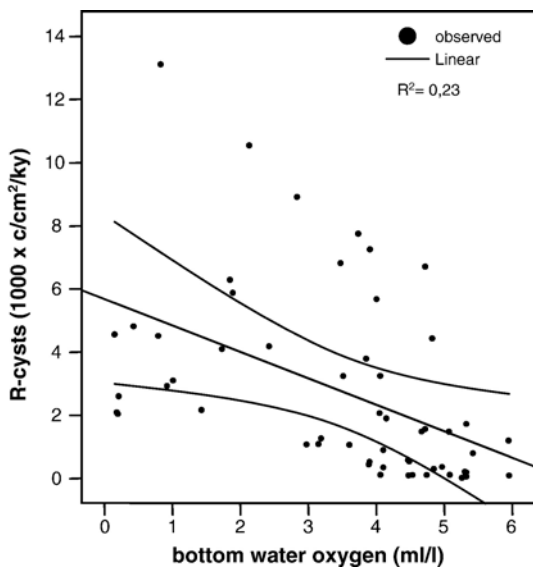

Fig. 5. Relationship between accumulation rates of R-cysts and bottom water [O$_2$]. Estimated linear relationship with 99.9% confidence limits of mean.
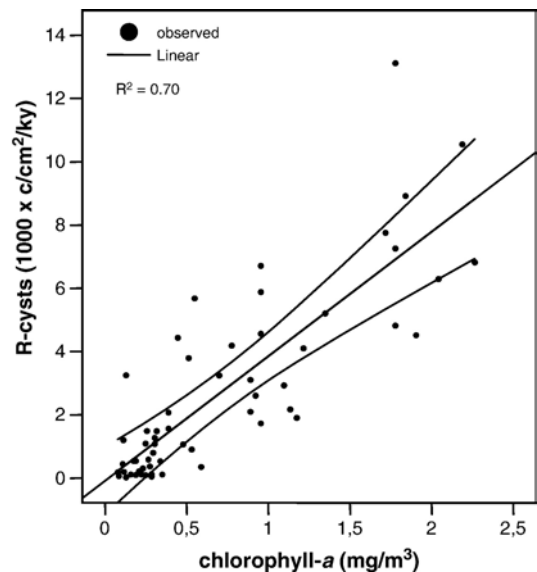

Fig. 6. Relationship between accumulation rates of R-cysts and mean annual upper water chlorophyll-a concentrations. Estimated linear relationship with 99.9% confidence limits of mean.
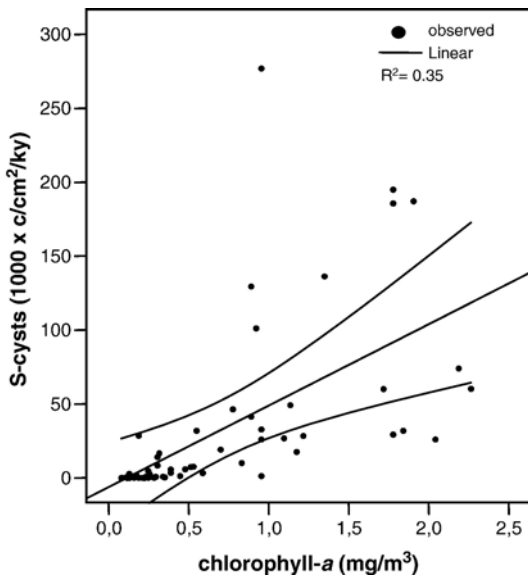
Fig. 7. Relationship between accumulation rates of S-cysts and mean annual upper water chlorophyll-*a* concentrations. Estimated linear relationship with 99.9% confidence limit of mean.

kt according to the following equation can be observed (Fig. 8B, Table 4)

$$[O_2] = 5.17/1 + e^{-1.23(kt-2.058)} \text{ with } R^2 = 0.846. \quad (3)$$

A weak relationship ($R^2 = 0.42$) can be observed between water depth and *kt* (Fig. 9, Table 4). *kt* decreases with increasing sedimentation rates (Fig. 10, Table 4).

Mean annual SST, SSS, P and N concentration show no significant or only a weak relationship between with R- and S-cyst accumulation rates (Fig. 11, Table 3). By correcting for this co-variation the variables water depth, SST, SSS, P and N did not account for variation within the dataset (Table 3).

