

EFFECTS OF PETROLEUM HYDROCARBON POLLUTION ON PHYTOPLANKTON PRIMARY PRODUCTION AND COMMUNITY RESPIRATION IN THE INNER SHELF OFF THE GULF OF GUINEA S. E. NIGERIA

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ABSTRACT

Diurnal rates of gross primary production, net community production and community metabolism were used to assess the impact of crude oil spill between 12th - 28th January, 1998, at the aftermath of Exxon Mobil (Idoho-QIT) Pipeline rupture, using invitro changes in dissolved oxygen at polluted and unpolluted sites in the Gulf of Guinea. Integrated gross production from the surface to about 1% light level was lower at non-oiled areas ($48.2 \text{ mmol O}_2 \text{ m}^{-2}\text{d}^{-1}$) than at the oiled area ($53.6 \text{ mmol O}_2 \text{ m}^{-2}\text{d}^{-1}$), although the integrated community respiration was higher at non-oiled areas ($48.2 \text{ mmol O}_2 \text{ m}^{-2}\text{d}^{-1}$) than at the oiled areas ($18.2 \text{ mmol O}_2 \text{ m}^{-2}\text{d}^{-1}$). The difference in gross production was ascribed to difference in photosynthetic activities in the study area, which was more at the non-oiled zones, while the difference in community respiration was due to heterotrophic respiration. This suggests that micro heterophs play a major role in overall rate of community respiration in the Gulf of Guinea. The ecological implications of these findings are discussed in the light of material cycling within the Guinea Gulf.

Keywords: Petroleum hydrocarbon, primary production, phytoplankton, Gulf of Guinea.

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INTRODUCTION

The continental shelf off the coast of S.E. Nigeria is plagued with petroleum activities ranging from exploration, drilling and transportation from the numerous oil companies operating in the region. On January 12, 1998, a 24-inch oil pipeline ruptured at Exxon - Mobil Idoho offshore platform releasing approximately 45,000bbl of crude oil into the continental shelf waters of the Guinea Gulf. Pollution biologists generally consider the impact of petroleum on plankton as an extremely difficult problem to assess in field studies. Due to turbulent mixing, probable long-term impact are considered relatively minor, compared to those on the benthos except in special cases of massive spill such as the present case or chronic contamination of water body with restricted flushing. Since the phytoplankton are the major primary producers in the oceans, factors affecting their rates of carbon fixation will have important repercussions on the entire food web. Both inhibition and stimulation of phytoplankton have been measured in field and laboratory cultures. Defined as the sum of autotrophic and heterotrophic respiration,

phytoplankton photosynthesis and community respiration play important roles as a sink and source of carbon dioxide in the ocean.

Although pelagic primary production has been extensively studied by ¹⁴C techniques since the introduction of the radiotracer method (Nielsen 1952). Few studies have been conducted on autotrophic and heterotrophic respiration in the ocean, particularly with regard to oceanic oil pollution. Considerable improvements made in the precision of the Winkler titration method enable direct measurement of planktonic respiration from changes in dissolved oxygen concentration to be made in the open ocean (Bryan *et al.*, 1976; Williams and Jankinson, 1982; Culberson & Huang, 1987; Furuya & Harada, 1995; Waku & Furuya, 1998). The techniques have been used to report active community respiration from various oceanic regions and the role of respiratory activity in material cycling is well evaluated and documented (Williams *et al.*; 1993, Williams & Purdie, 1991, Odate & Furuya, 1995).

The Nigerian coastal marine off the Atlantic Guinea Gulf is characterized by a complex circulation pattern and by high eddy activity (Dittmer, 1992), and although we seem to

know a great deal about the distribution and variation of primary production in adjacent near shore marine waters by estuaries and bays (Ewa-Oboho, 1992), planktonic respiration and primary productivity in the off-shore oceanic waters of the Gulf of Guinea is little understood particularly after a major oil spill. In studying phytoplankton production and respiration of the Gulf area, a gap would have been closed in the understanding of the dynamics in lower tropic levels shortly after oiling.

