OCEANOLOGICA ACTA - VOL. 17 - N°6

Variability of $\partial^{13}C$ of ΣCO_2 in ocean waters of the Equatorial Pacific

$\partial^{13}C$
Upwelling
Pacific
Anthropogenic CO_2

$\partial^{13}C$
Upwelling
Pacifique
CO_2 anthropogénique

Elzbieta LAUBE-LENFANT and Catherine PIERRE

UMR: CNRS/ORSTOM, Université Pierre et Marie Curie, laboratoire d'Océanographie Dynamique et de Climatologie, 4, place Jussieu, 75252 Paris Cedex 05, France.

Received 22/03/94, in revised form 5/10/94, accepted 18/10/94.

ABSTRACT

The transect from East to West Pacific realized along the equator during the Alize 2 cruise (January-March 1991) offers a unique opportunity to evaluate the effect of the equatorial upwelling on the $\partial^{13}C$ values of ΣCO_2 in oceanic waters. The surface $\partial^{13}C$ distribution from 95°W to 165°E is characterized by a general increase from 0.90 to 1.54 ‰ which parallels the temperature rise from 23 to 30°C, both giving a signature of the upwelling and of the westward advection of superficial waters: the ^{13}C depletion in the ΣCO_2 marks the progressive influence of upwelled waters which are rich in ^{13}C-depleted CO_2 generated by organic matter remineralization. The vertical $\partial^{13}C$ distribution from the surface down to 1000 metres shows that the upper thermocline and the oxygen minimum are two major boundaries between which the regeneration of organic matter mainly occurs. Furthermore, the comparison of our measurements with those obtained by Kroopnick in 1970 at the same location (150°W) shows that $\partial^{13}C$ values in surface waters have decreased by 0.5 ‰ during the last twenty years period as a result of anthropogenic CO_2 inputs .

RÉSUMÉ

Variabilité du $\partial^{13}C$ du ΣCO_2 des eaux océaniques du Pacifique équatorial.

Le transect d'Est en Ouest du Pacifique le long de l'équateur réalisé pendant la campagne Alizé 2 (janvier-mars 1991) offre l'occasion d'évaluer l'effet de l'upwelling équatorial sur les valeurs de $\partial^{13}C$ du ΣCO_2 des eaux océaniques. La distribution des valeurs de $\partial^{13}C$ en surface de 95°W jusqu'à 165°E est caractérisée par une augmentation progressive depuis 0,90 jusqu'à 1,54 ‰ qui se corrèle avec une augmentation de la température de 23 à 30°C ; les variations de ces deux paramètres marquent l'amortissement graduel vers l'Ouest du Pacifique de l'influence de l'upwelling qui injecte en surface des eaux froides et chargées en CO_2 appauvri en ^{13}C provenant de la reminéralisation en profondeur de la matière organique. La distribution verticale des valeurs de $\partial^{13}C$ depuis la surface jusqu'à 1000 mètres de profondeur montre que la thermocline supérieure et le niveau du minimum d'oxygène sont deux discontinuités majeures entre lesquelles se produit l'essentiel de la reminéralisation de la matière organique. Par ailleurs, la comparaison de nos données avec celles de Kroopnick obtenues en 1970 sur la même radiale transéquatoriale à 150°W montre une baisse générale de 0,5 ‰ des valeurs de $\partial^{13}C$ du ΣCO_2 pendant les vingt dernières années qui est due à l'injection dans l'océan de CO_2 d'origine anthropogénique.

Oceanologica Acta, 1994. **17**, 6, 633-641.

INTRODUCTION

Upwelling of nutrient and CO_2-rich subsurface waters in the central and eastern Equatorial Pacific causes high biological productivity in this region. The enhanced primary productivity level is particularly evident when it is compared with the oligotrophic conditions which are characteristic of the low latitude gyres of the adjacent North and South Pacific. The equatorial zonal belt several degrees wide is also considered as a major CO_2-source for the atmosphere (Lefèvre and Dandonneau, 1992; Tans *et al.*, 1989).

