Dissolved Organic Matter in Coral-Reef Lagoons, as determined by in vitro UV absorption 

Preliminary Results

J. Pagès, J.-P. Torrèront and S. Andréouès

OSTROM BP 529 Papeete, French Polynesia

LGMT, Université Française du Pacifique, BP 6570 Faa’a Aéroport, French Polynesia

Abstract

Light absorbance by water samples of 16 lagoons was measured between 250 and 400 nm. From these readings, we extract absorbance at 254 nm (A254), and spectrum slope, S*. These two descriptors are negatively correlated, so that samples are distributed along a hyperbola, between an "oceanic" (or oligotrophic) pole and a "eustrophic" (or coastal) pole. We determine an "optical oceanic index", GOI as the curvilinear abscess of each sample along the A254-S* hyperbolic regression curve. GOI exhibits significant correlations with several water characteristics (particulate organic matter, total dissolved nutrients). It also correlates well with an estimator of potential flushing rate based on reef morphometry and swell energy distribution. GOI thus appears adequate as a highly sensitive, and at least semi-quantitative, estimator of the oceanic/coastal gradient. Absorbance can be used as a rapid, sensitive, and relatively cheap method for studying DOC distribution qualitative and quantitative, in coral-reef lagoons. An improvement of the data base is planned, and necessary to confirm the present results.

Introduction

Since Forel's studies on lakes and Kalle's (1938) work on "Gelboff, in seawater, water color has been recognized as a simple, yet effective, means of classifying water masses. Numerous authors have studied spectral characteristics of waters, largely from two perspectives. One viewpoint is related to primary production modeling. Many studies describe the underwater light field as a control of photosynthesis, while another viewpoint is to use optical properties to assess the concentration of "Gelboff," or "oil" (Erik, 1983), which corresponds to most portion of dissolved organic matter (DOM), either as an index of terrestrial influence or as a substrate for heterotrophic activity. In this latter aspect, spectroscopy is still a well-used technique, although fluorometry is increasingly employed (e.g. Coble et al., 1993).

We have used spectrophotometry in several coral-reef environments, as a semi-quantitative tool for assessment of DOM. We show that spectral characteristics of water in the UV allow a quick and effective characterization of DOM in reef lagoon waters.

Material and Methods

Study sites and sampling

The work described here took place in the Tuamotu archipelago (French Polynesia, Fig. 1). Our observations were part of several programs (Tatafol, CyEL, FORM) studying the general biological production of atoll lagoons, and more specifically the biological and chemical processes in the water column.

The Tuamotu archipelago (North-East of Tahiti) stretches about 1700 km, between 14 and 21°S. The whole area has a tropical humid climate, with two seasons: the "dry" season (June to October) and the rainy season.

Most of the atolls studied are quite ordinary as atolls go, with a chain of islets (the motu) circling an inner lagoon. Atolls may or may not have a pass, of varying size. A typical feature is found in the Tuamotu: the hoa flat spillways) collect the water overlapping the reef crest, and lead it into the lagoon. The number and width of these hoa are variable.

A first series of samples was gathered in May-June 1993 in the Tikehau atoll lagoon (program CyEL). Additional samples were taken in Takapoto in January 1994 (program FORM). The two main series of samples were taken during two surveys done in November 1994 ("Tatafol 1") and November 1995 ("Tatafol 3") at a total of twelve atolls in the Tuamotu. While the samples from Tikehau and Takapoto were collected during a lengthy study (about two weeks for each, with daily sampling), the Tatafol 3 samples were collected during one morning on each atoll, at 5 to 8 locations in the main lagoon. Open-sea samples were collected during Tatafol 3 near six atolls.

As a rule, we took subsurface samples, using an acid-rinsed 2-l glass jar with plastic screw-on cover. A 1.7-l Niskin bottle was used for "deep" (10-40 m) samples. We transferred sub-samples for spectrophotometry with a 60-ml Terumo 3-parts syringe fitted with a stainless steel 1.5 mm needle. Delays were mostly short enough (1-3 hrs) that an ice box was sufficient to keep samples cool and dark. No preservative was used, although chloroform (at 0.05 mol.l-1) was found satisfactory. Mercuric chloride and NaN3 seriously interfere with spectrum scanning.