4. Discussion

Our results document marked difference in relationship of accumulation rates of R-cysts and S-cysts to environmental gradients in upper water masses and bottom waters. The final recovery of dinoflagellate cysts is depending on numerous factors such as their initial production, degradation in the water column and sediment as result of scavaging, bacterial activity or chemical processes and lateral translocation during their downward transport through the water column or post-depositional as result of sediment movement. In the following chapters we discuss how these processes are related to our results.
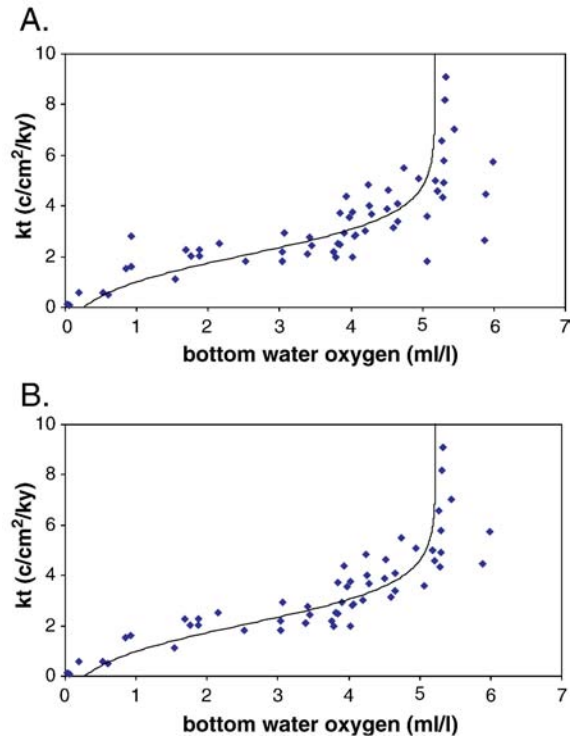

Fig. 8. Relationship between the degradation expressed of S-cysts by *kt* and bottom water [O$_2$]. (A) with outliers, (B) without outliers.

4.1. Cyst production

The initiation of dinoflagellate sexuality and, as a result, cyst production is influenced by environmental
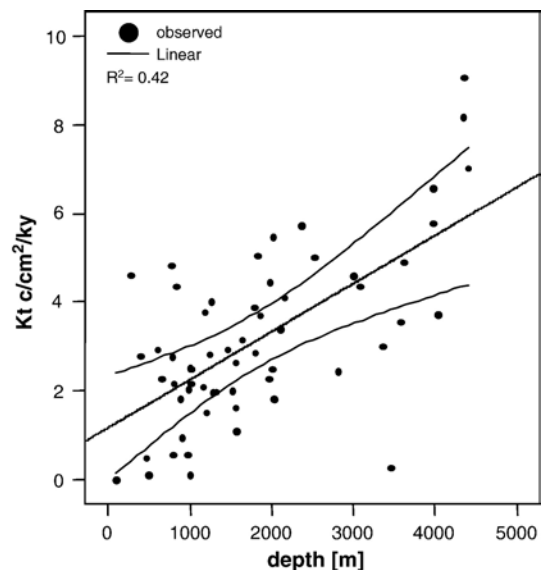

Fig. 9. Relationship between the degradation expressed of S-cysts by *kt* and water depth at the sample sites. Estimated linear relationship with 99.9% confidence limits of mean.
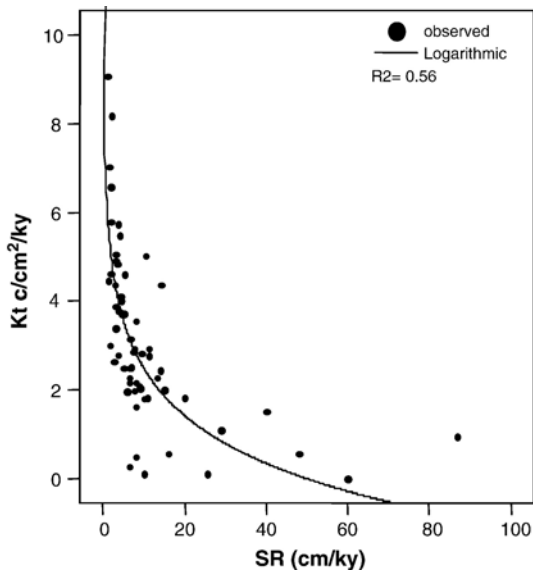
Fig. 10. Relationship between the degradation expressed of S-cysts by *kt* and the sedimentation rates at the sample sites.