The $\partial^{13}C$ value of ΣCO_2 of surface waters is controlled by biological and inorganic processes. The assimilation of dissolved inorganic carbon by phytoplankton is accompanied by large isotope fractionation, giving organic matter with $\partial^{13}C$ values of about -22 ‰ in the region near the equator, and causing the ^{13}C enrichment of the remaining ΣCO_2 (Deuser *et al.*, 1968; Goericke and Fry, 1994; Rau *et al.*, 1982, 1989). Conversely the decomposition of organic matter releases ^{13}C-depleted CO_2, causing $\partial^{13}C$ decrease of the ΣCO_2 reservoir. The formation of calcium carbonate does not change the carbon isotopic composition of ΣCO_2, since this process occurs with a small isotope fractionation and removes only minor amounts of bicarbonate from the ΣCO_2 pool. In the evasion process the carbon isotope ratio of the CO_2 crossing the air-sea interface is lighter than that of the surface water ΣCO_2 (Mook *et al.*, 1974; Tans *et al.*, 1993). Thus the release of CO_2 by degassing surface ocean water would provoke the ^{13}C enrichment of the remaining ΣCO_2 (Inoue and Sugimura, 1985).

In the water column, the $\partial^{13}C$ values of ΣCO_2 in the subsurface, intermediate and deep waters are controlled by the oxidation of organic matter, and below the lysocline by the dissolution of carbonate shells (Kroopnick, 1985).

With the change of $\partial^{13}C$ of the atmospheric CO_2, due to combustion of fossil fuels, ^{13}C-depleted CO_2 is introduced into the atmosphere, and the $\partial^{13}C$ values of ΣCO_2 in the ocean also change gradually due to permanent air-sea exchanges (Keeling, 1992; Quay *et al.*, 1992; Tans *et al.*, 1993). At the present time in the equatorial region of the Pacific, the $\partial^{13}C$ value of the atmospheric CO_2 is around – 7.8 ‰ *i.e.* lower by $\approx$1.5 ‰ compared to the pre-industrial estimations (Keeling, 1992).

This paper presents carbon isotope measurements of ΣCO_2 in surface waters and in the water column from the Equatorial Pacific. The water samples were collected during the French oceanographic cruise Alize 2 (*R.V. Le Noroît*–January-March 1991) (Fig. 1). Among the 110 hydrological sections realized during this cruise, a total of 46 surface stations and ten vertical profiles from surface the down to 1000 or 2000 m distributed on the ship track along the equator (95°W, 104.9°W, 114.9°W, 134.5°W, 150°W, 160.5°W, 168.3°W, 178°W, 173.8°E, 165°E) have been selected for stable isotope analysis (Tab. 1, 2, 3). The comparison of the horizontal and vertical distributions of $\partial^{13}C$ values with the distributions of other parameters (temperature, dissolved oxygen and nitrate) measured during the cruise appears very useful in relating the carbon isotope variations to the specific physical and biological processes induced by the large-scale equatorial upwelling.

METHODOLOGY

The sea-water samples for stable isotopic analysis were siphoned from Niskin bottles into 125 ml-glass flasks and immediately poisoned with 1 ml of a saturated solution of $HgCl_2$. Technical procedures used for the preparation of the CO_2 gas samples correspond to the classical method: extraction of the total dissolved inorganic carbon by acidification of water samples with phosphoric acid and collection of the CO_2 gas in the vacuum system. The ^{13}C measurements were made on a VG Sira 9 mass spectrometer triple collector with a reproducibility of ± 0,05 ‰. The $\partial^{13}C$ values are reported relative to the PDB reference :

$$\partial^{13}C = [\ (^{13}C/^{12}C)\text{sample} / (^{13}C/^{12}C)\text{PDB} - 1]\ * 10^3$$

RESULTS AND DISCUSSION

The equatorial upwelling in the Pacific Ocean originates in the divergence of surficial waters which causes the upward migration of waters from the uppermost part of the thermocline near the core of the undercurrent (Wyrtki, 1981). During the Alize 2 cruise, temperature, salinity, nutrient and dichlorodifluoromethane distributions indicated that the source of upwelled waters was lying at rather shallow depths below 50 m at 95°W and 110 m at 140°W (Lefèvre *et al.*, 1994). The upwelling is submitted to seasonal variations because the trade winds regime changes throughout the year, but the most important climatic changes which control the oceanographic circulation are due to the influence of the ENSO events. The periods 1986/1988 and