In the present investigation, phytoplankton photosynthesis and community respiration at two stations; oiled station 1, 20m near the Idoho platform and a non-oiled station 2 approximately 5km east of the spill point were studied. Based on the observed respiration, the relative contribution of photo-autotrophic and heterotrophic organisms to overall plankton community respiration in the polluted and the non oil-polluted waters of Gulf of Guinea using *in vitro* change in dissolved oxygen in water are presented.

MATERIALS AND METHODS

Field experiments were carried out during a MV Regina cruise on 12th to 28th January at two locations viz 4° 32'.06N and 08° 4'.46'E as Station 1 and 4° 01'.08N and 08° 32'.50'E as Station within the inner shelf of the Gulf of Guinea (West Africa). Before dawn, water samples were taken with Niskin bottles mounted on a rosette sampler fitted with a multi-sensor array, Octopus (Ishimaru *et al.*, 1984). No metal part was used inside the bottles and care was taken to avoid metal contamination throughout the handling of water samples.

Samples for incubation experiments were collected from six to seven depths in the upper 26 and 28m water columns at stations 1 and 2 respectively. Since the underwater light field was not measured before dawn, reference is made to those of the neighbouring stations on determination of the sampling depths. The 26 and 28m depths were proximate to the 1% light levels of the surface. Therefore, the euphotic zone is regarded to be the water column between the surface and its 1% light level. The sample was introduced into a 9-L polycarbonate carboy through silicon rubber tubing, and was then carefully siphoned into five glass bottles of 100-mL nominal volume and 10 borosilicate 200-ml bottles and the rest for dark. The light and dark bottles were incubated under simulated *in situ* conditions for 24h from dawn to dawn in an on-deck incubator cooled with running surface seawater. The dark bottles were kept within dark bags. Dissolved oxygen was determined by Winkler titration with potentiometric end-point

detection (Furuya & Harada, 1995). Titration was performed on board within 24hrs after fixation of oxygen. Net *in vitro* changes in light and dark bottles gave net community production and respiration, for the oil and the unoled areas respectively.

The gross production was obtained from difference in dissolved oxygen between the light and dark bottles after incubation. Chlorophyll *a* for the incubated water was determined fluorometrically (Turner Design/ OR) for particles collected on a Whatman GF/F glass fiber filter, extracted in N,N-dimethylformamide (Suzuki & Ishimaru 1990). Water temperature and salinity was measured using temperature and salinity meters. Under water photon flux was measured using a radiometer (Biospherical MER 2040) photosynthetic available radiation (PAR) and was monitored at every 10 mins on average (Li-1900s, LiCor). Nitrate was determined using an Auto analyzer (Bran - Luebbe TRAACS 2000).

Aliquots of the water samples were filtered for accessory pigment analysis through 47mm Whatman G/F filters with less than 150 mmHg of vacuum. The samples were stored in liquid nitrogen. The filtered samples were freeze-dried just prior to extraction and ground in 5mL of N, N- dimethylformamide with a glass homogenizer until the filtrates were completely crushed. The extract was mixed with 1M ammonium acetate as the ion-pairing reagent and filtered through 0.2µm PTFE filter before injection into a HPLC system. The advent system reported by Furuya *et al* (1998) and used pigment peaks were identified by comparison of retention time and absorption spectra to those of commercially available pigments including chlorophyll *a*, chlorophyll *b*, chlorophylls *c* and *c*₂, alloxanthin, fucoxanthin, 19-hexanoyloxyfucoxanthin, neoxanthin and violaxanthin (Water Quality Inst., Denmark). All the pigments (above) were quantified by weight from peak area calibrated against that of the standard solution, the concentration of which was determined spectrophotometrically. Primary production at both stations 1 and station 2 were determined both by bio-optical model (Furuya *et al*, 1998) and by *in situ* uptake of H ¹³C0 - on a 24-hr basis (Saino & Goes, 1997).

