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# Dissolved organic carbon in coral-reef lagoons, by high temperature catalytic oxidation and UV spectrometry

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1997

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**Abstract** Two surveys were carried out on ten atolls in the Tuamotu archipelago (French Polynesia, Pacific Ocean). *In vitro* UV (250–400 nm) spectra of water samples gave absorption at 254 nm,  $A_{254}$ , and spectrum slope,  $S^*$  (computed from  $\ln A_\lambda$  versus  $\lambda$ ). These two descriptors are negatively correlated, and data points are arrayed along a hyperbola spanned between an oceanic pole (high  $S^*$ , low  $A_{254}$ ) and a confined pole (low  $S^*$ , high  $A_{254}$ ).

Dissolved organic carbon (DOC) concentrations, [C], as assessed by HTOCO, exhibit a narrow range (0.7–1.0 mg C.L<sup>-1</sup> for most lagoons) contrasting with the wide diversity of optical characteristics. [C] and  $A_{254}$  are positively correlated, with a significant intercept (0.5 mg C.L<sup>-1</sup>) representing non-chromophoric DOC. Carbon-specific absorption,  $\epsilon_{254}$ , increases (from 0.4 to 1.3 m<sup>2</sup>.g<sup>-1</sup>) with increasing [C], mainly according to the literature) owing to increased average molecular weight (MW) of the chromophoric DOC fraction, which also lowers  $S^*$ .

Our optical data thus illustrate a gradient of confinement (or residence time) that corresponds to a continuum in DOC nature, especially in MW and hence in bioavailability. Optical methods are confirmed as quick and effective means of assessing DOM distribution.

**Keywords:** Coral reef lagoons, Dissolved organic carbon, Specific UV absorption, Tuamotu, France.

## Résumé Carbone organique dissous dans des lagons d'atoll, par combustion catalytique à haute température et par spectrophotométrie

Deux campagnes ont prospecté dix lagons d'atoll des Tuamotu (Polynésie française, océan Pacifique). Sur des échantillons d'eau, le spectre UV (250–400 nm) *in vitro* est décrit par l'absorption à 254 nm,  $A_{254}$ , et la pente,  $S^*$  (régression de  $\ln A_\lambda$  vs  $\lambda$ ). Ces deux descripteurs sont négativement corrélés. Les points s'organisent le long d'une hyperbole entre un pôle océanique (fort  $S^*$ , faible  $A_{254}$ ) et un pôle confiné (faible  $S^*$ , fort  $A_{254}$ ).

Le carbone organique dissous (COD) présente des concentrations ([C], déterminées par HTOCO) peu variables (0,7–1,0 mg C.L<sup>-1</sup>), contrastant avec la large diversité des propriétés optiques. [C] et  $A_{254}$  ont une corrélation positive, avec une ordonnée à l'origine significative (0,5 mg C.L<sup>-1</sup>) correspondant à une fraction « non chromophorique » du COD. L'absorption spécifique ramenée au carbone,  $\epsilon_{254}$ , croît (de 0,4 à 1,3 m<sup>2</sup>.g<sup>-1</sup>) pour des [C] croissantes, surtout (d'après la littérature) en relation avec une augmentation du poids moléculaire moyen, qui abaisse les valeurs de  $S^*$ .

Nos mesures optiques décrivent ainsi un gradient de confinement (ou de temps de séjour) qui correspond à un continuum dans la nature du COD, dont son poids moléculaire et donc sa susceptibilité à une action biologique. Cette méthode rapide confirme son efficacité pour la description de la distribution de la MOD.

**Mots clés :** Lagons d'atoll, Carbone organique dissous, Absorption spécifique UV, Tuamotu, France.

### Note

présentée par  
Georges Pedro.

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acceptée après révision  
le 24 février 1997.

Version  
française  
abrégée

**M**ALGRÉ l'importance quantitative de la matière organique dissoute (MOD) marine dans le cycle global du carbone, seule une faible fraction de cette MOD peut être identifiée chimiquement. Or, la nature de la MOD conditionne, entre autres, son utilisation par les bactéries hétérotrophes. Si l'identification fine est exclue, la reconnaissance de grandes catégories (par exemple sur la base du poids moléculaire) semble possible par des méthodes non chimiques. Nous avons employé la spectrophotométrie dans l'ultraviolet (entre 250 et 400 nm), qui permet un classement semi-quantitatif de types de MOD. Parallèlement, un dosage classique du carbone organique dissous (COD; Shimadzu TOC-5000) fournit une comparaison avec les données optiques, en même temps que des valeurs absolues. Les observations, réalisées dans le cadre du programme TypAtoll, ont été effectuées sur dix atolls des Tuamotu, au cours de deux campagnes.

