Suspended particulate organic carbon and phytoplankton in the Cananéia Estuary (25° S 48° W), Brazil

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Abstract

High concentrations of suspended particulate organic carbon have been registered at three stations along the Cananéia Estuary, Brazil. On annual basis POC ranged from 40 to 3240 µg C. l⁻¹. Phytoplankton carbon estimated from cell volume and counts, constituted over the year, a small fraction of the POC, except during bloom periods. The magnitude of bacterial and heterotrophic organisms contribution to the POC pool have been discussed. Apparently in surface waters large quantities of non phytoplanktonic suspended detrital organic carbon dominate the particulate matter in the Cananéia Estuary.

Key words : Organic suspended matter – Phytoplankton – *Skeletonema* – Chlorophyll – Detritus – Sapropel — Estuary – Brazil.

Résumé

Carbone organique particulaire et phytoplancton dans l'estuaire du Cananéia (25° S, 48° W), Brésil

De fortes concentrations de carbone organique particulaire (POC) ont été relevées à trois stations dans l'estuaire du Cananéia, Brésil. Le POC varie dans l'année de 40 à 3240 µg C. l⁻¹. Le carbone phytoplanctonique, évalué d'après le volume cellulaire et le nombre de cellules, ne représente tout au long de l'année qu'une faible fraction du POC, sauf en périodes de bloom. L'importance de la contribution des bactéries et des organismes hétérotrophes à l'ensemble du POC est examinée. Il apparaît que ce sont de grosses quantités de carbone organique d'origine détritique et non phytoplanctonique qui forment l'essentiel de la matière particulaire dans les eaux de surface de l'estuaire du Cananéia.

Mots-clés : Matière organique particulaire – Phytoplancton – *Skeletonema* – Chlorophylles – Détritus — Saproplancton — Estuaire – Brésil.

INTRODUCTION

There is strong evidence that the macrophytes are the greater generators of particulate organic matter (POM) in estuarine ecosystems. Phytoplankton seems to contribute comparatively less to the POM pool (Van Valkenburg *et al.*, 1978; Odum and de la Cruz, 1967; Moss, 1970; Mann, 1972). The implications of those findings on the food web structure have been discussed extensively in the literature.

In the present account an attempt is made to assess the relative importance of the phytoplankton as a source of organic matter in the Cananéia Estuary, Brazil.

Many aspects of the phytoplankton communities in the area has been previously studied (Besnard, 1950; Teixeira *et al.*, 1965; Tundisi, 1969 a and b; Kutner, 1972; Tundisi and Tundisi 1972; Tundisi *et al.*, 1973). Particulate organic carbon and phaeopigment *a* have now been analysed for the first time.

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THE AREA STUDIED

The Cananéia Estuary, on the south coast of Brazil, has an area of approximately 10.000 ha (Besnard, 1950; Gerlach, 1958; Miniussi, 1959), an average depth of 6 m (Wakamatsu, 1973) and is approximately 110 km long. Of great significance for the hydrography of the estuary is the flux of two major water masses. One is the Ribeira do Iguape River which provides, during summer, a maximum daily average of 1500 m^3/s of freshwater (Diegues, 1975). The other is the oceanic water that flows into and out of the Estuary through the Cananéia Bar (Besnard, 1950; Gerlach, 1958; Miniussi, 1959). There is a marked salinity gradient from the inner parts of the estuary towards the sea (Teixeira *et al.*, 1965). The mangrove vegetation which surrounds a major part of the estuary is continuously washed by the tides, constituting, beside the Ribeira do Iguape River, a considerable source of organic matter.

The rainfall regime can be described as very wet without a pronounced dry season. In general, the months of lower rainfall are June-July-August. The heavy summer rains begin in December and lasts over March (Occhipinti, 1963) and are responsible for a marked decrease in surface water salinity during the summer season.

MATERIAL AND METHODS

Surface water samples were collected from three stations located along the Cananéia Estuary 25° S-48° W), Brazil (Fig. 1). Station I is located near the entrance of the oceanic water (Cananéia Bar) and Station III is in the inner part of the estuary, at the mouth of the Maria Rodrigues tidal channel. Station II occupies an intermediate position. On account of their geographical positions the stations differ by their depth, terrestrial and freshwater influence.

Samples at Sts. I and II were taken at the same date, and the total time elapsed between them was at most 40 minutes. At St. III, water samples were obtained 24-48 hours after sampling at Sts. I and II. Water sampling was taken irrespective of the phase of the tide, although always at the same time of day (between 09:00 and 10:00 a.m.). No detailed comparisons of the absolute values observed and the monthly variation between the stations were made, because of the sample variability due to the extremely variable estuarine conditions.

Field sampling was carried out at monthly intervals, during the period January 1976 to December 1976, using a 9,0 l PVC Van-Dorn bottle. Water temperature was measured at the sampling time.

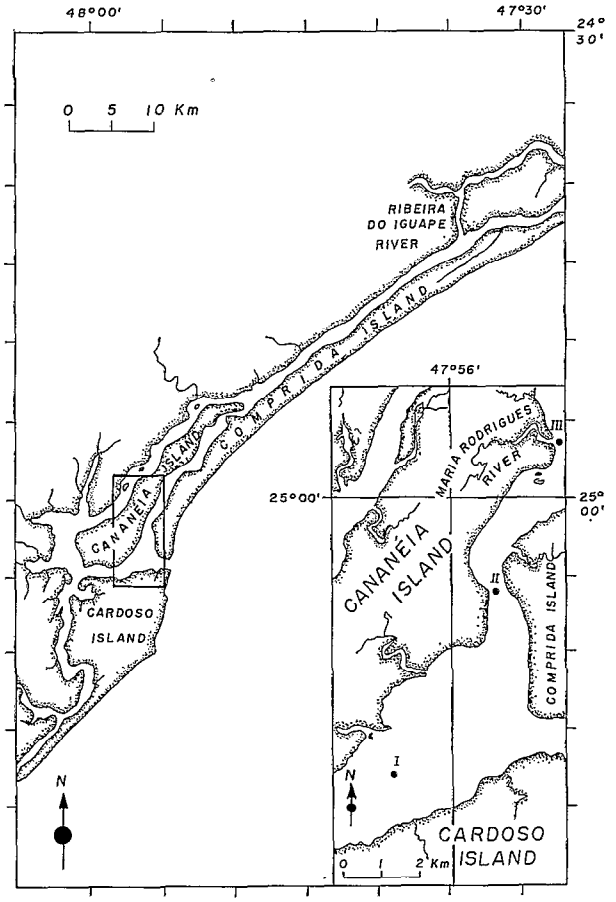

Fig. 1. — Cananéia Estuary sampling stations: I. Trapandé, II. Argolão and III. Maria Rodrigues.