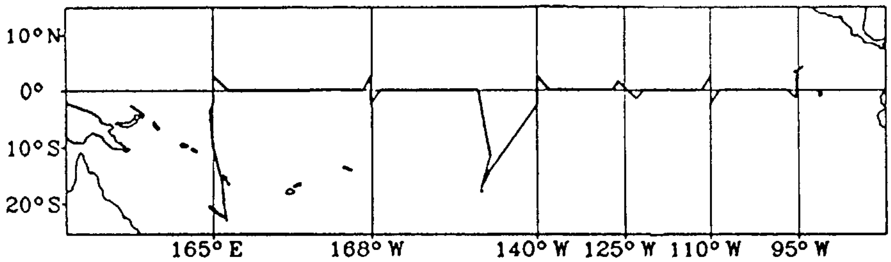

Figure 1

Schematic map of the Alize 2 cruise track in the Equatorial Pacific.

Carte schématique du Pacifique équatorial et trajet suivi au cours de la campagne Alizé 2.

N° station	latitude	longitude	S °/°°	T°C	∂13C °/°°
11	0,00S	95,39W	34,707	23,320	1,07
15	0,00S	97,00W	34,706	23,118	0,90
16	0,00S	98,46W	34,753	23,169	1,19
17	0,00S	99,76W	34,841	23,121	1,03
18	0,00S	101,33W	34,339	23,352	1,04
19	0,00S	102,87W	33,930	25,825	1,13
20	0,00S	104,93W	34,187	25,379	1,32
21	0,00S	106,70W	34,517	24,322	1,11
22	0,00S	108,47W	34,845	23,788	1,02
28	0,00S	110,00W	34,485	24,279	1,09
34	0,00S	111,50W	34,417	24,553	0,94
36	0,00S	114,90W	34,857	24,360	1,13
37	0,00S	116,49W	34,827	24,341	0,86
38	0,00S	118,40W	34,815	24,728	0,98
43	0,20N	124,78W	34,976	25,054	1,11
45	0,00S	127,25W	34,615	25,284	1,36
46	0,00S	128,59W	34,688	26,097	1,31
47	0,00S	130,65W	34,852	25,505	1,10
48	0,00S	132,63W	35,183	25,627	1,10
49	0,00S	134,55W	35,208	25,909	1,10
50	0,00S	136,37W	35,215	25,997	1,15
51	0,00S	137,92W	35,210	26,376	1,07
57	0,02N	140,18W	35,213	26,398	1,16
71	0,00S	150,00W	35,001	27,269	1,20
72	0,00S	152,85W	34,995	27,072	1,17
73	0,00S	154,73W	34,977	27,043	1,16
74	0,00S	156,42W	35,053	26,761	1,14
75	0,02S	158,32W	35,023	26,925	1,10
76	0,00S	160,55W	35,254	27,007	1,13
77	0,00S	162,47W	35,189	27,572	1,23
78	0,00S	164,62W	35,192	27,691	1,20
79	0,00S	166,58W	35,256	27,872	1,11
85	0,00S	168,25W	35,276	27,975	1,29
91	0,02S	169,53W	35,282	27,805	1,17
92	0,00S	172,20W	35,276	27,824	1,07
93	0,00S	174,27W	35,322	27,821	1,16
94	0,00S	176,25W	35,270	27,967	1,18
95	0,00S	178,25W	35,295	28,420	1,29
96	0,00S	179,75E	35,248	28,216	1,15
97	0,00S	177,75E	35,191	28,554	1,22
98	0,00S	175,75E	35,205	28,727	1,27
99	0,00S	173,82E	35,176	28,918	1,28
100	0,00S	171,75E	35,341	29,341	1,32
101	0,00S	169,75E	35,330	28,881	1,26
102	0,00S	167,75E	35,113	29,601	1,41
108	0,02N	165,00E	34,790	29,866	1,54

Table 1

Salinity, temperature, $\partial^{13}C$ values of ΣCO_2, of the surface waters from the Equatorial Pacific collected during the Alize 2 cruise (January-March 1991).

Salinité, température et valeurs de $\partial^{13}C$ du ΣCO_2 des eaux de surface prélevées dans le Pacifique équatorial au cours de la campagne Alizé 2 (janvier-mars 1991).

1988/1989 corresponded to El Niño and La Niña situations (Philander, 1990); the Alizé 2 cruise in early 1991 corresponded to quite normal conditions, where the minimum sea surface temperature was situated at the equator between 180°W and 95°W. However the SST values were higher than those measured a few months before suggesting that the upwelling was in a weak phase of its development (Lefèvre *et al.*, 1994).