19-butanofloxyfucoxanthin was identified on the basis of absorption spectra (Wright & Jeffrey, 1987). Assuming that the molar specific extinction coefficient of 19-butanofloxyfucoxanthin is equal to that of 19-hexanoyloxyfucoxanthin (Goericke & Repeta, 1993), 19-hexanoyloxyfucoxanthin was quantified in terms of weight.

RESULTS

PHYSICO-CHEMICAL CONDITIONS

Both water temperature and salinity were vertically homogeneous throughout the euphotic zone at stations 1 and 2 (Figs. 1(a) and 1(b)). Temperature and salinity at both oiled and unoled stations were uniform in the upper 25m-

water column. But below this depth at oiled station 2, there were slight decrease with depth of temperature and salinity, producing a weak pycnocline around 28m depths. Sufficient nitrate $>5\mu\text{m}$ existed throughout the euphotic zone at both stations (Fig. 1(c)).

Table 1: Daily respiration of phytoplankton group (R), chlorophyll a specific maintenance respiration (R_o) and the linear coefficient of increase of dark respiration with photosynthesis (R_D) at the study area during the Idoho - off-shore oil pipeline rupture in 1998.

Phytoplankton Types/class	R	R_o	mmol O_2 $m^{-2}d^{-1}$	
			Un-oil water station 1	Oiled water station 2
Chryptophytes	0.018	0.088	0.31	7.24
Chrysophytes	0.016	0.082	2.01	1.32
Chlorophytes	0.008	0.058	5.10	3.30
Diatoms	0.005	0.084	0.38	0.29
Prymesioophytes	0.019	0.065	6.67	4.23