Les spectres d'absorption sont décrits par leur pente,  $S^*$ , et l'absorption à 254 nm,  $A_{254}$ . Ces deux descripteurs présentent une corrélation négative (fig. 1;  $r^2 = 0,60$ ,  $n = 327$  points). Chaque lagon fournit un nuage de points bien groupés, nettement séparé de celui des autres lagons. Nous déterminons que la distribution des échantillons le long de la courbe de régression correspond à un gradient de confinement entre deux extrêmes: d'une part, des eaux « océaniques », oligotrophes, à fort  $S^*$  et faible  $A_{254}$ , d'autre part des eaux « confinées », ou mésotrophes, à fort  $A_{254}$  et faible  $S^*$ .

Les concentrations en COD,  $[C]$ , sont assez homogènes (0,7 à 1,0 mg C.L<sup>-1</sup>) dans la

plupart des lagons. Rekareka et Taiaro, lagons confinés, font exception ( $[C]$  de 1,1 et 1,8 mg C.L<sup>-1</sup> respectivement). Le COD est bien corrélé avec  $A_{254}$  ( $r^2 = 0,8$ ), malgré les échantillons océaniques, à léger excès de COD par rapport à leur  $A_{254}$  (fig. 2). Cette régression présente une ordonnée à l'origine d'environ 0,5 mg C.L<sup>-1</sup> qui correspond à une fraction optiquement inactive. L'absorption spécifique (ramenée au COD),  $\epsilon_{254}$ , varie entre 0,4 et 1,4 m<sup>2</sup>.gC<sup>-1</sup>. Elle présente une corrélation négative avec  $S^*$  ( $1/\epsilon_{254}$  vs  $1/S^*$ ;  $r^2 = 0,62$ ).

Nous vérifions que la concentration en COD prédite à partir de  $A_{254}$ ,  $[C_A]$ , diffère peu ( $\pm 0,1$  mg C.L<sup>-1</sup> en moyenne) de la concentration déterminée par HTCO,  $[C_m]$  (fig. 3).

Une part de la variation de  $\epsilon_{254}$  (augmentation pour des  $[C]$ , et des  $A_{254}$ , croissants) peut être due au seul artefact « mathématique » de la présence du COD optiquement inactif, mais la proportion de COD « chromophorique » peut aussi varier. Enfin, selon la littérature, l'évolution de  $\epsilon_{254}$ , et de  $S^*$ , reflète aussi la variation du poids moléculaire moyen de cette fraction optiquement active. Les caractéristiques optiques du COD varient beaucoup plus que la valeur globale fournie par le dosage HTCO « classique », en relation avec la nature de la MOD, et donc en fonction de son histoire. Sa susceptibilité à une attaque biologique en dépend.

Les méthodes optiques sont rapides, et nous confirmons leur efficacité pour l'étude qualitative et semi-quantitative de la distribution de la MOD naturelle.

## I. INTRODUCTION

It is well accepted that dissolved organic matter (DOM) represents the main organic compartment in the global aquatic carbon stock. Despite this importance, several authors have explicitly underlined that only a small part (5–30%) of marine DOM can be chemically characterized (Collins and Williams, 1977; Chen and Bada, 1992; Benner et

al., 1992; Lee and Henrichs, 1993; Amon and Benner, 1996). This has a direct consequence on the perspectives of assessing DOM's bioavailability, which is at least as important as knowing total DOC concentration (see example in Benner et al., 1995). Describing "bulk characteristics" of marine DOM will thus remain a plausible aim, while it would be

useful to recognize some broad categories (Hobbie, 1992), for instance through non-chemical methods (Coble *et al.*, 1990).

Among these, optical characteristics have been widely used, perhaps more often in continental waters (partial review in Moore, 1987) than in open-sea waters. We applied spectrophotometry to characterize the waters of several coral-reef lagoons, with the initial aim of a typological, semi-quantitative classification (Pagès *et al.*, 1997). We could thus describe the distribution of qualitative characters of DOM (or at least of its "chromophoric" part) among different lagoons. Here, we compare these results with those of the classical HTCO (high temperature catalytic oxidation) assessment of DOC concentration, to determine whether i) there is a relationship between optical properties and DOC concentration, and ii) we can predict DOC from optics.