Spectrophotometry

The core of our study is in vitro spectrophotometry, done very classically by scanning the absorption spectrum between 250 and 400 nm, using a 100 nm quartz cell. In most cases, we used a Milton Roy "Spectronic 1201", measuring absorption (A) at 12 discrete wavelengths against distilled water blanks. As a rule, samples were not filtered. Absorption was not corrected for scattering as described by Frison et al. (1981) and by Davies-Colley and Vant (1987).

The classical exponential decrease of A at increasing wavelength λ is described by spectrum slope, S*, calculated from the regression of ln A vs. λ across the rectilinear portion...
of the absorption spectrum (250 to 320 nm at least; $r^2 > 0.990$). We also noted absorbance at 254 nm, $A_{254}$. Samples with high $S^*$ and low $A_{254}$ values raise the question of confidence limits on $S^*$. We did replicate spectrum scanings, either by successive scanings of the same sample or by combining successive sub-samples. Standard error on $A_2$ seldom reached 0.02 m$^{-1}$, while standard error on $S^*$ was between 0.0002 and 0.0006 (for $S^*$ values of 0.0150 and 0.0250 m$^{-1}$ respectively). We also tried to introduce an 'artificial error' in $A_2$ into an actual spectrum; we injected a random error of ± 0.02 in $A_2$ values (with an actual $A_{254}$ of 0.40 m$^{-1}$). In these 'worst case' conditions, extreme 'erroneous' $S^*$ values were 0.0257 and 0.0222, straddling the actual value of 0.0228 m$^{-1}$. We then see that our high $S^*$ values, while necessarily less precise than lower ones, are still reasonably reliable.

Other water characteristics
In addition to the classical "dissolved" descriptors of water quality (nutrients, etc.), we considered some particulate matter descriptors. Particulate organic carbon (corrected for carbonate) and nitrogen (POC, PON) were determined with a Leco CHN analyzer. Chlorophyll was determined by fluorometry on methanol extracts of GF/F filters, without correction for phaeopigments.

Atoll flushing rate
To develop a semi-quantitative estimation of potential flushing rate for each atoll, we combined morphometry and swell height data. Morphometry was obtained from high-resolution satellite (SPOT) images, from which we determined the width $L_1$ of each atoll. We distinguish a "maximum width", $L_{max}$, corresponding to the highest water level, and a "minimum width", $L_{min}$, corresponding to moderate swell conditions. From semi-quantitative ground-truth observations, we admitted that $L_{max}$ has a "weight" of 1.5 against a weight of 1 (unity) for $L_{min}$. We did these calculations in each octant (N, NE, E, etc.) of each atoll. Swell energy distribution was calculated from averaged observations of swell height and period, by combining swell measurements in Moruroa (Anon., 1989) and observations done in the region by merchant ships (Anon., 1979). We assumed that energy ($E_i$), and hence the amount of water overlapping across the reef, was proportional to the square of swell height and period. The potential flushing rate $F = L_1 / L_i$ of a given atoll is calculated from the relative distributions of $L_1$ and wave energy in each of the 8 octants. This rate has the dimension of a flow rate (m$^2$.s$^{-1}$) but has not yet been properly calibrated. This approach is described in some more detail elsewhere (Pagès et al., in prep.).

RESULTS
Environmental characters
We shall briefly comment here some descriptive parameters of the atolls, and of their waters.

Flushing rate
As already stressed, our "potential flushing rate" has the dimension of a flow rate (m$^2$.s$^{-1}$) but still must be considered as given in arbitrary units. The figures of $F = L_1 / L_i$ range between 14, for well-flushed and semi-open lagoons such as Tikehau and Rangiroa, to < 1 for nearly closed lagoons like Takapoto and Tepoto, with a raised atoll, has only one hoa which is seldom functional; this lagoon is hence not really amenable to our calculation of a flushing rate.