conditions in surface waters such as nutrient availability, temperature, irradiance, turbulence and by endogenic encystment rhythms. (e.g. Pfiester and Anderson, 1987). Although salinity is an important parameter influencing the geographic distribution of dinoflagellates, it is not known to trigger or influence their sexuality and cyst production. Laboratory experiments show that cyst production can often be induced when phototrophic dinoflagellates are grown under nitrogen or phosphate limitation and when cultures of heterotrophic dinoflagellates are exposed to food limitation (e.g. Anderson and Lindquist, 1985; Ishikawa and Taniguchi, 1996; Montresor et al., 1998; Sgrosso et al., 2001; Olli and Anderson, 2002; Alexandra Kraberg, pers. comm, 2005). However, studies in natural environments show that maximal cyst production occurs during or just after dinoflagellate cyst blooms, when nutrients in the water column are not limiting (Ishikawa and Taniguchi, 1996; Montresor et al., 1998; Kremp and Heiskanen, 1999; Godhe et al., 2001). Results of a long-term sediment trap study from just outside the upwelling region off NW Africa, covering a time interval of 5 years, shows that cyst export production of phototrophic dinoflagellates is increased when more nutrients in the upper water column are available and that cyst production of a group of heterotrophic dinoflagellates is positively related to the export production of diatoms. In turn, export production of diatoms, the main food source of dinoflagellates, follows nutrient availability in upper waters (Susek et al., 2005). As a possible explanation for this paradox it is suggested that at maximal vegetative

growth, nutrient depletion can occur within individual cells or their microhabitat and as such triggering enhanced sexuality. The amount of gametes produced is therefore related to the amount of motiles but individual specimens are triggered to produce gametes by nutrient or food depletion. Nevertheless, independent of if this hypothesis is true or not, in natural environments, for both groups of dinoflagellates (R-cysts and S-cysts) increased cyst production is related to enhanced production of motiles which in turn is observed when nutrient, trace element or food conditions are favorable.

Numerous studies show that dinoflagellates have complex ecologies with the cyst production of every species dependent on biotic and a-biotic factors (e.g. Marret and Zonneveld, 2003; Rochon and Marret, 2004; Harland et al., 2004). Within this study we have grouped cysts with different ecologies. By doing so, we expect that environmental factors that influence the cyst production, transport and preservation of all species in the group in a similar way, will have a strong relationship with the total cyst accumulation of that group. On the contrary, a damped effect is expected for factors that influence only part of the species within the group, or influence individual species of the group in different ways. We have correlated the a-biotic environmental factors; bottom water $[O_2]$, water depth, mean annual chlorophyll-*a*, SST, SSS, nitrate and phosphate concentrations, with total accumulation rates of R-cysts and S-cysts. The multivariate ordination analysis shows that mean annual SST, SSS, nitrate and phosphate concentrations do not show a significant relationship to the variation in accumulation rates of R-cysts or S-cysts (Fig. 11, Table 4.). We therefore suggest that they had differential effects on the production of individual cyst
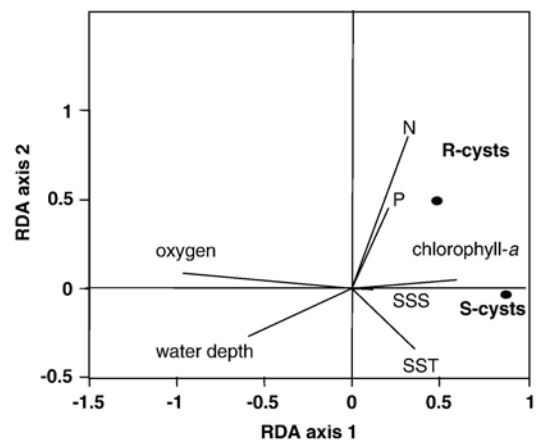

Fig. 11. RDA diagram of R-cyst and S-cyst accumulation rates with environmental variables.

species within the groups. Only the factors bottom water [O_2], chlorophyll-*a* and water depth showed a significant relationship with accumulation rates of R-cysts and S-cysts. With exception of chlorophyll-*a* these factors can not directly influence cyst production in upper water masses.