Surface waters

The $\partial^{13}C$ variations of ΣCO_2 in surface waters (collected at depths between 2 and 4 m) were observed along the equator in the east-west direction of the surface current, and compared with the changes in temperature, ΔpCO_2 and nitrate concentrations.

The $\partial^{13}C$-temperature relationship

Along the equatorial transect of the Pacific Ocean, the $\partial^{13}C$ values of ΣCO_2 of surface waters increased from 0.90‰ at 97°W to 1.54‰ at 165°E, which directly parallels the temperature increase from 23°C to 30°C (Fig. 2a). These parameters are both affected by the upwelling and the westward advection of surface waters of the South Equatorial Current: the decrease by 0.64‰ of the $\partial^{13}C$ values in the ΣCO_2 at the easternmost side marks the progressive influence of ^{13}C-depleted upwelled waters, which are also 7°C colder than at the westernmost side. Under conditions

station 11 (0,00S, 95,39W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	34,707	23,320	1,11
20	34,782	22,370	1,02
30	34,882	22,206	1,01
40	35,042	21,882	0,85
61	34,871	18,949	0,64
81	35,226	17,836	0,64
93	35,261	17,020	0,71
100	35,169	16,283	0,74
118	35,012	14,629	0,67
159	34,937	13,570	0,56
399	34,742	10,181	-0,16
1991	34,640	2,328	-0,18

station 20 (0,00S, 104,90W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	34,187	25,379	1,32
20	34,250	25,155	1,21
30	34,370	24,810	1,22
39	34,487	24,447	1,18
48	34,744	23,123	0,92
59	34,785	22,546	0,92
79	34,752	19,498	0,42
100	34,899	15,484	0,31
118	34,879	14,230	0,22
158	34,885	13,024	0,33
327	34,808	11,441	-0,17
2002	34,634	2,289	-0,30

station 36 (0,00S, 114,90W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	34,857	24,360	1,07
20	34,871	24,298	1,15
40	34,913	24,203	1,03
49	34,952	24,155	1,16
58	35,007	24,005	1,03
70	35,120	23,669	1,01
83	35,057	22,133	0,80
94	35,075	20,197	0,60
118	35,079	16,852	0,77
158	34,903	13,530	0,48
351	34,766	10,669	-0,05
1499	34,607	2,935	-0,26

station 49 (0,00S, 134,55W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	35,208	25,909	1,10
25	35,216	25,912	1,14
48	35,201	25,844	1,11
74	35,217	25,768	1,14
99	35,299	25,228	0,91
119	35,568	22,833	0,94
139	34,951	17,984	0,57
161	34,999	15,583	0,61
200	34,922	13,357	0,43
300	34,837	11,842	-0,01
381	34,693	9,395	0,08
998	34,552	4,615	-0,01

station 71 (0,00S, 150,00W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
4	35,001	27,269	1,20
23	35,000	26,742	1,16
33	35,003	26,727	1,24
43	35,010	26,698	1,12
63	35,080	26,668	1,13
83	35,210	26,668	1,19
104	35,419	24,991	0,92
124	35,003	19,554	0,51
163		14,694	0,01
303	34,826	11,652	0,04
599	34,573	6,824	0,01
1009	34,551	4,648	-0,08

station 76 (0,00S, 160,55W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	35,254	27,007	1,13
20	35,252	26,912	1,05
30	35,254	26,909	1,05
40	35,254	26,906	0,94
59	35,261	26,904	1,02
80	35,274	26,881	1,02
99	35,400	26,459	1,07
119	35,635	24,018	0,96
159	35,166	16,763	0,73
299	34,807	11,360	0,19
599	34,575	7,151	-0,05
1004	34,552	4,392	-0,15

station 85 (0,00S, 168,25W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	35,279	27,795	1,29
20	35,263	27,644	
29	35,265	27,611	
40	35,267	27,583	1,18
61	35,351	27,411	1,12
80	35,372	27,280	1,08
100	35,397	26,824	1,05
120	35,605	25,814	0,97
159	35,234	16,988	0,71
300	34,812	11,469	0,02
600	34,569	6,952	-0,05
1005	34,550	4,692	-0,05

station 95 (0,00S, 178,25W)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	35,295	28,420	1,29
20	35,310	28,023	1,20
30	35,318	27,955	1,11
39	35,302	27,905	1,15
60	35,302	27,813	1,06
80	35,346	27,817	1,08
99	35,375	27,759	0,89
121	35,546	26,402	0,84
160	35,159	17,777	0,53
300	34,835	11,570	0,17
599	34,583	7,323	0,10
1015	34,561	4,200	-0,09

station 99 (0,00S, 173,82E)