Stations d'échantillonnage dans l'estuaire de Cananéia: I. Trapandé, II. Argolão, III. Maria Rodrigues.

Salinity and oxygen data were obtained by Harvey's and Winkler's methods, respectively.

Suspended particulate matter with a size range from 0,45 to 100 μm was quantitatively analysed. Particulate organic carbon (POC), chlorophyll *a*, and cell numbers, in concentrates obtained using Acropor Gelman membrane filters 0,45 μm pore size, were analysed. The concentration procedure basically followed that of Dodson and Thomas (1964). The concentrate for cell counting and cell volume assessment was preserved in 3 % formalin. Cell counts were undertaken under an HBO 200 mercury lamp (fluorescence microscopy), using a 20 μl aliquot of the concentrate stained with acridine orange (Wood, 1962). The cell volume was obtained from another aliquot stained with Rose Bengal and observed under transmitted light microscope.

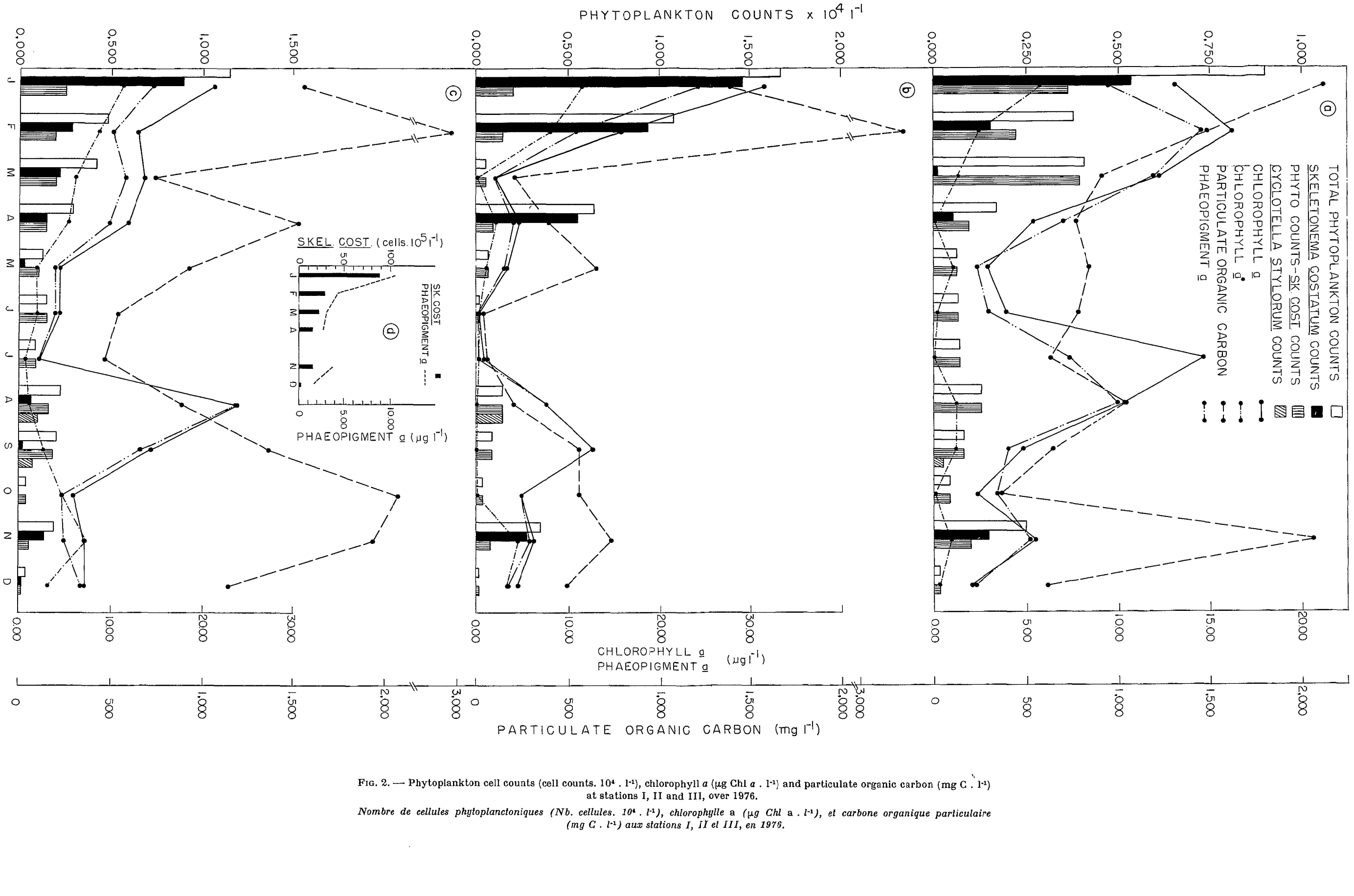

FIG. 2. — Phytoplankton cell counts (cell counts. 10^4 . l^{-1}), chlorophyll *a* (µg Chl *a* . l^{-1}) and particulate organic carbon (mg C . l^{-1}) at stations I, II and III, over 1976.

Nombre de cellules phytoplanctoniques (Nb. cellules. 10^4 . l^{-1}), chlorophylle a *(µg Chl* a *. l^{-1}), et carbone organique particulaire (mg C . l^{-1}) aux stations I, II et III, en 1976.*

In the case of Chl *a* determinations, before filtration of the concentrate, 1 ml of 1 % suspension of $MgCO_3$ was added to the filter. Immediately upon completion of filtration, the filter was folded in half and stored at 4 °C. At the laboratory, the filters were ground in 90 % acetone with a Teflon homogenizer. Chlorophyll *a* in the extracts were determined spectrophotometrically following LORENZEN (1967) and the trichromatic procedure of STRICKLAND and PARSONS (1968). Phaeopigment *a* was determined by acidification of the chlorophyll extracts and remeasurement at 665 and 750 nm.

Particulate organic carbon (POC) was determined by exothermic heating and oxidation of the organic matter trapped on the filter, with 0,5 N potassium dichromate solution in concentrated H_2SO_4. The excess dichromate was titrated with ferrous ammonium sulphate solution using as indicator orthophenantroline monohydrate in 0,7 % ferrous sulphate solution. The amount of carbon in the sample was estimated by reference to a standard glucose solution processed in the same way as the sample. Precombusted Whatman GF/C filters were used in both chlorophyll and particulate organic carbon determination. POC is defined in the present paper as "all organic carbon, both living and dead, that is retained on a Whatman GF/C filter".