## II. MATERIAL AND METHODS

Our observations were part of several programs studying the general biological produc-

tion of atoll lagoons, and more specifically the processes in the water column. The main series of samples was taken during surveys (the "Typatoll" cruises) carried out in November 1995 ("Typatoll 3") and March 1996 ("Typatoll 4"), during which we studied a total of ten atolls in the Tuamotu archipelago (15–18°S, 141–146°W). Open-sea samples were also collected. Some characteristics of the lagoons studied here are given in **table I**.

Sampling was performed within a few hours on each atoll, at 5–8 stations (see details in Pagès *et al.*, 1997).

Spectrophotometry was performed on board during the surveys. We used a Milton Roy "Spectronic 1201" fitted with a 100 mm quartz cell. We measured absorption ( $A_\lambda$ ) at 12 discrete wavelengths between 250 and 400 nm against blanks of distilled de-ionized water. Reproducibility of absorption values is good. Mean coefficient of variation on 71 duplicates (either successive sub-samples or duplicate samples) is 0.019 (i.e. less than 2%).

For DOC assessment, samples (11-mL) were not filtered (De Baar *et al.* 1993), but preserved with  $\text{HgCl}_2$  (200  $\mu\text{L}$  of a 0.5  $\text{g}\cdot\text{L}^{-1}$

**Table I** Some averaged characteristics of the lagoons studied (lagoons in alphabetical order).

*Données moyennes des lagons étudiés (par ordre alphabétique).*

Lagoon	Area	Z	$A_{254}$		$S^*$		DOC		$\epsilon_{254}$		POC	
			T3	T4	T3	T4	T3	T4	T3	T4	T3	T4
Haraiki	10.4	8.3	0.80	0.93	0.018	0.015	0.88	0.78	0.91	1.19	0.11	0.18
Hikueru	82.5	18	0.67	0.74	0.023	0.025	1.05	0.96	0.65	0.77	0.05	0.11
Hiti	15.3	8	0.79	0.75	0.020	0.019	0.96	0.95	0.83	0.79	0.11	0.12
Kauehi	315	32	0.47	0.55	0.022	0.024	0.91	0.85	0.52	0.65	0.05	0.09
Marokau	217	20	0.61	0.65	0.024	0.021	0.76	0.88	0.80	0.74	0.09	0.11
Nihiru	79	18	0.74	0.71	0.021	0.018	0.075	0.74	0.99	0.97	0.06	0.11
Rekareka	0.74	1.0	1.43	1.28	0.016	0.015	1.20	1.03	1.18	1.25	0.22	0.23
Taiaro	11.8	12	2.58	2.13	0.022	0.025	1.91	1.72	1.36	1.24	0.18	0.20
Tekokota	5.1	3	0.45	0.43	0.022	0.019	0.75	0.74	0.61	0.58	0.05	0.09
Tepoto Sud	1.6	5	0.68	0.47	0.018	0.023	0.90	0.76	0.77	0.62	0.13	0.12
Ocean	—	—	0.40	0.37	0.036	0.043	0.98	1.03	0.42	0.36	0.05	0.05

Each figure is based on six separate stations. For each characteristic, twin columns give the results from Typatoll 3 (T3) and Typatoll 4 (T4) surveys. Lagoon area in  $\text{km}^2$ ; averaged depth (Z) in m; absorption  $A_{254}$  in  $\text{m}^{-1}$ ; spectrum slope  $S^*$  in  $\text{nm}^{-1}$ ; carbon-specific absorption  $\epsilon_{254}$  in  $\text{m}^2\cdot(\text{g}\cdot\text{C})^{-1}$ ; DOC and POC in  $\text{mg}\cdot\text{C}\cdot\text{L}^{-1}$ .

*Chaque valeur est fondée sur six stations distinctes. Pour chaque paramètre, deux colonnes donnent les résultats des deux campagnes, Typatoll 3 (T3) et Typatoll 4 (T4).*

solution) and HCl (50  $\mu\text{L}$  of a 6 N solution), and kept at 5 °C on board. Measurements were made (at least in duplicate) with standard HTCO techniques on a Shimadzu TOC 5000. Mean standard error on duplicates was 0.046 mg C.L<sup>-1</sup>, i.e. 4.3%. These TOC figures were then corrected for particulate organic carbon (POC), which we determined with a Leco CHN analyzer.