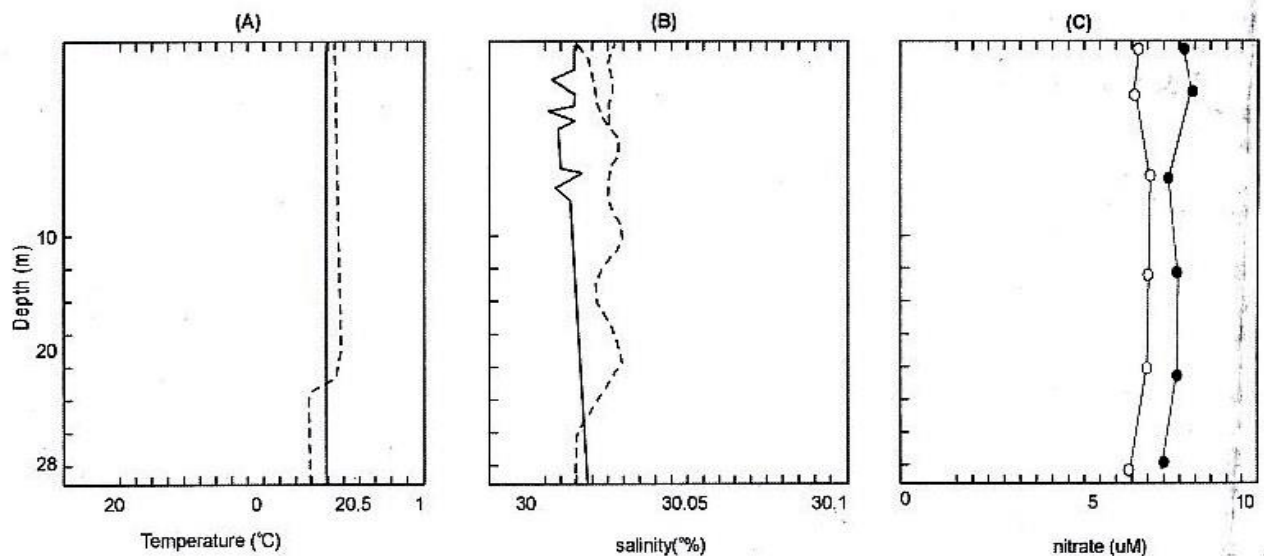


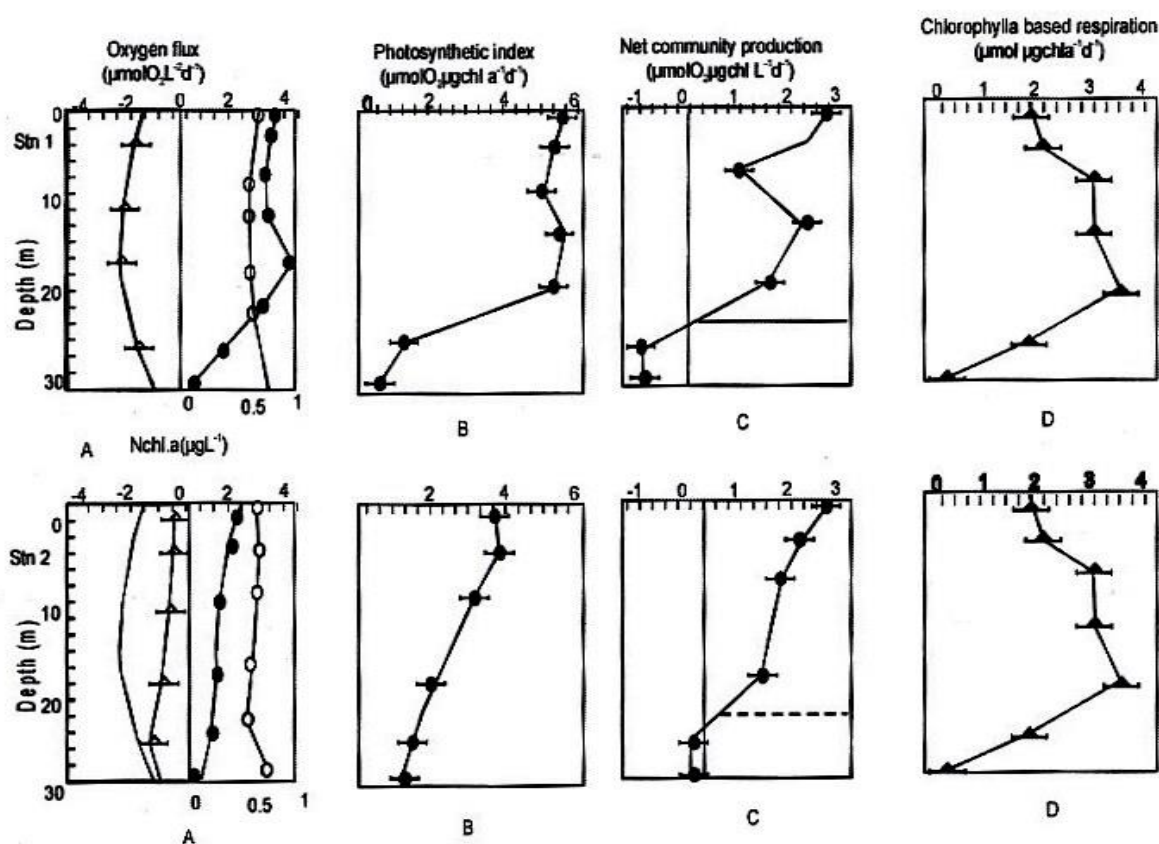
Fig 1: Vertical profiles of temperature (A) and (B) at station 1 unoled (solid line) and oiled station 2 (broken line) and nitrate (C) at station 1 (closed circles) and 2 (open circles).