To date, satellite measurements routinely provide global chlorophyll-*a* biomass. Since the remote sensing determination of phytoplankton carbon has been proven to be elusive, net primary production estimates use chlorophyll-*a* as an index of phytoplankton biomass (e.g. Campbell et al., 2002). Although the above mentioned method has constrains and it is assumed that about 30% of daily watercolumn photosynthesis is missed by satellite based estimates (e.g. Behrenfeld et al., 2005; Mouw and Yoder, 2005), we can safely assume that mean annual chlorophyll-*a* is a qualitative reflection of mean annual net primary production. Assuming that more cysts of heterotrophic dinoflagellates might be produced when more food is available we could expect to find a positive causal relationship between mean annual chlorophyll-*a* concentration and S-cyst accumulation rates. However, although a trend is visible the relationship is weak ($R^2 = 0.35$, *F*-value = 30.36 on 1 and 57 degrees of freedom, Fig. 7, Table 4). A possible explanation for this could be that the cyst production of S-cysts is related to the presence of individual phytoplankton prey species rather than to the phytoplankton community as a whole.

The positive relationship between R-cysts and upper water mean annual chlorophyll-*a* concentrations suggests that the accumulation of R-cysts is somehow related to the total phytoplankton production in upper waters (Fig. 5). We do not think this relationship to be causal but assume that chlorophyll-*a* and R-cyst accumulation rates react on similar factors, although we can not exclude a causal relationship completely, given the fact that many, if not all, dinoflagellates that are capable of photosynthesis, are capable of heterotrophy (Schnepf and Elbrächter, 1999; Smayda and Reynolds, 2003 and references therein). However, within our database we find one exception at site GeoB 3607. At this site chlorophyll-*a* values are a factor 100 higher than at the other studied sites whereas accumulation rates of R-cysts have intermediate values. This sample is located at the edge of an active upwelling cell along the Namibian coast. In contrast to all other studied sites, considerable mixing of waters takes place in the upper water column at this site. Field and laboratory studies show that dinoflagellate growth and cyst production can be strongly (negatively) influenced by turbulence intensity and the duration of turbulent

phases (e.g. Thomas et al., 1995; Gibson and Thomas, 1995; Gibson, 2000; Smayda and Reynolds, 2001). They appear to be much more sensible for turbulence than other groups of primary producers such as diatoms. In high productivity areas such as upwelling regions it is often observed that dinoflagellates become abundant in the phytoplankton at times of upwelling relaxation when the watercolumn becomes more stratified or in the more stratified upwelling filaments (e.g. Shannon and Pillar, 1986; Mitchell-Innes and Walker, 1991; Pitcher et al., 1991; Veldhuis et al., 1997; Smayda and Reynolds, 2003). At site GeoB 3607 turbulence might therefore be the limiting factor for cyst production.

4.2. Transport

Apart from reflecting differences in initial production and preservation processes at the sediment–water interface, accumulation rates can be affected by processes of winnowing or focussing. Winnowing or focussing result in an underestimation or overestimation of the accumulation rates compared to the real influx of cysts into the sediments. Regarding the fact that the size and cyst-outlines of the grouped species are comparable indicates that the processes of winnowing/focussing will have a similar effect on both groups. The marked differences in relationship of R- and S-cysts with upper water and bottom water conditions can, therefore, not be the result of winnowing or focussing.

Several authors have suggested that lateral transportation of cysts during downward migration within the water column or after deposition might form an important factor affecting the cyst distribution (e.g. Dale and Dale, 1992; Harland and Pudsey, 1999). However, with the exception of mass transport (e.g. turbidites) studies on distribution patterns of cysts in modern undisturbed sediments as well as sediment trap studies that evidence of lateral transport, document small scale transport only (e.g. (Zonneveld and Brummer, 2000; Marret and Zonneveld, 2003; Susek et al., 2005). As far as we know no evidence is found that species selective cyst transport occurs in natural environments. We therefore assume that species specific transport of cysts is not the cause of the observed differences in relationship between R-cysts and S-cysts and bottom water [O_2], water depth and upper water chlorophyll-*a*.