Appropriate corrections for sample concentration were made to the values of chlorophyll *a*, particulate organic carbon and phytoplankton cell numbers.

Cell volume was computed from linear dimensions, assuming the cells to be spherical, cylindrical, or ellipsoidal (HOLM-HANSEN, 1969). Cellular phytoplankton carbon was estimated from cell volume (V, in μ^3_m) by use of the following equations (STRATHMANN, 1967), for *Skeletonema costatum* and *Cyclotella stylorum*:

$$\log_{10} C \text{ (in pg)} = 0{,}758 \cdot \log_{10} V\text{-}0{,}422$$

for other phytoplankton cells:

$$\log_{10} C \text{ (in pg)} = 0{,}866 \cdot \log_{10} V\text{-}0{,}460$$

"Detritus+heterotrophic organisms carbon" was obtained by subtracting phytoplankton carbon from total particulate organic carbon.

The standard deviation (SD) of the particulate organic carbon (POC) determination was 50 $\mu g\ C.l^{-1}$ or approximately 15 % of the mean.

The standard deviation of the carbon data is included to indicate the amount of variability in the data.

Skeletonema costatum has been chosen as an indicator of the physiological conditions of the phytoplankton, since, it is easily recognizable, and in the Cananéia Estuary it has been shown to constitute the most frequent and abundant species. During the summer, when there is a phytoplankton bloom, it may constitute over 80 % of the phytoplankton population (KUTNER, 1972). *Skeletonema costatum* cells showing bright red fluorescence under U. V. light, were classified as "healthy" cells (H SK). Those cells showing comparatively duller or weaker fluorescence were considered "senescent-like or precarious cells" (P SK). A miscellaneous assemblage of phytoplanktonic organism with no clear predominance of any particular species was referred as "the other members of the phytoplankton population" (OMP).

Consideration of the physiological conditions of the phytoplankton population using *Skeletonema costatum* as an indicator does not exclude the fact that other members of the phytoplankton population may be dead or in poor physiological conditions.

RESULTS

Hydrological data (table I)

Surface salinity increased from St. III to St. I, but no similar trends were observed in the temperature and oxygen data. The dissolved oxygen, percent saturation, varied from 72,2 to 103,0 %. Supersaturation occurred only a few times during the year and seems to be phytoplankton related.

Clorophyll *A* and phaeopigment *A* (table II)

The chlorophyll *a* concentration not corrected for phaeopigment *a* (Chl *a*) varied between 0,27 and 31,65 $\mu g/l$. The chlorophyll *a* corrected for phaeopigment *a* (Chl *a**) varied from 0,18 to 24,47 $\mu g/l$. The maximum value of surface Chl *a* was found in January and the minimum in June, both at St. II.

Phaeopigment *a* concentration (Phaeo *a*) in the water, was usually low and generally, constituted less than 50 % of the Chl *a*. Only in February at St. II and January and November at St. III, Phaeo *a* was about 50 % of the Chl *a*.

The relationship between chlorophyll *a* and phaeopigment *a* is shown in Fig. 2. Except for St. I, Phaeo *a* variation pattern follows that of Chlorophyll *a* (Chl *a* and Chl *a**).

Unless contrarily stated, all the analyses were made considering the chlorophyll *a* data obtained by the Strickland and Parson's method (Chl *a*), since the chlorophyll *a* variation patterns obtained by the two methods were closely related.

Cell number (table III)

The highest phytoplankton counts were recorded at St. II, in January. High values were also found in

TABLE I

Monthly hydrological data at stations I, II and III. Sampl. day = Sampling day; T (°C) = Water temperature; S(‰) = Salinity; D.O. (ml/l) = Dissolved oxygen; % O_2 Sat. = Percentage oxygen saturation.

Données hydrologiques mensuelles aux stations I, II et III. Sampl. day = date d'échantillonnage; T (°C) = Température de l'eau; S (‰) = Salinité; D.O. (ml/l) = Oxygène dissous; % O_2 Sat. = pourcentage de saturation d'oxygène.

STATION	I					II					III				
MONTH	Sampl. Day	T (°C)	S (‰)	D.O. (ml/l)	% O_2 Sat.	Sampl. day	T (°C)	S (‰)	D.O. (ml/l)	% O_2 Sat.	Sampl. day	T (°C)	S (‰)	D.O. (ml/l)	% O_2 Sat.
January	21	27,8	18,01	4,33	87,4	21	26,5	8,23	4,19	78,2	23	26,5	5,38	4,17	76,5
February	17	26,0	17,36	3,94	76,9	17	26,0	12,22	3,90	73,7	19	26,2	6,33	4,46	81,5
March	24	25,8	15,13	4,58	87,7	24	25,5	3,83	4,42	78,9	25	25,0	4,53	4,08	72,2
April	22	25,0	20,16	4,83	93,8	20	23,8	12,12	5,26	95,5	20	23,8	9,91	5,01	89,5
May	18	22,2	21,58	4,86	90,0	18	22,2	20,71	4,81	88,4	19	22,8	13,83	4,56	82,0
June	22	19,5	21,0	5,64	98,9	22	19,0	13,33	5,42	87,4	23	19,5	11,66	4,68	77,7
July	20	18,5	17,46	5,98	100,5	20	18,5	8,68	5,81	93,1	21	19,0	6,73	5,88	93,9
August	24	18,5	24,30	5,54	96,8	24	18,5	14,53	6,22	103,0	25	18,5	11,48	6,10	99,5
September	14	19,5	23,44	5,44	97,5	14	19,5	18,22	5,90	101,7	15	19,5	11,22	6,38	101,2
October	20	22,0	26,60	4,81	89,6	19	22,0	24,46	4,81	90,7	19	23,5	16,16	4,04	74,8
November	23	25,8	26,46	4,73	96,5	23	25,8	23,58	4,87	97,8	24	25,8	15,92	4,18	80,5
December	14	28,0	19,24	4,80	99,6	14	27,2	12,20	4,64	89,9	15	27,8	7,44	4,38	83,4

January at Sts. I and III. In general *Skeletonema costatum* was the most conspicuous species over the year at St. III, but was dominant at St. II only in January, February, April and November, and in January and November at St. I. In August at Sts. II and III, and September at Sts. I and III, there was a bloom of *Cyclotella stylorum*, which largely dominated over the other members of the phytoplankton population. Looking at the proportion of senescent-like or "precarious" *Skeletonema* cells to the remainder of the phytoplankton population (excluding *Skeletonema* cells) it was observed that by the time *Skeletonema* was dominant over the phytoplankton population (over 50 % of the phytoplankton population), the proportion of "precarious" *Skeletonema* cells was rather high. This proportion varied from 58 to 60 % at St. I, from 46 to 85,4 % at St. II, and from approximately 15 % (single value below 40 %) to 72,3 % at St. III. Only in January, at St. III, was a high proportion of *Skeletonema* cells in "healthy" conditions found.