CHLOROPHYLL a, PRIMARY PRODUCTION AND COMMUNITY METABOLISM

At both oiled and unoiled stations 2 and 1, chlorophyll a was distributed almost uniformly in the euphotic zone. Its concentration however, was slightly higher at, unoiled station ($0.53\text{--}0.65\mu\text{gL}^{-1}$), than at oiled station 2 ($0.52\text{--}0.56\mu\text{gL}^{-1}$), (Figs. 2(a) and 3(a)). The integrated amount of chlorophyll a in the euphotic zone was almost identical between the oiled and non-oiled stations 22.8mgm^{-2} and 25.2mgm^{-2} respectively.

Gross primary production showed a surface maximum followed by a decrease with depth at both oiled and un-oiled stations, while

there was a subsurface maximum at 16-m depth at station 1 (unoiled), than those at station 2 (oiled) [Figs 2(a) and 3(a)]. The rates tended to be higher at station 1 than at station 2, the higher rates ranging between 2.8 and $4\mu\text{mol O}_2$ occurred in the upper 17-18m at station 1. On the other hand high rates of $>2\mu\text{mol L}^{-1}\text{d}^{-1}$ were found only in the upper 8-10m at oiled station 2. The integrated gross production was $82.2\text{mmol O}_2\text{ m}^{-2}\text{ d}^{-1}$ at un-oiled station 1, 52% higher than $53.6\text{mmol O}_2\text{ m}^{-2}\text{ d}^{-1}$ at oiled station 2.



Figs. 2 and 3: Gross production (closed circles), community metabolism (open triangles) and chlorophyll a (open circles) at oiled station 2 and un-oiled station 1, photosynthetic index (b), net community production (c), and respiration per chlorophyll a (d) are also shown. Bars indicate standard deviation. Broken line denotes community compensation depth (CCD).