Depth m	S°/°°	T°C	∂13C°/°°PDB
2	35,176	28,819	1,28
20	35,181	28,845	1,26
30	35,190	28,842	
40	35,198	28,833	1,23
60	35,243	28,802	1,25
78	35,293	28,632	1,26
100	35,356	25,482	0,91
120	35,292	22,645	0,85
157	35,263	18,172	0,60
299	34,840	11,727	0,39
600	34,564	6,920	0,22
1020	34,556	4,379	0,04

station 108 (0,02S, 165,00E)

Depth m	S°/°°	T°C	∂13C°/°°PDB
3	34,790	29,866	1,54
20	34,798	29,849	1,50
30	34,809	29,845	1,50
40	34,849	29,844	1,53
60	34,966	29,672	1,46
78	35,175	29,299	1,35
99	35,293	26,853	1,24
120	35,353	24,266	0,96
158		20,754	0,59
299	34,856	12,088	0,55
599	34,572	7,016	0,19
1008	34,554	4,467	-0,09

◀ Table 2

Vertical distribution of salinity, temperature and $\partial^{13}C$ values of ΣCO_2, of the waters from ten hydrological sections from the Equatorial Pacific collected during the Alize 2 cruise (January-March 1991).

Distribution verticale de la salinité, de la température et des valeurs de $\partial^{13}C$ du ΣCO_2 des eaux prélevées en dix stations hydrologiques dans le Pacifique équatorial au cours de la campagne Alizé 2 (janvier-mars 1991).

of isotopic equilibrium and assuming a $\partial^{13}C$ value of – 7.8‰ for the atmospheric CO_2 (Keeling, 1992), the $\partial^{13}C$ values of ΣCO_2 would be inversely related to temperature by the equation (1) of Mook *et al.* (1974) :

$$\partial^{13}C\ eq = 9483\ T^{-1} - 31.7 \qquad (1)$$

However, the lack of correlation between temperature and $\partial^{13}C$ values of ΣCO_2 shows that the ΣCO_2 of the surface ocean is far from isotopic equilibrium with the atmospheric CO_2 (Fig. 2b). Previous studies have shown that in general the system does not reach carbon isotope equilibrium because the rate of CO_2 exchange at the ocean-atmosphere boundary is not fast enough and the residence time of surface waters is not infinite (Broecker and Peng, 1982; Murnane and Sarmiento, 1993). At all events, the amplitude of the deviation from isotopic equilibrium would give an interesting indication on the nature of the processes causing this departure. In that respect, the highest carbon isotope enrichments (1.3 to 1.9‰) relative to equilibrium values are encountered west of 150°W where temperatures are maximum, while eastward, the increasing upwelling of ^{13}C-depleted CO_2 in the surface waters brings $\partial^{13}C$ values close to equilibrium values (Fig. 2b).

A few anomalies of high $\partial^{13}C$ values are well correlated with the local presence of warm-low saline and nutrient-poor waters with near-zero CO_2 fluxes, which are introduced from the north by equatorial long-waves. These anomalies are more important in the eastern part of the Equatorial Pacific. West of 135°W the well developed westward zonal current reduces the fluctuations caused by equatorial long waves (Eldin *et al.*, 1992; Lefèvre and Dandonneau, 1992; Lefèvre *et al.*, 1994).

The $\partial^{13}C$-ΔpCO_2 relationship

Although the measurements of ΔpCO_2 (pCO_2water-pCO_2air) represent snapshots during the annual variations of the Equatorial Pacific, the inverse correlation which is observed between the CO_2 fluxes (Lefèvre and Dandonneau, 1992) and the $\partial^{13}C$ values of the ΣCO_2 of surface waters is rather conspicuous (Fig. 3). In fact, the outgassing of CO_2-rich waters should induce an increase of the $\partial^{13}C$ values of the ΣCO_2. The inverse correlation between CO_2 fluxes and $\partial^{13}C$ values indicates that the upwelling of ^{13}C depleted waters rich in CO_2 due to organic matter remineralization is the prevailing factor which influences the $\partial^{13}C$ values in surface waters of that region therefore masking the isotope enrichment due to CO_2 degassing.