### III. RESULTS

#### 1. Spectral parameters and qualitative aspects

Most of this section has been expounded elsewhere (Pagès *et al.*, 1997), but must be briefly recalled for comprehension of the following.

Absorption spectra show the classical linear relation between  $\ln A_\lambda$  and  $\lambda$  (Bricaud *et al.*, 1981). Spectrum slope ( $S^*$ ) values range between 0.009 and 0.030 nm<sup>-1</sup> in atolls, while oceanic samples exhibit higher values, up to 0.040 nm<sup>-1</sup> (table I). Absorption at 254 nm

( $A_{254}$ ) mostly ranges between 0.5 and 0.8 m<sup>-1</sup>, with lower values (0.4 m<sup>-1</sup>) in oceanic samples, and higher values (up to about 2 m<sup>-1</sup>) in some confined lagoons (Rekareka and Taiaro).

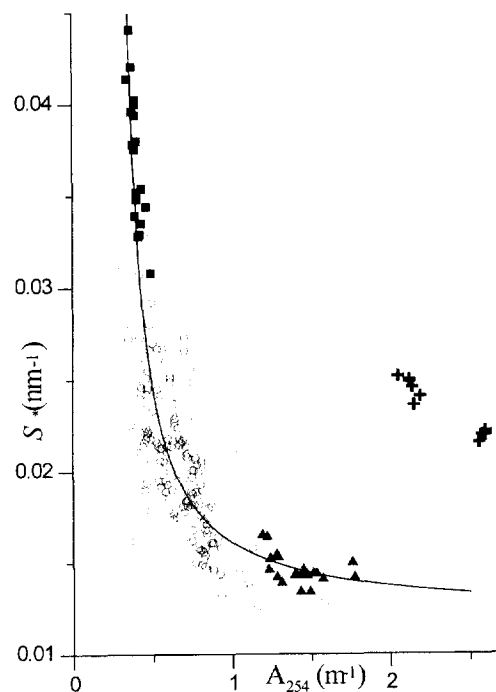
A plot of  $A_{254}$  against  $S^*$  for all lagoon and seawater samples (fig. 1) shows an inverse correlation between these two descriptors. The waters from Taiaro, a closed lagoon with abundant terrestrial vegetation, are conspicuous outliers. Their abnormally high  $S^*$  values stem from the presence of lignin degradation products and humic acids (ms in prep.). Excluding this lagoon, the best fit ( $r^2 = 0.60$ ) is given by the regression of  $(1/S^*)$  against  $(1/A_{254})$  (see table II).

Data points are not randomly distributed along this hyperbolic regression curve. Spatially detailed observations in Tikehau lagoon (see details in Pagès *et al.*, 1997) show that data points are arranged between an “oceanic” pole, with high  $S^*$  values ( $\sim 0.04$  nm<sup>-1</sup>) and low  $A_{254}$  (0.4 m<sup>-1</sup>), and a “eutrophic” pole, with low  $S^*$  ( $< 0.01$  nm<sup>-1</sup>) and high  $A_{254}$  ( $> 2$  m<sup>-1</sup>). By mixing different water types, we could see that the observed hyperbola corresponds to mixtures, in varying proportions, between two main types of water reflecting the above description of the two poles. We are thus dealing with a continuum of waters between which there is no basic difference, but only a continuous variation of proportions.

#### 2. Quantitative aspects: DOC and carbon-specific absorbance

##### (a) DOC concentrations

For most lagoon samples, DOC concentrations [C] exhibit a narrow range, from 0.7 to 1.0 mg C.L<sup>-1</sup> (table I), against [C] values of  $\sim 1.0$  mg C.L<sup>-1</sup> in oceanic samples. Relatively high DOC concentrations are only found in Rekareka and Taiaro (averaging 1.11 and 1.82 mg C.L<sup>-1</sup>). Intra-lagoon variability is very low in most cases. Coefficient of variation (CV) for a given lagoon on a given survey generally amounts to  $\sim 5\%$ , and this includes the (low) analytical variability. If we consider only “normal” lagoons and oceanic samples,



**Fig.1** Spectrum slope,  $S^*$ , versus absorption at 254 nm,  $A_{254}$ . Symbols represent oceanic waters (■), Rekareka (▲), Taiaro (+), and other atoll lagoons (○). Solid curve represents the functional linear regression of  $1/S^*$  versus  $1/A_{254}$  (see table II).