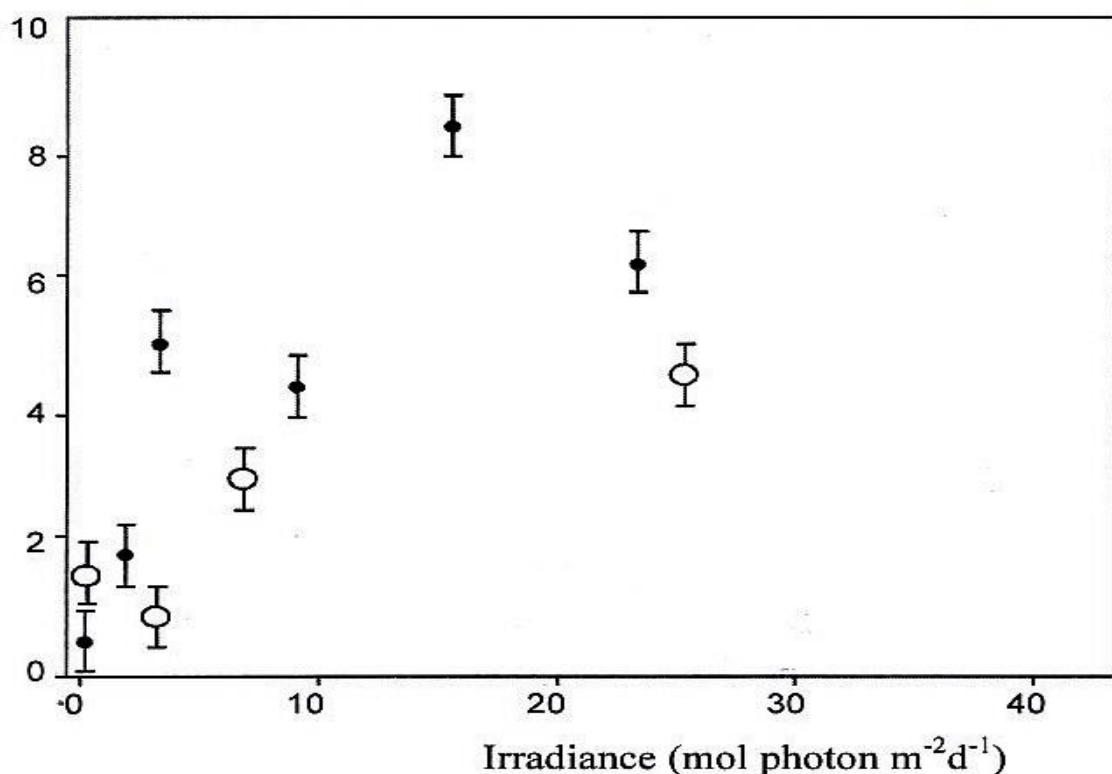


Fig4: Photosynthetic index at various depth versus insitu daily irradiance at non-oiled station 1 (closed circles) and oiled station 2 (open circles).

The photosynthetic index was generally higher at unoiled station 1 than at oiled station 2, varying from 0.3 to 5.68 $\mu\text{mol O}_2$ or $(\mu\text{gchl.a})^{-1} \text{d}^{-1}$ in the euphotic layer at station 1 and from 0.72 to 3.21 $\mu\text{mol O}_2$ or $(\mu\text{gchl.a})^{-1} \text{d}^{-1}$ at station 2 (Figs. 2(a) and 2(b)). Therefore the different magnitudes of gross production between both stations were primarily ascribed to difference in photosynthetic activity in the oiled and non-oiled station. A plot of photosynthetic indices at various depths against daily photonflux showed a photosynthetically more active population at non-oiled station 1 than oiled station 2 (Fig 4).

Dissimilar profiles of community respiration were obtained at both stations as a result of the oil spill incidence. Profiles showed a subsurface maximum at 16m depth at station 1 while at station 2 it was substantially low, ranging from 0.06 to 0.82 $\mu\text{mol O}_2 \text{ l}^{-1} \text{d}^{-1}$. The integrated community respiration was higher at non-oiled station 1 (48.2 $\text{mmol O}_2 \text{ m}^{-2} \text{d}^{-1}$) than at oiled station 2 (18.6 $\text{mmol O}_2 \text{ m}^{-2} \text{d}^{-1}$) as was the case for gross production. A difference in both gross production and community metabolism between the oiled and non-oil-polluted stations gave a clear contrast in vertical distribution of community metabolism. Net community production showed a double maximum at the surface and at about 16-m depth at station 1 (Fig 3[c]), positive net community production were found in upper 18m at this station and above 20m

at oiled station 2. The depth where net community production became zero, was defined as the community compensation depth (CCD) (Williams & Purdie 1991). The CCD was 23m and 25m at station 1 (non-oiled) and station 2 (oiled) respectively (Figs 2 [c] and 2[d]), approximately 12-14m shallower than the 1% light level depth. The level of the CCD was 6% at non-oiled station 1 and 4% at oiled station 2 respectively. The net community production integrated in the euphotic zone, was positive at both station, but higher at the non-oiled station 1 (being 36.2 $\text{mmol O}_2 \text{ m}^{-2} \text{d}^{-1}$) at the oiled station 2 (30.1 $\text{mmol O}_2 \text{ m}^{-2} \text{d}^{-1}$). Community respiration normalized for unit, chlorophyll a was also higher at non-oiled station 1 than at oiled station 2 ranging from 0.59 to 3.58 $\mu\text{mol O}_2$ or $(\mu\text{g.chla})^{-1} \text{d}^{-1}$ (Figs. 2[d] and 3[d]).

The dominant phytoplankton pigments detected using high-performance liquid chromatography (HPLC) were chlorophyll a, chlorophyll b, chlorophylls c and c₂, 19-hexanoyloxyfucoxanthin, 19- butanoylOxyfucoxanthin, fucoxanthin, alloxanthin neoxanthin and violaxanthin, neoxanthin and violanthin at stations 1 and 2.