Cell volume (table IV)

No significant difference in *Skeletonema costatum* average cell volume was found among the stations, in January. Therefore, cell volume was assessed over the year only at St. II. The average cell volume found for St. II was assumed for the other two stations, in the remaining months. Table IV shows the average phytoplankton cell volume, apart from *Skeletonema* and *Cyclotella* cell volumes.

Skeletonema costatum and *Cyclotella stylorum* average cell volumes were between 310 and 606 μm^3, and 8,310 and 11,564 μm^3, respectively.

Phytoplankton average cell volume (*Skeletonema* and *Cyclotella* volumes computed apart) varied from 123 to 2430 μm^3 over the year.

Carbon (table V)

Total phytoplankton carbon (including *Skeletonema costatum* and *Cyclotella stylorum* carbon), estimated from the average cell volume, varied between 7 and 1280 µgC/l. The highest values occurred in January and February at all three stations, and also in August and September at Station III.

A characteristic of the three stations is the high content of POC. Throughout, POC concentration ranged from 40 µgC/l in winter to 3240 µgC/l, in summer. Concentrations at St. II were usually lower than those observed at Sts. I and III. St. II registered the highest and the lowest POC value observed

TABLE II

Monthly concentration of chlorophyll *a* ($\mu g \cdot l^{-1}$) and phaeopigment *a* ($\mu g \cdot l^{-1}$) at stations I, II and III. CHL *a* = Chlorophyll *a* not corrected for phaeopigment *a*; CHL *a** = Chlorophyll *a* corrected for phaeopigment *a*; PHAEO *a* = Phaeopigment *a*; PHAEO (% CHL *a*) = Phaeopigment *a* as a percentage of CHL *a*.

Concentrations mensuelles de chlorophylle a *($\mu g \cdot l^{-1}$) et de phéopigment* a *($\mu g \cdot l^{-1}$) aux stations I, II et III. CHL* a = *chlorophylle* a *non corrigée du phéopigment* a; *CHL* a*: *Chlorophylle* a *corrigée du phéopigment* a; *PHAEO* a = *Phéopigment* a; *PHAEO (% CHL* a*)* = *Phéopigment* a *en pourcentage de la CHL* a.

STATION	MONTH	CHL a	CHL a*	PHAEO a	PHAEO (% CHL a)
	January	13.17	9.45	5.81	44.1
	February	16.25	14.54	2.36	14.5
	March	12.23	11.95	1.29	10.5
	April	5.41	7.06	0.00	0.0
	May	2.92	2.33	0.99	33.9
I	June	3.90	2.97	0.17	4.4
	July	14.67	7.37	0.00	0.0
	August	10.32	9.95	1.18	11.4
	September	4.79	4.03	1.15	24.0
	October	2.31	3.38	0.06	2.6
	November	5.50	5.25	0.88	16.0
	December	2.07	2.22	0.35	16.9
	January	31.65	24.47	10.86	34.3
	February	15.80	10.65	7.99	50.6
	March	2.01	2.16	0.00	0.0
	April	4.66	4.14	1.10	23.6
	May	3.38	3.15	0.52	15.4
II	June	0.27	0.18	0.13	40.1
	July	0.44	0.35	0.14	31.8
	August	7.77	7.61	0.00	0.0
	September	12.72	12.60	0.00	0.0
	October	4.90	4.93	0.00	0.0
	November	6.34	4.91	2.23	35.2
	December	4.52	3.49	1.61	35.6
	January	21.49	14.59	10.60	49.3
	February	13.03	10.24	4.31	33.0
	March	13.80	11.74	3.11	22.5
	April	12.02	9.89	2.72	22.6
	May	4.52	3.95	0.89	19.7
III	June	4.51	4.00	0.94	20.8
	July	2.20	2.21	0.33	15.0
	August	24.03	23.73	0.52	2.2
	September	14.53	13.44	1.28	8.8
	October	6.35	4.84	2.41	37.9
	November	7.21	5.00	3.66	50.8
	December	7.98	6.89	1.60	20.0

TABLE III

Monthly phytoplankton cell counts (cells . l^{-1}) at stations I, II and III. SK = *Skeletonema*; P = Precarious *Skeletonema* cells; H = Healthy *Skeletonema* cells; OMP = Other members of the phytoplankton population; CY = *Cyclotella*.

Nombres mensuels de cellules phytoplanctoniques (par litre) aux stations I, II et III. SK: Skeletonema; *P = Cellules « sénescentes »* de Skeletonema; *H = Cellules valides de* Skeletonema; *OMP = Autres membres de la population phytoplanctonique; CY* = Cyclotella.

STATION	MONTH	TOTAL PHYTO X 10^4	SK X 10^4	SK% PHYTO	P SK/ OMP	H SK/ OMP	CY X 10^4	CY% PHYTO
	January	899	534	59.3	1.38	0.03	0	0
	February	379	155	41.0	0.14	0.32	0	0
	March	408	11	2.7	0.00	0.02	0	0
	April	171	76	44.4	0.50	0.17	0	0
	May	59	0	0	0.00	0.00	0	0
I	June	64	0	0	0.00	0.00	0	0
	July	71	0	0	0.00	0.00	0	0
	August	127	0	0	0.00	0.00	0	0
	September	81	0	0	0.00	0.00	24	29.4
	October	42	0	0	0.00	0.00	0	0
	November	249	149	59.8	1.49	0.00	0	0
	December	15	0	0	0.00	0.00	0	0
	January	1674	1467	87.6	1.03	0.75	0	0
	February	1080	935	86.6	0.85	0.75	0	0
	March	53	0	0.0	0.00	0.00	0	0
	April	647	557	86.1	5.88	0.04	0	0
	May	67	0	0.0	0.00	0.00	0	0
II	June	18	0	0.0	0.00	0.00	0	0
	July	no sample	-	-	-	-	-	-
	August	147	0	0.0	0.00	0.00	145	98.9
	September	85	0	0.0	0.00	0.00	0	0
	October	32	0	0.0	0.00	0.00	0	0
	November	350	273	78.0	3.54	0.00	0	0
	December	11	0	0	0.00	0.00	0	0
	January	1148	893	77.8	0.17	0.74	0	0
	February	481	288	59.9	0.89	0.24	0	0
	March	421	223	53.0	0.90	0.11	0	0
	April	295	148	50.0	0.50	0.25	0	0
	May	125	22	17.6	0.20	0.01	0	0
III	June	150	0	0.0	0.00	0.00	0	0
	July	89	0	0.0	0.00	0.00	0	0
	August	228	68	29.8	0.37	0.04	100	44.0
	September	201	14	7.0	0.06	0.01	75	37.1
	October	39	0	0.0	0.00	0.00	0	0
	November	192	139	72.4	2.62	0.00	0	0
	December	36	19	52.8	1.12	0.00	0	0