Pente des spectres d'absorption  $S^*$  par rapport à l'absorption à 254 nm,  $A_{254}$ . Symboles : eaux océaniques (■); eaux des lagons, Rekareka (▲), Taiaro (+), autres (○). La courbe continue est celle de la régression linéaire fonctionnelle de  $1/S^*$  en fonction de  $1/A_{254}$  (voir tableau II).

**Table II** Functional correlations (Ricker, 1973) between variables.

Corrélations fonctionnelles (Ricker, 1973) entre variables.

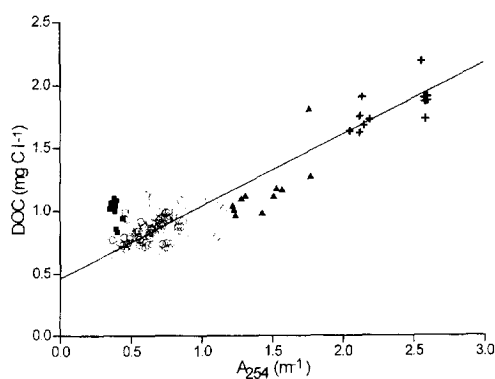
X	Y	Data	Slope	Intercept	r <sup>2</sup>	n	P
1/A <sub>254</sub>	1/S*	all data	-16.6	75.3	0.60	327	< 0.001
A <sub>254</sub>	[C]	all data	0.553	0.508	0.76	142	< 0.001
A <sub>254</sub>	[C]	without oceanic samples	0.580	0.465	0.83	130	< 0.001
1/S*	1/ε <sub>254</sub>	without oceanic samples	-0.034	3.069	0.62	130	< 0.001
[C <sub>Δ</sub> ]	[C <sub>m</sub> ]	lagoon averages, without oceanic samples	0.898	0.075	0.86	20	< 0.001

[C]: Dissolved organic carbon concentration, in mg C.L<sup>-1</sup>; [C<sub>m</sub>]: measured DOC concentration [C<sub>Δ</sub>]: DOC concentration; computed from A<sub>254</sub> and the A<sub>254</sub>-versus-[C] regression (without oceanic samples).

they exhibit a 1.5-fold amplitude for [C], against a two-fold one for A<sub>254</sub> (see **table I**).

Absorption, A<sub>254</sub> (in m<sup>-1</sup>), is correlated with DOC concentration (**fig. 2** and **table II**). The overall regression (r<sup>2</sup> = 0.76) is slightly improved (r<sup>2</sup> = 0.84) when oceanic samples exhibiting “too much” DOC are excluded. We can note that this correlation is acceptable only after including the “high DOC” lagoons (Taiaro and Rekareka); with “normal” lagoons only, the correlation is statistically significant (r = 0.521, n = 107, P > 0.001) but the regression is worthless in terms of predicting [C] from A<sub>254</sub>. The other salient point is the intercept, amounting to about 0.5 mg C.L<sup>-1</sup> of DOC without optical activity.

Inspection of the results indicates that A<sub>254</sub> allows a better discrimination between lagoons than does [C]. To quantify the discriminative potential of A<sub>254</sub> and [C], we tested the null hypothesis of a homogeneous population comprising all stations in all lagoons and the ocean during the two surveys (22 sets of six data each), using the Kruskal–Wallis one-way analysis by ranks (two-by-two comparison on rank sums of adjacent sets; 21 comparisons). Significance of the differences between lagoons was also tested using the Mann–Whitney test (two-by-two comparison on all data; 213 (i.e. 21 + 20 + 19 + ...) comparisons). Results of the two tests confirm that optics are more able to discriminate between lagoons than chemical (HTCO) DOC measurements.



**Fig. 2** DOC concentration versus A<sub>254</sub>. Same symbols as in figure 1. Oceanic samples are not included in the fitted line.

COD en fonction de A<sub>254</sub>. Les symboles sont les mêmes que ceux de la figure 1. Les échantillons océaniques sont exclus de la ligne droite.

#### (b) Specific absorption

We computed carbon-specific absorption as ε<sub>254</sub> = A<sub>254</sub>/[C], with A in m<sup>-1</sup> and [C] in mg C.L<sup>-1</sup>. Values of ε<sub>254</sub> (see **table I**) range between 0.5 and 1.0 m<sup>2</sup>.g<sup>-1</sup> in “normal” lagoons, but are higher for Rekareka and Taiaro lagoons (1.2–1.3 m<sup>2</sup>.g<sup>-1</sup>), while oceanic samples exhibit low ε<sub>254</sub> values (~0.4 m<sup>2</sup>.g<sup>-1</sup>).