DISCUSSION

PRIMARY PRODUCTION

The low gross production at oiled station 2 was due to low photosynthetic activity (Figs 2[b], 3[b]

and 4). Daily incident flux of PAR during incubation was 39.0 at station 1 and 18.1 $\text{Em}^{-2}\text{d}^{-1}$ at station 2. Oil slicks and sheens on the water surface at station 2 probably reduced the intensity of light penetration into the subsurface seawater.

Therefore the low integrated gross production at 2 can be partially ascribed to the low photon flux in the water. The photosynthetically active population at station 1 seemed to be responsible for the high production at that station (Fig 1), since there was no surface slicks or sheen on the water surface to have obstructed light penetration. Determination of primary production by bio-optical model yielded average value of 42.6 $\text{mmol Cm}^{-2}\text{d}^{-1}$ and / oiled stations 1 and 2, while in situ uptake of $\text{H}^{13}\text{CO}_3^-$ on a 24-hr basis yielded 33.2 $\text{mmol Cm}^{-2}\text{d}^{-1}$ and 16.8 $\text{mmol Cm}^{-2}\text{d}^{-1}$ respectively at both stations.

The former values seem to be closer to the gross production than the latter values (Furuya *et al*, 1998). The model calculation was based on parameters of photosynthetic - irradiance curves obtained by incorporation of $\text{H}^{13}\text{CO}_3^-$ into particles retained on Whatman GF/F Filters. The apparent photosynthetic quotients of 3.6 at non-oiled station 1 and 1.8 at the oiled station 2 were obtained from our estimate and the bio-optically derived production. The oxygen method determined production of both particulate and dissolved fractions, while the model calculation was made only on particulate fraction. The quotients are over estimation, and values observed at the stations seem considerably high around the upper limits of the reported values. (McAllister *et al*, 1961, Platt *et al*, 1987).

Although, ammonia concentration and nitrate uptake rate were not determined during the cruise, phytoplankton likely depended on replete nitrate supply at both stations. Thus, the apparent photosynthetic quotient tended to be high according to a stoichiometric consideration (Geider & Osborne, 1992). Because the quotients are influenced by numerous factors, no immediate and adequate explanation is available for the high value recorded in the study area.

Phytoplankton Taxa and Chlorophyll a Distribution

On the basis of the concentration of biomarker pigments, the contribution of prymnesiophytes, chrysophytes and diatoms to the total chlorophyll a biomass was calculated for each class by algorithm (Litelier *et al*, 1993; Andersen *et al*, 1996). The class-specific chlorophyll a of the three classes summed up to 40% and 35% of integrated chlorophyll at control station 1 and the oiled station 2 respectively. Since a high amount of chlorophyll b and alloxanthin was observed at the stations, the remaining chlorophyll a was attributed to chlorophytes and chryptophytes. The

concentration of chryptophytes to total chlorophyll a was calculated using a chlorophyll a: alloxanthin ratio of 3.04 (Tester *et al*, 1995). The remainder of the chlorophyll a (36 and 38% of integrated chlorophyll a at stations 1 and 2 respectively) was assigned to chlorophytes.