during the present study. In general, there was no clear evidence of a direct link between seasonal variation in POC and Chl *a* (Fig. 2: *a*, *b*, *c*).

"Detritus + heterotrophic organisms carbon" (DET C), obtained from the difference between particulate organic carbon (POC) and total phytoplankton carbon (Phy C), generally showed high values at the three stations. In January at St. I, January, April and August at St. II, and January and August at St. III, phytoplankton carbon was greater than the "detritus+heterotrophic organisms carbon". The $SD_{\bar{x}}$ (standard deviation of the mean) of the DET C and POC data were greater than that of the Phy C, at all the stations (table V).

TABLE IV

Monthly phytoplankton average cell volume (μm^3) for stations I, II and III. PHYTO -(SK+Cy) = Average cell volume of phytoplankton, discounting *Skeletonema* and *Cyclotella* average cell volumes; SK = *Skeletonema* average cell volume; Cy = *Cyclotella* average cell volume.

Volumes cellulaires moyens du phytoplancton (μm^3), par mois, pour les stations I, II et III. PHYTO -(SK+Cy) = Volume cellulaire moyen du phytoplancton, soustrait des volumes cellulaires moyens de Skeletonema *et* Cyclotella*; SK = Volume cellulaire moyen de* Skeletonema*; Cy = Volume cellulaire moyen de* Cyclotella.

MONTH	PHYTO - (SK + Cy) AVERAGE CELL VOLUME	SK AVERAGE CELL VOLUME ST. I	II	III	Cy AVERAGE CELL VOLUME
January	2430.5	422	486	455	-
February	1772.8		428		-
March	123.5		362		-
April	468.5		334		-
May	1595.6		310		-
June	645.6		382		-
July	1951.0		no sample		-
August	200.1		212		8310
September	318.0		441		11564
October	2175.1		606		10477
November	317.2		446		-
December	398.3		351		-

Relationships between pairs of variables

STATION I

A good agreement between Chl *a* and cell number is seen, at St. I, over the year, except for January, February, March and July (Fig. 2 *a*). From January to February an increase in Chl *a* is accompanied by a decrease in phytoplankton cell number. An assessment of the physiological conditions of the phytoplankton population by considering the ratio H SK/OMP (Table III), shows that there is an improvement in the physiological conditions of the population from January to February. Phaeopigment *a*, as a percentage of Chl *a*, shows a rather marked decrease from January to February, reinforcing the suggestion of an improvement in the physiological conditions of the phytoplankton population during this time. On the other hand, the decrease in Chl *a* from February to March is concomitant to a sharp decrease in the H SK/OMP ratio, in spite of the relative small increase in the total phytoplankton cell counts. These factors may account for the discrepancies found in January, February and March, in the relationship, between Chl *a* concentration and phytoplankton cell number.

Consideration of the physiological conditions of the phytoplankton population based on the ratio H SK/OMP in the remainder of the year was not made on account of the low frequency of *Skeletonema* at those times of the year. In St. I this species occurred only in January, February, March, April and November, and its percentage of the phytoplankton population varied from 2,7 to 59,8 (table III).

No apparent association is found between Chl *a* and POC, from January to June (Fig 2 *a*). From July onwards there is a general agreement between the variations of the two variables. Phytoplankton carbon constitutes over the year only a small fraction of the suspended POC (table V), except in January (60,4 %). In July low POC/Chl *a* and Phy C/Chl *a* ratios are found concomitantly to a high Chl *a*/cell ratio (Fig. 3) and absence of Phaeo *a* in the water. Oxygen oversaturation was detectable at this time (table I).

STATION II

At St. II a reasonably good relationship is found between Chl *a* and phytoplankton cell counts, with the exception of August, September and

TABLE V

Monthly concentration of particulate organic carbon, total phytoplankton carbon and "detritus+heterotrophic organisms carbon" (in $\mu g \cdot l^{-1}$), at stations I, II and III. POC = Particulate organic carbon; PHY C = Total phytoplankton carbon; DET C = "Detritus+heterotrophic organisms carbon"; % POC = Phytoplankton carbon as a percentage of POC; $\bar{x}$ = Data mean; SD = Standard deviation of the mean.

Concentrations mensuelles (en $\mu g \cdot l^{-1}$) de carbone organique particulaire, de carbone phytoplanctonique total, et de "carbone des détritus et organismes hétérotrophes", aux stations I, II et III. POC = Carbone organique particulaire; PHY C = Carbone phytoplanctonique total; DET C = "Carbone des détritus et organismes hérétotrophes"; % POC = Carbone phytoplanctonique en pour cent du POC; $\bar{x}$ = Moyenne des données; SD = Ecart-type des données.

STATION	I				II				III			
MONTH	POC	PHY C	DET C	(% POC)	POC	PHY C	DET C	(% POC)	POC	PHY C	DET C	(% POC)
January	2120	1280	840	60.4	1400	1236	164	88.2	1560	1109	451	71.0
February	1490	563	927	37.8	3240	677	2563	20.9	3170	543	2627	17.1
March	910	93	817	10.2	210	12	198	5.7	740	130	610	17.6
April	770	97	673	12.6	400	237	163	59.1	1530	158	1372	10.3
May	840	109	731	13.0	660	138	522	20.9	930	220	710	23.6
June	780	60	720	7.7	40	17	23	42.2	550	141	409	25.6
July	630	174	456	27.6	60	no sample	-	-	470	218	252	46.4
August	1040	43	997	4.2	210	257	-47	100.0	890	491	399	55.1
September	640	168	472	26.3	560	211	349	37.7	1370	500	870	36.5
October	360	113	247	31.4	660	118	542	17.9	2080	105	1975	5.0
November	2060	119	1941	5.7	740	144	596	19.5	1940	90	1950	4.6
December	610	9	601	1.5	490	7	483	1.4	1150	18	1132	1.5
$\bar{x}$	1020	235	785		722	292	560		1365	310	1063	
SD	570	356	421		875	370	730		768	307	765	

November (Fig. 2 *b*). From August to September, the decrease in cell number, is followed by an increase in Chl *a*. In these months a bloom of *Cyclotella stylorum* is found, characterized by a large volume per cell unity (table IV).