Salinity
Open seas in the Tuamotu region often have high salinities, about 36.5 at the end of the dry season (December; Rancher and Rougerie, 1993). The various lagoons exhibited uniform salinities in the same range. Some outstanding exceptions appear, there being hypohaline waters (up to 43 in Tairao) as well as slightly hypohaline lagoons (Tepoto).
Dissolved Organic Matter in Atoll Lagoons

Tikehau lagoon was surveyed at a much smaller spatial scale than that used in the Typatoll surveys (see methods). Data points from this lagoon are not randomly distributed (fig. 3) and correspond to 3 locations: i) the open sea outside the lagoon, ii) the lagoon itself, and iii) several hoa. These data points are arranged between an "oceanic" pole, with high $S^*$ values ($0.04 \text{ nm}^{-1}$) and low $A_{254}$ ($0.4 \text{ m}^{-1}$), and a "eutrophic" pole, with low $S^*$ ($< 0.01 \text{ nm}^{-1}$) and high $A_{254}$ ($>2 \text{ m}^{-1}$). A "coastal", or at least confined, character for this pole is confirmed by additional samples taken in particular locations, such as a sort of ox-bow pond on the side of a hoa, or a sample taken at the wharf, in shallow waters near the village.

Such a distribution between "oceanic" and "eutrophic" poles may also be seen for the Typatoll samples. Small lagoons or pools, nearly closed and/or with abundant terrestrial vegetation nearby, are on the "eutrophic" side, together with a lagoon (Hikueru) which had recently suffered a severe dystrophic event. On the other side of the plot are found lagoons with wide openings toward the ocean, and the open sea samples themselves.

To understand the aspect and meaning of the $S^*$-vs-$A_{254}$ plot, we mixed two different water types. Waters from two semi-enclosed coves in Haraiki lagoon were mixed in six different ratios. We reasoned that the absorption spectrum ($A$ vs. $A_{254}$) of a mixture should reflect the additive combination of both "parent" spectra while conforming to Beer-Lambert's law. We hence computed the resulting spectra of the various mixtures (fig. 4).

The close correspondence between the computed characteristics ($S^*$ and $A_{254}$) and actual values allows us to simulate any mixture between two water types. Such simulations (not shown) along with the "Haraiki experiment" give data points which are arrayed, in the $A_{254}$-vs-$S^*$ plane, along a hyperbola similar to our general regression. We may then consider that the lagoon samples represent mixtures in various proportions between two types of water: an "oceanic" one and a more eutrophic one (see discussion).

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As we shall focus here upon the qualitative aspects of carbon-specific absorption, it is highly correlated with concentrations in hard-water systems" (italics from us). The negative correlation we observe between $A_{OM}$ and $S^*$ also appears in other studies (Kirk, 1983 (p. 54); Donard et al., 1989; Green and Blough, 1994), but is not evident from the illustrations in Bricaud et al. (1981). We have sought an explanation for this negative relation, which is too frequent to be random. A first hint is given by our mixing experiments. The various lagoon waters would then result from mixing oceanic water with a 'confined' water (or 'eutrophic') end-member. A second indication can be obtained from the fact that $A_{OM}$ indicates an averaged molecular weight (Chen et al. 1977, Stewart and Wetzel, 1980, De Haan et al. 1987, Beaud et al. 1988) while $A_M$ increases with DOC concentration (see above). Our "oceanic pole", with its high $S^*$ and low $A_{OM}$ values, would then represent a lower carbon concentration made of small molecules, while our "confined" pole (low $S^*$ and high $A_{OM}$) represents a higher carbon concentration made of rather large molecules.

Another point in this $A_{OM}$ vs. $S^*$ distribution concerns the mathematical form chosen. We kept an hyperbolic expression mainly because of its good fit at extreme (high or low) values of both $A_{OM}$ and $S^*$. More important, an homogeneous set of samples (such as our present set of atoll lagoons) can be characterized by its asymptotic value for $S^*$. Our atolls would have an end-member with an $S^*$ of about 0.012 nm. It remains to be seen whether there are other "families" of waters, with other asymptotes which might be related to particular characteristics. The closed lagoon of Taiaro, with its abnormally high $S^*$ values (not due to humics, which have very low $S^*$), could then be an isolated example of a high $S^*$ curve. This would open a possibility of classifying various water bodies by their "confined" end-member, while the "open-sea" pole should remain common to all mixtures.

"Oceanic index" from optics

Our $OII$ values are expressed, as stressed before, in arbitrary units. An added arbitrary factor is the location of the origin, that we set beyond the most oligotrophic oceanic waters we had found. Still, more oligotrophic waters might yield negative $OII$ values, in the other direction (toward the "eutrophic" pole), our $OII$ scale is a priori open since we cannot define (at least not a priori) the end-member's maximum possible $A_{OM}$ value.