Community Metabolism

The obvious distinction of community metabolism between the oil and the un-oiled stations was perhaps due to a difference in heterotrophic activities, since chlorophyll a concentration in the euphotic zone at oiled station 2 and un-oiled station 1 were the same. Algal respiration was estimated after Langdon (1993) and assumed light and dark respiration to be equal. Daily respiration was estimated group by group and was divided into two components, the maintenance respiration and a growth-rate-dependent component (Verity, 1982. Langdon, 1988). Daily algal respiration R ($\mu\text{mol O}_2 \text{L}^{-1}\text{d}^{-1}$) is expressed as $R = 24 \cdot B (R_0 + R_D P^B)$, where B is the chlorophyll a concentration of each algal group ($\mu\text{g L}^{-1}$), R_0 is the chlorophyll-specific maintenance respiration ($\mu\text{O}_2 [\mu\text{g chl.a}]^{-1}\text{h}^{-1}$), R_D is the linear coefficient of increase of chlorophyll-specific dark respiration with chlorophyll-specific gross production and P^B is the chlorophyll-specific gross production ($\mu\text{mol O}_2 [\mu\text{g chl. a}]^{-1}\text{h}^{-1}$) (Langdon 1993). Values of R_0 and R_D have been compiled according to taxonomic groups for diatoms, chlorophytes, chrysophytes and prymnesiophytes, Table 1 (Langdon 1993). Because the effects of temperature on R_0 is negligible and R_D is temperature dependent (Verity, 1982), to obtain means values for each taxon, the compiled R_D values were normalized to 10°C by the following equation (Langdon, 1993) : $R_D(10^\circ\text{C}) = R_D(T) \exp \{C \cdot 0.1 \ln Q_{10} (T - 10) -$ where T is temperature in $^\circ\text{C}$ and the value of Q_{10} is assumed to be 2.

In Table 1 the daily respiration(R) of each group of phytoplankton is shown for both oiled and un-oiled stations together with their chlorophyll a - specific maintenance respiration (R_0) and the linear coefficient of increase of dark respiration with photosynthesis (R_D). The total autotrophic respiration was obtained by summing algal respiration rates for each group of phytoplankton. The algal respiration varied from 0.21 to 1.2 $\mu\text{mol O}_2 \text{L}^{-1}\text{d}^{-1}$ vertically at the oiled station 1. Heterotrophic respiration which was subtracted from community respiration ranged from 0.18 at 30m to 1.8 $\mu\text{mol O}_2 \text{L}^{-1}\text{d}^{-1}$ at 18m depth. Depth integrated heterotrophic respiration was 28.9 $\text{mmol O}_2 \text{m}^{-2}\text{d}^{-1}$, accounting for 65% of the community respiration, and 34% of the gross production. The calculated algal maintenance respiration ranged from 0.18 to 0.22 $\mu\text{mol O}_2 \text{L}^{-1}\text{d}^{-1}$ at oiled station 1 and was almost equivalent to

community respiration. Depth - integrated phytoplankton respiration was $18.0 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$, comparable to the integrated community respiration of $2.1 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. It could however be suggested that heterotrophic respiration is quite low at the oiled station 1 compared to un-oiled station 1. Respiratory activity of small plankton ($<3 \mu\text{m}$) could be significant during diatom bloom due to non-photosynthetic organisms (Williams, 1981). This suggests that micro heterotrophs play a major role in overall rate of community respiration in the Gulf of Guinea. Although earlier studies have emphasized the importance of microheterotrophs such as bacteria in material recycling via microbial food webs (Iriarte *et al.*, 1991), petroleum can inhibit bacterial heterotrophic activity in natural waters (Griffiths *et al.*, 1981). This probably is responsible for the observed reduction in community respiration at the oiled station compared with the non-oiled stations.

Phytoplankton stimulation or inhibition has been reported in several oil pollution incidents. Increase productivity was indicated after the Bravo Spill (Lannergren, 1978) and the Tsesis Spill (Johansson, 1980) during the Torrey Canyon Spill, there were some indications of increased number of flagellates (Smith, 1970). In the present investigation the algal community exhibited inhibitory behaviour as both carbon fixation and community metabolism was significantly lower at oiled sites than at the un-oiled station.

CONCLUSION

Although phytoplankton abundance and composition were almost identical between the oiled station 2 and the un-oiled station 1 in the study off shore area, gross primary production showed a marked difference which was ascribed to variations in photosynthetic activity of the population, perhaps due to the presence of oil. Heterotrophic organisms appeared to be an important biological factor in determining the magnitude of net community production being that they actively consumed the products of algal carbon fixation during the study period.

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