The carbon isotope budget

The chemical carbon budget could not be calculated directly because no measurements of ΣCO_2 concentrations were made during the cruise. The ΣCO_2 concentrations were thus deduced from nitrate concentrations using Redfield stoechiometry in order to establish the isotopic mass balance calculations between 165°E and 95°W and to estimate the respective parts of biological processes (the production-regeneration budget) and of CO_2 outgassing. The stations at 165°E and 95°W are considered as the two end members of the surficial Equatorial Pacific system, where turbulent meridional advection is assumed to be small. The

Table 3

Salinity, temperature, $\partial^{13}C$ values of ΣCO_2, of the surface waters from the submeridional transect between 140°-150°W in the Equatorial Pacific collected during the Alize 2 cruise (January-March 1991).

Salinité, température et valeurs de $\partial^{13}C$ du ΣCO_2 des eaux de surface prélevées le long d'une radiale subméridienne entre 140° et 150°W dans le Pacifique équatorial au cours de la campagne Alizé 2 (janvier-mars 1991).

N° station	latitude	longitude	S ‰	T °C	$\partial^{13}C$ ‰
52	2,50N	140,00W	37,847	26,897	1,28
53	2,00N	140,00W	34,880	26,943	1,26
54	1,50N	140,00W	34,827	26,028	1,21
55	1,00N	140,00W	34,922	25,804	1,01
56	0,50N	140,00W	35,069	26,143	1,05
57	0,02 N	140,00W	35,213	26,398	1,16
58	0,50S	140,00W	35,238	26,426	1,03
59	1,00S	140,00W	35,260	26,512	1,17
60	1,50S	140,00W	35,250	26,484	1,16
61	2,00S	140,00W	35,165	26,489	1,05
62	2,50S	140,00W	35,207	26,657	1,14
63	5,67S	142,20W	35,380	26,932	1,07
64	7,09S	143,17W	35,733	27,905	1,28
65	8,79S	144,37W	35,786	28,316	1,45
66	10,52S	145,55W	37,776	28,855	1,52
67	12,20S	146,73W	35,958	28,814	1,57
68	13,30S	147,50W	35,953	29,164	1,38
69	15,10S	148,63W	35,929	29,046	1,56
70	16,00S	148,90W	35,959	29,620	1,38

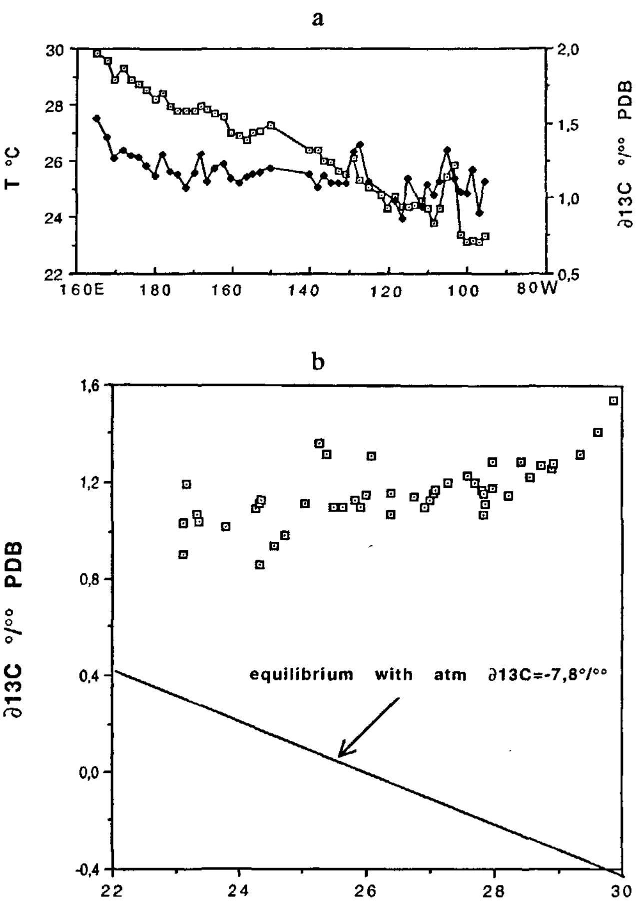

Figure 2

a) Variations along the equator of temperature (open squares) and of $\partial^{13}C$ values of ΣCO_2 in the surface waters of the Pacific ocean (filled rhombs).