Apart from this, we have to discuss two aspects: i) the very principle of this "index", its possible meaning and its relationship with other descriptors, and ii) its intrinsic accuracy.

In regards to the latter point, low $OII$ values correspond to oceanic waters, in the high-$S^*$ portion of the regression. We have seen above that accuracy of $S^*$ is necessarily worse in this region, since absorption values (used to compute $S^*$) are then low. The precision we observe for open-sea samples is nonetheless still ordinary spectra. The only point deserving some comment is the magnitude of spectrum slope. We have chosen to express it by $S^*$, following Bricaud et al. We noted that our high $S^*$ values are reasonably reliable despite the low $A_{OM}$'s used for calculation. So, we arrive for $S^*$ at figures higher than the "norm" of about 0.014 mm$^{-1}$ for seawater (Bricaud et al., 1981; Davies-Colley, 1992). But already remarked by Bricaud et al. (ibid.), they had already remarked on a gradient stretching between "pure" seawaters, with high $S^*$ values, and land-bound water bodies like coastal waters or Baltic Sea, with low $S^*$'s. While some confusion by inter-calibration is still necessary, we may accept our $S^*$ values as real, and representative of an oligotrophic oceanic origin.
tolerable, be it for $S^*$ or for OOI; with seven replicates, on two occasions we arrive at coefficients of variation of ca. 30%.

We must now consider the principle of our index.

The first point is the possible loss of information incurred when replacing a pair of coordinates by a single value. This loss remains tolerable, but only as long as we deal with groups of samples, when small errors cancel each other out. We must stress again that OOI is the estimator of total DOC. Apart from the above difficulties, we already recalled that several authors explicitly differentiate between "chromophoric substances" and total dissolved organic matter.

As a second point, we may remark that OOI has the advantage of characterizing a water body by a single number. While handling two numbers is no difficulty in statistics (especially with a computer), mental representation is somewhat easier with only one number. Qualitatively, then, OOI performs efficiently: seeing that it correlates well with several factors expressing an oceanic/coastal (or eutrophic/oligotrophic) gradient. This agreement is rather clear-cut with the several "classical" descriptors. Lower concentrations in particulate organic matter, either living (microorganisms) or undifferentiated (POC) point to an oceanic, open-sea water. In the case of chlorophyll concentrations, which are very robust (if simplistic) and a lot of the correlation observed here between $B_{Mac}$ and OOI are to be compared with observations relating phytoplanktonic biomass with residence time, in freshwater systems (Séballe and Kimmel, 1987) as well as in coral-reef environments (Purnas et al., 1990; Delesalle and Sournia, 1992). We would thus have a supplementary, if indirect, indication of the effectiveness of OOI as an estimator of relative residence time, or confinement.

Correlations of OOI with "dissolved" parameters give a less clear-cut view. We have found two opposite sequences with salinity. We saw analogous two-pronged relations, between salinity and $\delta^18$O, in coastal lagoons (Jusserrand et al., 1989); this analogy would suggest that OOI reacts (somewhat like $\delta^18$O) to residence time or confinement much better than does salinity. Among the waters we studied then, the high-OOI ones would show the effect of a long residence time, and not only of evaporation.

Water renewal and optics

The correlation between OOI and flushing rate, $EL^*$, is highly significant. We have thought to remember that "Potential flushing rate" is obtained by considering in each oceant of the reef the product of relative aperture by relative swell energy. As signalled, $EL^*$ has the dimension of a flow rate and might be expressed in $m^3.s^{-1}$ - except that we have not yet determined a proper proportionality factor. Our $El^*$ figures are thus in arbitrary units as those of OOI. Despite this, the good correlation obtained between OOI and $EL^*$ shows that the principle is sound, and that the figures are meaningful, suggesting internal consistency.

CONCLUSION

The major point of our results is that optical characteristics allow differentiation of water types when $\delta^18$O or "classical" descriptors yield a very narrow range of undifferentiating values. We deem this fact alone as an interesting and useful property. A connection with optics (under- or above-water) in the visible range should be explored. On a quantitative basis, spectrophotometry has already yielded an approximation of DOC (or DOM) concentration, but the method still demands improvements because of its sensitivity to the molecular characteristics of DOM. A major material advantage is the relatively low cost in equipment and workload, simplifying large-scale field surveys.

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