4.3. Preservation

We observe a significant exponential relationship between S-cysts accumulation rates and bottom water

[O$_2$] (Fig. 4, Table 4). As discussed above, this relationship can not be explained by differential production related to upper water conditions and selective transport. Our results are consistent to earlier studies that conclude S-cysts to be extremely sensitive for degradation based on similar relationships and comparison with chemical data (Zonneveld and Brummer, 2000; Zonneveld et al., 2001; Versteegh and Zonneveld, 2002; Hopkins and McCarthy, 2002; Reichart and Brinkhuis, 2003; Bockelmann and Zonneveld, submitted for publication) Again consistent with earlier studies we find no clear relationship between R-cysts accumulation rates and bottom water [O$_2$] subscribing the assumption that they are minimally affected by aerobic degradation (Fig. 5, Table 4). We assume that the difference in relationship between R-cysts and S-cysts with [O$_2$], can be subscribed to a fundamental difference in the chemistry of the cyst walls of both groups. Such a difference has previously been evidenced by differences in fluorescence, vulnerability to staining or oxidative laboratory treatments by various authors (e.g. Dale, 1976; Marret, 1993; Elbrächter, 1994 and references therein). To date, chemical data of dinoflagellate cyst walls are limited but indicate that they are composed of complex biomolecules (Kokinos et al., 1998; Versteegh and Blokker, 2004; de Leeuw et al., 2006). Nuclear magnetic resonance (NMR) analysis of the fossillisable organic inner-wall of *Scrippsiella* sp. (a peridinioid) cysts that are included into the species *Brigantedinium* spp. by palynologists, suggests that the macromolecules contain a substantial aliphatic component (Hemsley et al., 1994). A comparable aliphatic component is absent in the dinoflagellate cyst walls of *Lingulodinium polyedrum* (a gonyaulacoid) in contrast to the presence of condensed and predominantly aromatic components (Kokinos et al., 1998). Furthermore, laboratory experiments based on cyst cultures and sediments suggest that gonyaulacoid cysts consists of a high proportion of carbon and ether-linked macromolecular building blocks, whereas the building blocks of peridinoid macromolecules are much more ester linked (for an overview see Versteegh and Blokker (2004)). Versteegh and Blokker (2004) suggested that there are two variables influencing cyst wall composition, (1) the proportion of aliphatic versus aromatic moieties and (2) the proportion of ether- and carbon-bonds versus ester-bonds.

Sediment trap studies have so far revealed no evidence that organic-walled dinoflagellate cysts are prone to degradation during their transport within the water column (Zonneveld and Brummer, 2000; Susek et al., 2005). This might be the result of the fact that cyst accumulation is thought to be a rather fast process resulting in a relatively short reaction time. Within this study we observe a weak negative relationship between S-cysts accumulation rates and water depth that might suggest a degradation of these cysts within the water column. However, water depth co-varies with bottom water [O$_2$] and after correction for this co-variance, no significant relationship can be documented (Table 3).

4.4. Cyst accumulation rates as a tool to estimate past net primary productivity?

One of the aims of this study is to discuss if we can use accumulation rates of R-cysts to estimate past net primary productivity. We observe a significant positive relationship between accumulation rates of R-cysts and chlorophyll-*a*, according to Eq. (2) (Fig. 6, Table 4). Given the discussion above we can assume that this equation has the potential to be used as a past productivity proxy. We realise that this suggestion will cause controversy within the dinoflagellate research community given the discussions that are being held about al attempts to digitalise past environmental conditions using dinoflagellate cyst associations (e.g. Dale et al., 2002; de Vernal et al., 2005). However, we suggest this relationship to be tested in palaeostudies to obtain insight in its usability and limitations. Our results already point out that this relationship cannot be used in environments that are characterised by strong or long-lasting turbulence or in case other environmental factors influence dinoflagellate growth and cyst production differently from production of other phytoplankton groups. Nevertheless, the empirical relationship appears to be clear in a large variety of environments.

4.5. Degradation rates of dinoflagellate cysts as a tool to estimate past deep ocean oxygen concentrations

The calculation of the degradation (expressed by *kt*) of sensitive dinoflagellate cysts assumes that the initial production of sensitive dinoflagellate cysts is related to the production of resistant dinoflagellate cysts in all studied environments. This is based on the relationship we found in various regions, in sediment trap samples and samples from anoxic environments, where selective degradation can be expected to be minimal and where cyst accumulation rates of both groups can be assumed to reflect changes in their initial production (e.g. Reichart and Brinkhuis, 2003). As far as we know, there is no evidence from the literature that our assumption does not hold. Furthermore, if our assumption is wrong we would expect to find a random signal

between kt and environmental gradients (such as bottom water [O_2]; Fig. 8).