Skeletonema costatum constituted the dominant phytoplankter in January, February, April and November. In these months, *Skeletonema costatum* cells showed apparently poor chlorophyll conditions. Generally over 50 % of the whole phytoplankton population was constituted of senescent *Skeletonema costatum* cells. Looking at the ratio H SK/OMP and judging the physiological conditions of the phytoplankton population from this standpoint, it is observed that there is a deterioration of the phytoplankton population in April (table II). This coincides with a slight increase in the chlorophyll *a* concentration (Fig. 2 *b*). Although *Skeletonema* is numerically an important member of the phytoplankton community in April, it does not seem to account for the increase in chlorophyll *a*. It seems likely however, that at this time "other members of the phytoplankton community" are responsible for the levels of chlorophyll *a*, either by the presence of a specific phytoplankton population characterized by higher content of Chl *a* or by the occurrence of a phytoplankton population in a growth phase characterized by higher levels of Chl *a*.

In november the discrepancy between cell number and Chl *a* may be explained by the large numbers of *Skeletonema* cells in apparently very "poor chlorophyll conditions".

Phytoplankton carbon contributes little to POC, with the exception of January, April, June and August when it constitutes on an average 72,4 % (table V). The POC/Chl *a* ratio was relatively low only in January, August and September. A low POC/Chl *a* ratio coincides with relatively high Chl *a*/cell ratio only in August and September, suggesting a bloom of the phytoplankton population. The Phy C/Chl *a* ratio was 33,1 in August, and 16,6 in September (Fig. 3). At this time, no phaeopigment *a*

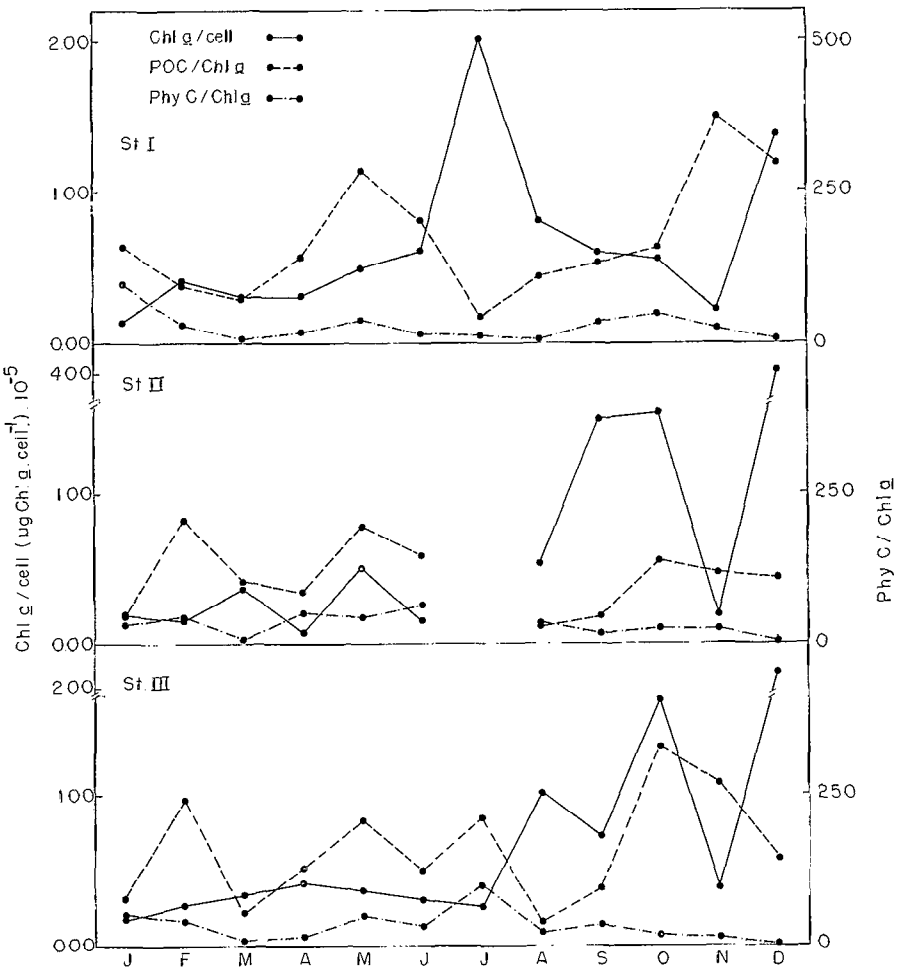

FIG. 3. - - Chlorophyll *a*/cell (μg Chl *a* . cell^{-1}), particulate organic carbon/chlorophyll *a* (POC/Chl *a*) and phytoplankton carbon/chlorophyll *a* (Phy C/Chl *a*) ratios at stations I, II and III.

Chlorophylle a/cellule (μg Chl a . cell^{-1}), et rapports carbone organique particulaire/chlorophylle a (POC/Chl a) et carbone phytoplanctonique/chlorophylle a (Phy C/Chl a), aux stations I, II et III.

was detected and the water was oversaturated with oxygen (tables I and II).

In fact, in August there was a *Cyclotella* bloom and the POC value was lower than the estimated phytoplankton carbon (table V). It is possible that large errors have been introduced in measuring cell volume and transforming cell volume into carbon. Less probable is that the precision and accuracy of the analytical method used to measure POC are below the actual levels of carbon, although the analytical error is large enough to account for the difference observed.

The trend followed by the POC over the year is not accompanied by similar variation of the Chl *a* (Fig. 2*b*). No improvement in the relationship is found if phytoplankton carbon is considered.

Phaeo *a* variation over the year showed close association to Chl *a* variation (Fig. 2*b*).