Comparison between ε<sub>254</sub> and spectrum slope S\* shows a general inverse trend (high ε<sub>254</sub> values for low S\*), with Taiaro samples as prominent outliers (figure not shown). Excluding Taiaro, the best fit is given by a hyperbolic (1/ε<sub>254</sub> versus 1/S\*) equation with significant correlation (r<sup>2</sup> = 0.62, P < 0.001 for n = 130). Data points appear too widely scattered (figure not shown) for a satisfactory prediction of ε<sub>254</sub> from S\*.

## (c) Prediction of DOC concentration

The various correlations seen above should allow determination of DOC concentration,  $[C]$ , from optical properties, in particular from the regression between  $A_{254}$  and DOC concentration. We obtain a set of computed values,  $[C_A]$ , which we compare with actual (measured) values  $[C_m]$  (see **fig. 3**).

In the narrow range of "normal" lagoons ( $n = 96$ ), mean values ( $\pm$  s.d.) agree very well: 0.852 ( $\pm 0.096$ ) for  $[C_m]$ , against 0.827 ( $\pm 0.083$ ) for  $[C_A]$ . For oceanic samples,  $[C_A]$  values are underestimated (0.68 mg C.L<sup>-1</sup> instead of 1.00), in accordance with the divergence between  $[C_m]$  and  $A_{254}$  (section (a)). Considering now the whole range, with the two "eutrophic" lagoons (Rekareka and Taiaro), we obtain a high correlation ( $r^2 = 0.857$ ) between  $[C_m]$  and  $[C_A]$  (see **fig. 3** and **table II**).

## IV. DISCUSSION

The relations we found between optical properties and DOC concentration,  $[C]$ , have two aspects: i) quantified prediction of  $[C]$  and ii) semi-quantified evaluation of the nature of the DOC.

Optics, and especially absorption at a given wavelength, have been widely used as a proxy estimator (or a "surrogate parameter" (Summers *et al.*, 1987)) of DOM concentration, in the laboratory or in the field. Even if caution is necessary in some particular environments, such as hard-water lakes (Stewart

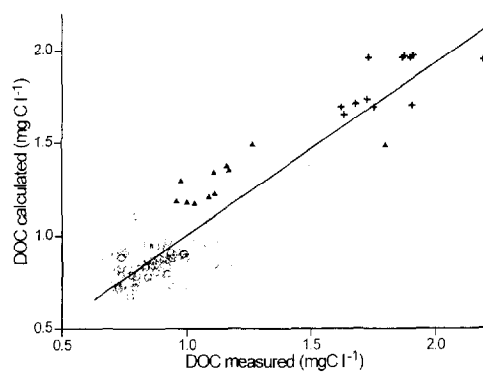
and Wetzel, 1981), optical measurements provide an interesting method for DOC assessment, once duly calibrated. In our case, agreement between measured  $[C_m]$  and computed  $[C_A]$  is reasonable ( $r^2 \sim 0.86$ ) across the whole range studied here (including Rekareka and Taiaro).

Excluding Rekareka and Taiaro, the "normal" lagoons show a small relative variation in total DOC concentration (range 0.74–1.05 mg C.L<sup>-1</sup>). This contrasts with the much wider variation in absorption ( $A_{254}$  ranging between 0.43 and 0.93 m<sup>-1</sup>). We have seen that  $A_{254}$  discriminates better between lagoons than does bulk DOC concentration. The sensitivity of optical characteristics (both  $\epsilon_{254}$  and  $S^*$ ) to minute variations in DOM nature and/or concentration has been shown in a previous paper (Pagès *et al.*, 1997).

The DOC concentrations we found are quite normal for oligo- to mesotrophic waters (Martin and Fitzwater, 1992; Guo *et al.*, 1994; Carlson and Ducklow, 1995). In these "normal" lagoons, then, the purely quantitative aspect of optical measurements is useful only as a preliminary estimation of bulk DOC concentration, especially when considering the cost/benefit ratio (see the analogous conclusion reached by Moore, 1987).