A logical question arises; how causal is the relationship between kt and bottom water [O_2]. As explained in the Introduction part, individual OM components typically show a first order decay (e.g. Middelburg, 1989; Hartnett et al., 1998; Hedges et al., 1999). The cyst wall degradation can be considered to depend on the degradability of its biomolecules (expressed by their degradation constants k) and the oxygen exposure time (t). Other factors that are known to influence the rate of aerobic decay of organic matter such as bioturbation and sedimentation rates, oxygen concentration and water depth, are considered to actually modulate the effects of the oxygen exposure time (e.g. Hartnett et al., 1998; Sun et al., 2002; Keil et al., 2004). A decrease in rate of aerobic decay of organic matter with reaction time has often been observed and several mechanisms have been proposed to explain this phenomenon such as organic recalcitrance and biotic exclusion (e.g. Tegelaar et al., 1989; Derenne and Largeau, 2001; Mayer, 2004). For instance, complex biomolecules vary in their ease to disassembly, at monomer, polymer or supramolecular scales of organisation. In the case of organic-walled dinoflagellate cysts, it is therefore possible that for sensitive cysts the "degradation constant", k is not completely constant with the most labile species degrading first, therefore increasing the relative amount of the less sensitive species through time. Through biotic exclusion, some organisms, or their digestive agents, are excluded or inhibited from access to organic matter, for instance through the accumulation of harmful metabolites or by transporting material to anoxic environments through bioturbation processes. Indeed kt shows a decreasing relationship to increasing sedimentation rates (Fig. 10) which suggests that the degradation processes might take place in the upper sediments or at the sediment–water interface.

If dinoflagellate cyst degradation is a first order process there should be a constant or decreasing relationship between kt and all the factors reflecting oxygen exposure time. The relationship between kt and [O_2] is however more complex, suggesting a higher order degradation process. At low [O_2] there is a strong increase in the degradation with increasing [O_2] that becomes less intense at intermediate [O_2]. Above a [O_2] at 4 ml/l there is an exponential increase. This pattern can be explained when cysts are being degraded though a process with oxygen concentration being the limiting factor inhibiting the growth rate of degrading organisms (Jorge and Livingston, 1999; Guerra-Garcia and

García-Gómez, 2005). With the degrading organisms increasing in numbers with increasing oxygen concentration the rate of degradation will also increase. However, at a certain threshold oxygen concentration the population of the degrader increases to a point where all S-cysts are being consumed and kt values increase exponentially to ∞.

There are several methods to estimate past deep-ocean ventilation based on the sediment structure and the (bio-)chemical content of sediments including, numerical models, as well as the chemical and isotopic composition of microfossils (e.g. Francois et al., 1997; Toggweiler, 1999; Ninnemann and Charles, 2002; Matear and Hirst, 2003; McManus et al., 2004; Ivanochko and Pedersen, 2004). However, the estimation of past bottom oxygen concentrations is still problematic. The relationship documented here might form the basis of a new method that makes quantitative estimations of past deep-ocean oxygen concentrations possible. First applications of this method in sediments deposited during the last deglaciation, last 140 ky and between 3.2 and 2.5 Ma years BP imply ventilation changes of the deep equatorial Atlantic, South Atlantic and Southern Ocean (Atlantic Sector; Versteegh and Zonneveld, 2002; Bockelmann and Zonneveld, submitted for publication). Further studies are required to determine the accuracy and restrictions of the method.

4.6. General remarks

Our results are in opposition to the strong traditional belief within the dinoflagellate research community, that cyst forming dinoflagellates with a heterotrophic life strategy prefer high productivity regions characterised by eutrophic conditions, whereas phototrophic cyst forming dinoflagellates prefer low productivity, oligotrophic environments. This belief finds its basis in the results of the first pioneering studies on the geographic distribution of dinoflagellate cysts in modern environments carried out in the 60's and 70's of the last century. A strong dominance of cysts of photosynthetic species in the central oceanic basins was documented whereas the cyst associations of most coastal sediments appeared to be dominated by cyst of heterotrophic species (see overviews in Wall et al., 1977; Harland, 1983 and references therein). However, the lack of good dating methods prevented the calculation of accumulation rates in these studies. The recent compilation of large worldwide datasets show, that there are many sites from "low productivity, oligotrophic" regions that are dominated by heterotrophic taxa and vice versa (de Vernal et al.,