STATION III

Total phytoplankton cell numbers seem to follow the general trend shown by Chl *a* (Fig. 2*c*). Some considerations of the physiological conditions of the phytoplankton population and of its taxonomic composition, may be helpful in explaining the discrepancies observed. From February to March a slight increase of Chl *a* is accompanied by a decrease in total phytoplankton cell counts. The increase in Chl *a* from February to March, may be due to the slight increase in the number of the cells of "other members of the phytoplankton community".

The physiological conditions of the population seem rather poor from February to March, considering the ratio H SK/OMP (table III).

From July to October the changes in Chl *a* are accompanied by changes in cell number. However, there seems to be no simple proportionality between the two variables. This seems to be accounted for by the rather marked change in the community taxonomic composition. In August and September a diatom bloom occurred. At this time, the phytoplankton community was characterized by a high proportion of *Cyclotella stylorum* (Fig. 3*c*). This species shows large volumes per cell unity (table IV).

Skeletonema costatum cell density drops sharply from January to February. From February onwards *Skeletonema costatum* importance gradually decreases, being absent in June-July. In November, there is another burst of *Skeletonema costatum* growth as shown by the proportion of *Skeletonema costatum* cells to the phytoplankton population (table III). In November the lack of agreement between cell number and Chl *a* may be justified by the total dominance of the population by *Skeletonema* cells in "poor physiological conditions", as depicted by the fluorescence characteristics of their cells. Generally, except for January, *Skeletonema costatum* is found in very poor physiological conditions over the year accounting for a high proportion of the senescent cells of the phytoplankton population. The relationship between *Skeletonema costatum* cell counts and Phaeo *a* concentration seems better than that between Phaeo *a* and total cell counts. *Skeletonema* is dominant from January to April and in November-December. Considering only the months in which *Skeletonema* is dominant, one observes a close association between the number of *Skeletonema* cells and Phaeo *a* concentrations, suggesting that, at least, when *Skeletonema* is found, it constitutes a significant source of Phaeo *a* (Fig. 2*d*).

Phaeo *a* is closely related to Chl *a* (Fig. 2*c*). No doubt exists that the direct source of Phaeo *a* is the Chl *a* in suspension.

No clear association between POC and Chl *a* is found (Fig. 2*c*). The percentage of phytoplankton contribution to POC ranges from 1,5 to 71,0 % (table V), but only in January, July, August and September was the phytoplankton contribution to POC greater than 30 %.

The ratio POC/Chl *a* was relatively low only in March and August. The Phy C/Chl *a* ratio was 9,4 in March and 20,4 in August. The Chl *a*/cell ratio varied from 0,271 to $2{,}216 \times 10^{-5}$. μg Chl *a* . cell^{-1}. In March and August it was 0,328 and $1{,}054 \times 10^{-5}$. μg Chl *a* . cell^{-1}, respectively (Fig. 3). The water was oxygen oversaturated only in September (table I).

DISCUSSION

Tidal variations may account in part for the differences in the absolute values of the parameters studied and may explain in part, the monthly variations at each station since the samples were collected at different tide phases.

The input of terrestrial material to the estuary is apparently large, on account of the mangrove vegetation fringing the basin, the high rainfall regime and the Iguape River contribution. There exists the possibility of differential contribution to the stations of terrestrial and bottom material, because of their differences in depth and proximity to land. Station III, for instance, is liable to receive larger inputs of allochtonous organic matter because of its greater land proximity. Its lesser depth may favor the re-suspension of deposited organic matter or those originating from the benthic community.

The seasonal succession of phytoplankton in the Cananéia Estuary has been previously studied by KUTNER (1972). Generally the major growth pulse occurs during the rainy season (from December to March) and is dominated by diatoms. From this point on, the phytoplankton biomass begins to diminish, so that by June-July (the dry season) a comparatively low phytoplankton standing-stock is found. Occasionally, a second phytoplankton peak, also dominated by diatoms, occurs in September-October.

In the present investigation the first phytoplankton increase (cell counts and Chl *a* concentration) was found in January at Sts. II and III, and in January (cell counts) and February (Chl *a* concentration) at St. I. Toward June-July, Chl *a* concentration dropped to rather low levels. A second peak (Chl *a* and cell counts) was found in July-August at St. I, August-September at St. II, and August at St. III. An unusual occurrence was a third peak observed in November, at all the stations, dominated by the diatom *Skeletonema costatum*.

According to KUTNER (1972) temperature and nutritive elements brought by land drainage during the rainy season have strong influence in the phytoplankton seasonal cycle.

There seems to be a good association between phytoplankton cell number and Chl *a*, and the discrepancies found may be explained either by changes in the growth phase of the population, its taxonomic composition, or both. In January and November (St. II and III) the bloom was characterized by the flourishing of *Skeletonema costatum*, and in August and September (St. II and III) by *Cyclotella stylorum*. The physiological conditions of the phytoplankton population, as assessed by cell fluorescence, were different in each of the blooms: the good Chl *a* fluorescence shown by the

Cyclotella cells, was not observed in the *Skeletonema* cells. The Chl *a*/cell ratio at each of the blooms was distinctively different: it was low during the *Skeletonema* blooms and relatively high in the *Cyclotella* blooms. Pigment rich cells seem to be characteristic of early stages of development of phytoplankton blooms; a reduction in the pigment content of the cells occurs mainly in the later stages of a phytoplankton bloom (GIESKES and KRAAY, 1975; JENSEN and SAKSHAUG, 1973). Besides, the occurrence of diverse species alters the relationship between Chl *a* and cell density on account of the interspecific variability of pigment contents per cell (PAASCHE, 1960; EPPLEY and SLOAN, 1965).

Low and high Chl *a*/cell ratios with no definite interpretation were also found in the present work. Such ratios can only be explained in general terms. For instance, in February at St. I and in March at St. III, there had been an increase in Chl *a* in spite of the decrease in *Skeletonema costatum* cell number and in the total phytoplankton cell density. The increase in *Skeletonema costatum* "healthy" cells in the first case, and the increase in the "other members of the phytoplankton population" relative to *Skeletonema costatum* in the second case, may be responsible for the increase in the concentration of Chl *a*. The lack of agreement between Chl *a* and cell counts and the relatively low Chl *a*/cell ratio is probably the result of taking into account the total phytoplankton population irrespective of the physiological conditions of its members.

In July at St. I a high Chl *a*/cell ratio is found. By simple microscopical inspection of the population it was not possible to infer the occurrence of a phytoplankton bloom. However, the concomitant high Chl *a*/cell-low POC/Chl *a* ratios and the absence of phaeopigment *a* suggest its occurrence.