The semi-quantitative evaluation of DOC nature has higher potentials. Our argumentation is based on (i) the  $A_{254}$ -versus- $S^*$  distribution, and (ii) the correlation between  $[C]$  and  $A_{254}$ . This latter shows the existence of a "residual" colourless DOC fraction amounting to about 0.5 mg C.L<sup>-1</sup>. Such an optically inactive fraction (appearing as the intercept in the  $[C]$ -versus- $A_{254}$  regression) has been found in other environments, at concentrations ranging between 0.4 and 0.9 mg C.L<sup>-1</sup> in oceanic samples (Amador *et al.*, 1990; Vodacek *et al.*, 1995) and between 2 and 6 mg C.L<sup>-1</sup> in coastal or continental waters (De Haan and De Boer, 1987).

The relative increase in the ratio between active and inactive C at increasing  $[C]$  leads to the mathematical artifact of increasing  $\epsilon_{254}$ , even if the "true" specific absorption ( $\epsilon^*$ ) were constant, which is not necessarily true (see below).



**Fig. 3** DOC calculated from  $A_{254}$  compared to measured values. Same symbols as in figure 1.

COD calculé à partir de  $A_{254}$  par rapport aux valeurs déterminées expérimentalement. Symboles : voir la figure 1.



Our  $\epsilon_{254}$  varies between 0.6 and 1.4  $\text{m}^2\cdot\text{g}^{-1}$  in the lagoons studied. We found only one comparable value (0.29  $\text{m}^2\cdot\text{g}^{-1}$ ), obtained on marine fulvics (Carder *et al.*, 1989). Most other published values range between 3 and 11  $\text{m}^2\cdot\text{g}^{-1}$ , but were obtained with isolated fractions (humics or fulvics) of various aquatic origins (Summers *et al.*, 1987; De Haan *et al.*, 1988; Blough *et al.*, 1993).

Among the identified factors of variation of  $\epsilon$  (at any wavelength) are ionic strength (Summers *et al.*, 1987; De Haan *et al.*, 1987) and pH (De Haan *et al.*, 1983), which are irrelevant for our measurements on natural seawater. We deal here with marine DOM, which is an undetermined mixture of molecules (Amon and Benner, 1996). The chief factor controlling  $\epsilon$  in natural samples will be average molecular weight, MW, or "molecular size". Several studies show, more or less explicitly, a positive correlation between  $\epsilon$  and log MW, and a negative correlation between spectrum slope  $S^*$  (or the equivalent ratio  $E2/E3$ ) (De Haan *et al.*, 1988) and MW (Stewart and Wetzel, 1980; De Haan *et al.*, 1983; Summers *et al.*, 1987; Senesi *et al.*, 1989).

The "confined" pole, with high  $A_{254}$  (and high [C]) corresponds to gradually increased average MW (as evidenced by the low  $S^*$  values), as found in other environments (Tranvik, 1990; Guo *et al.*, 1994). The increase in  $\epsilon_{254}$  in this chromophoric portion may be also due to a parallel (and slight) increase in the proportion of high- $\epsilon^*$  molecules (Blough *et al.*, 1993), such as lignin derivatives, or UV-protecting compounds (Shick *et al.*, 1992).

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The continuity that we observe between lagoons suggests a continuum of MW, such as is described by several authors (Moran *et al.*, 1991; Guo *et al.*, 1994; Amon and Benner, 1996). This array of MWs can result in part from bacterial heterotrophic activity, which leads to decreased  $S^*$  (Blough *et al.*, 1993). Bacterial uptake induces very small variations in bulk properties (Brophy and Carlson, 1989), but may alter the more sensitive optical properties of DOM.

## V. CONCLUSIONS

Optical characteristics allow the prediction of DOC concentration with an accuracy of about  $\pm 0.1 \text{ mg C}\cdot\text{L}^{-1}$  (average absolute difference between  $[C_m]$  and  $[C_A]$ ). The main potential of optics lies though in the ability to detect minute variations, or alterations, in the nature of DOC, or at least of its "chromophoric" portion.

We have noted that our data points (our lagoon samples) are arrayed, in the  $A_{254}$ -versus- $S^*$  plane, between two poles. A distance along the regression curve (measured on the graph from the data points for open-sea samples) would then also correspond to a factual distance (in space and/or in time) between the open sea and a water body. Optical characteristics would then estimate confinement. We could verify their good correlation with chlorophyll concentration Pagès *et al.*, 1997), which has been shown to be related to water residence time (Furnas *et al.*, 1990; Delesalle and Sournia, 1992).

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