2001; Marret and Zonneveld, 2003). Furthermore, several photosynthetic R-cyst species have their highest abundances in regions where eutrophic conditions prevail. For instance *Dalella chathamensis* can dominate assemblages in sediments of the eutrophic Southern Ocean frontal zones (Marret and Zonneveld, 2003). *Nematosphaeropsis labyrinthus*, *Pentapharsodinium dalei* and *Pyxidinopsis reticulata* can dominate cyst associations in regions characterised by eutrophic upper water conditions whereas the distribution of *Impagidinium pallidum*, is even restricted to these environments (Marret and Zonneveld, 2003). Several heterotrophic dinoflagellates have their highest abundances in "oligotrophic regions". For instance *Polykrikos* species (such as *Polykrikos kofoidii* and *Polykrikos schwarzii*) and *Votadinium spinosum* have high or even their highest relative abundances in the oligotrophic part of the China Sea. These datasets indicate therefore, that the environmental "preferences" of cyst forming dinoflagellate species should not be generalised but have to be considered on an autoecological (= species) level and that the initial concept is due for revision.

Also in recent years many studies document that the cyst association of high productivity areas is dominated by heterotrophic species and conclude that dominance of hetrerotrophic species are characteristic for these regions (e.g. Hamel et al., 2002; Radi and de Vernal, 2004). These studies do, however, not consider the possible effect of selective preservation on the relative abundances of cysts and do not correct for differences in sedimentation rates in the studied region. Hence, although the conclusions that eutrophic regions are often characterised by a dinoflagellate association dominated by cysts of heterotrophic species whereas sediments of oligotrophic regions are characterised by a dominance of cysts of photosynthetic species are valid, the conclusion that cysts of both groups are produced in higher amounts in the respective regions can not be drawn. These studies give no support to the idea that heterotrophic dinoflagellates or phototrophic species "prefer" eutrophic or oligotrophic regions respectively. Our results indicate that cyst production has to be considered at an autecologic scale and that only in case of excellent preservation (as can occur in regions characterised by oxygen minimum zones) cyst accumulation rates of S-cysts reflect their export production. It can be expected that in these extreme conditions their accumulation rates co-vary with changes in total export productivity (Reichart and Brinkhuis, 2003). Consequently, the results of this study clearly demonstrate that the traditional view about the ecology of cyst forming dinoflagellates has to be evaluated.

5. Conclusions

Accumulation rates of dinoflagellate cyst species known to be resistant against (post-depositional-) aerobic decay (r) show a significant positive relationship with upper water chlorophyll-a concentrations (y) according to the equation: $y = 0.0002r + 0.2271$ ($R^2 = 0.70$). No relationship with bottom water oxygen concentrations, annual sea-surface temperature, salinity, nitrate and phosphate concentrations can be observed. This is in contrast to the general opinion that species producing these cysts are being produced in higher amounts in oligotrophic environments. The reason for this seemingly paradox is that previous studies considered relative abundances of cysts in sediments, did not correct of differential sedimentation rates or did not consider the possible effect of species selective preservation. Our study suggests that R-cyst accumulation rates might be a useful proxy to estimate net primary production in the past. Exception is found in regions with environments that are characterised by strong or long-lasting turbulence or in case other environmental factors influence dinoflagellate growth and cyst production differently from production of other phytoplankton groups.

Accumulation rates of dinoflagellate cysts known to be sensitive for aerobic degradation exponentially decrease in relation to bottom water oxygen concentration ($R^2 = 0.73$). Only a weak correlation can be found with upper water chlorophyll-a concentrations ($R^2 = 0.35$). This suggests that aerobic degradations might strongly overprint the initial production signal. Only in case of excellent preservation (as can occur in regions characterised by oxygen minimum zones) cyst accumulation rates of S-cysts reflect their export production.

The observed relationships between kt, water depth and sedimentation rates suggest that processes of organic recalcitrance and biotic exclusion might take place in the upper sediments rather than within the water column.

The positive relationship between degradation rates of S-cysts (kt) and bottom water $[O_2]$ according to the equation $[O_2] = 5.17 / 1 + e^{-1.23(kt - 2.058)}$ ($R^2 = 0.85$) suggests that S-cysts are being degraded according to a higher order decay process. This relationship forms the basis for a proxy that can be used to estimate past bottom water oxygen concentration.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. margeo.2006.10.023.

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