In healthy and actively growing phytoplankton cultures the Phy C/Chl *a* ratio has been found to vary from 35 to 70 (HARRIS and RILEY, 1956; MCALLISTER *et al.*, 1964). Higher ratios in cultures and natural populations seem to reflect the presence of dead cells or detritus (RYTHER and MENZEL, 1965). In the present account, PhyC/Chl *a* ratio lower than 70 occurred most of the year at the three stations. Only in January at St. I, and July at St. III, the Phy C/Chl *a* ratio was greater than 70. The "detritus+heterotrophic organisms carbon" percentage of the POC, and *Skeletonema costatum* precarious cells percentage of the total phytoplankton counts, varied from 0 to 82 % and from 0,7 to 85,4 %, respectively during the year. In the present study it seems that either the Chl *a*/cell, Phy C/Chl *a* or POC/Chl *a* ratios constitute (by themselves) poor indicators of either the growth phase of the phytoplankton population or the presence of detritus.

The concomitant association found between phaeopigment *a* and Chl *a* (at least at Sts. II and III), and Chl *a* and phytoplankton cell counts at the three stations, is an indication of the importance of the phytoplankton as a source of phaeopigment *a*. High levels of Chl *a* associated with low levels of phaeopigment *a*, as in July at St. I, have been found by MAYZAUD and TAGUCHI (1979) to coincide with diatoms and dinoflagellate blooms. JENSEN and SAKSHAUG (1973) found that between two spring blooms in the Trondheimsfjord (Norway), a new population of *Skeletonema costatum* flourished in surface waters, which was characterized by a high pigment content and none or very little degraded Chl *a*.

The great abundance of a defined species of phytoplankton, rich in degraded pigments, may largely dominate the production of phaeopigment. That seems to be the case in St. III where the phaeopigment is closely dependent upon the concentration of *Skeletonema costatum* over the year.

The results obtained in the present conflicts with the general papers dealing with similar environments. Moss (1970) found that in two English ponds Phaeo *a* was not correlated to Chl *a*. He also estimated that the amour of Phaeo *a* which originated from dead cells was insignificant. He concluded that the bulk of Phaeo *a* came from resuspension of the bottom sediments. Similar conclusions were found by GLOOSCHENKO *et al.* (1974) and TIETJEN (1968). Tidal resuspension of mud bottom was found to contribute largely to the levels of Chl *a* and detritus in the water column in Buzard Bay (ROMAN and TENORE, 1978).

RAI (1978) found in Lake Tupé (Central Amazon Region) that the Chl *a* maximum always coincided with phaeopigment maximum. However, he found relatively more phaeopigment *a* than Chl *a*. He suggested that a large quantity of detritus would enter the lake from the catchment area. In some Scottish sea lochs, SOLORZANO and GRANTHAN (1975), found that the main source of phaeopigment *a* was detrital material brought from land and the incoming sea water.

The levels of particulate organic carbon are within the range found for similar regions, in other parts of the world. They are usually high in inshore waters (ABDULLAH *et al.*, 1973; BIGGS and FLEMER, 1972; SEKIGUCHI, 1976). The extremely high levels of POC found in the present study are probably due to imputs from land and also to the generally high productivity of the estuary.

This surface waters POC of the Cananéia Estuary, apparently made up of large quantity of original land material, seems to have no significant pigment content.

In woodland soil the pigment concentration of leaves recently fallen is low (GORHAM and SANGER,

1967). Aged large plant material would be devoided of pigment.

In the present work plant tissue greater than a 100 μm, have been excluded by the screening of the samples. The remaining fragments would have been in the water, long enough to have their pigments completely destroyed, either by the activity of organisms, photobleaching or by the action of their own enzymes.

A size fractionation of the POC (unpublished) has shown the great predominance of particles between 0,45 μm and 10-50 μm. To attain this size range, mangrove leaves or river brought material would have remained in the water long enough to be completely deprived of their pigments (HEALD, 1969).

The contribution of phytoplankton to the POC pool only occasionally exceeded 30 %. This result is supported for inshore waters by many workers (PATTEN *et al.*, 1966; FINENKO and ZAIKA, 1970; STRICKLAND *et al.*, 1970; ZEITZSCHEL, 1970; SAUNDERS, 1972; MANUELS and POSTMA, 1974; FISHER, 1975; VAN VALKENBURG *et al.*, 1978). Generally, the particulate organic carbon seems to be deprived of pigment, as there seems to be no relationship between this particulate material and Chl *a*, except for St. I, from July to December. However, even in that case phytoplankton carbon constitutes only a small fraction of the suspended particulate organic carbon. In that case, POC levels may have reflected a high contribution by heterotrophs, most of them depending only indirectly upon the phytoplankton, or in other words represented the effect of total productivity (HOBSON *et al.*, 1973; WANGERSKY, 1977).

To date, the magnitude of the contribution of microheterotrophs to the POC pool in the Cananéia Estuary is unknown. Ciliates, meroplanktonic larvae and young stages of copepods were sometimes conspicuous. THAYER *et al.* (1974) found for the Newport River Estuary that there was 1,7 to 20 times more biomass of suspended phytoplankton than heterotrophic organisms. FISHER (1975) in the North Caroline Estuary showed that approximately 25 % of the organic carbon found was phytoplankton with the remainder being detritus and microfauna.

Bacterial contribution is probably small because of its low biomass despite its usually high density in estuarine regions. Certainly, bacterial contamination cannot be excluded without a direct estimate of bacterial carbon. An approximate value for bacterial biomass may be obtained by multiplying observed bacterial numbers (MESQUITA, 1978) by the average bacterial carbon content per cell ($3,5 \times 10^{-7}$ μg C/cell in HAMILTON and HOLM-HANSEN, 1967). In this way 10^7-10^9 cells/l (the order of magnitude found in the Cananéia Estuary) would represent 3,5-350 μg C/l. This represents only 0,5 to at most 25 % of the suspended POC. Considering that the screening of the samples excluded organisms greater than 100 μm, and consequently the majority of larger zooplankton, and that bacterial biomass is usually small (EPPLEY *et al.*, 1977) it seems that in surface waters detritus carbon largely dominates the particulate organic carbon pool in Cananéia and that in the present study, with the methodology used, either Chl *a*/cell, C/Chl *a* or Phy C/Chl *a* ratios constitute (by themselves) poor indicators of either the growth phase of the phytoplankton population or of the presence of detritus.

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