Variations le long de l'équateur de la température (carrés blancs) et des valeurs de $\partial^{13}C$ du ΣCO_2 des eaux de surface dans l'océan Pacifique (losanges noirs).

b) Relationship between temperature and $\partial^{13}C$ of ΣCO_2 in surface ocean waters from the Equatorial Pacific.

Relation température-$\partial^{13}C$ du ΣCO_2 dans les eaux de surface du Pacifique le long de l'équateur.

ΣCO_2 of East Pacific surface waters (with an isotopic composition labelled as $\partial^{13}C_{east}$) is thus considered resulting from the simple mixing of the ΣCO_2 of oligotrophic West Pacific surface waters (with an isotopic composition labelled as $\partial^{13}C_{west}$) and of the CO_2 added by upwelled waters (with an isotopic composition labelled as $\partial^{13}C_{o.m.}$). The fraction x of CO_2 which comes from organic matter oxidation is calculated assuming an average ΣCO_2 concentration of 2040 µmol kg^{-1} in the oligotrophic surface waters at 165°E (Inoue and Sugimura, 1992), a Redfield ratio C/N = 106/16, and nitrate concentrations of 0 µmol kg^{-1} at 165°E and of 11 µmol kg^{-1} at 95°W (Reverdin *et al.*, 1991). The mixing equation (2) thus becomes :

$$\partial^{13}C_{east} = [\partial^{13}C_{west} * (1-x)] + [(\partial^{13}C_{o.m.}) * x] \qquad (2)$$

The difference between the calculated and measured $\partial^{13}C$ values ($\Delta^{13}C_{c-m}$) is equal to 0.4‰ at 95°W and should correspond to the overall isotopic effect due to the CO_2 evasion from the ocean to the atmosphere. The carbon enrichment factor ε at equilibrium between ΣCO_2 and gaseous CO_2 is equal to 8.15‰ at 23°C (Mook *et al.*, 1974). The fraction f of ΣCO_2 remaining in the sea surface after outgassing may be estimated by the Rayleigh equation: $\Delta^{13}C_{0.m.} = -\varepsilon \ln f$; it is equal to 0.95 which means that about 5 % of the aqueous ΣCO_2 escapes as gas toward the atmosphere at 95°W in the zone of active upwelling.

The $\partial^{13}C$-Nitrate relationship

In the westernmost Pacific at 165°W the nitrate concentration of oligotrophic surface waters is below detection. The injection of nutrients from underlying waters increases progressively toward the east so that the nitrate concentration reaches 11 µmol kg^{-1} at 95°W. A plot of nitrate concentrations against $\partial^{13}C$ values (Fig. 4) clearly shows the linear relationship between these two parameters. This suggests that surface water nutrients are contributed by an unique source which is organic matter oxidation, a process which also adds ^{13}C-depleted CO_2 to the ΣCO_2 reservoir. The relationship between $\partial^{13}C$ values and $[NO_3]$ concentrations in the Pacific surface waters (3) may be defined as Broecker and Maier-Raimer (1992) proposed for the $\partial^{13}C$-$[PO_4]$ relationship.

$$\partial^{13}C_{surf} - \partial^{13}C_{m.s.o.} = [\Delta photo/\Sigma CO_2 m.s.o. * C/Norg] \; [(NO_3)surf - (NO_3)m.s.o.] \qquad (3)$$

where surf and m.s.o. refer respectively to surface and mean surface ocean, photo is the carbon isotope fractionation during marine photosynthesis, and C/Norg is the Redfield ratio. Taking the following parameters for the Equatorial Pacific (Δphoto= −22 ‰ , C/N org = 106/16, ΣCO_2m.s.o.= 2040 µmol kg^{-1}), the equation becomes :

$$\partial^{13}C_{surf} - \partial^{13}C_{m.s.o.} = -0.0714 \, [(NO_3)surf - (NO_3)m.s.o.] \qquad (4)$$

For the mean surface ocean values measured in the Pacific ($\partial^{13}C$ =1.16‰, (NO_3) = 4.81 µmol kg^{-1}) the production-remineralization line is given by the following equation :

$$\partial^{13}C_{surf} = -0.0714 \, (NO_3) + 1.50 \qquad (5)$$

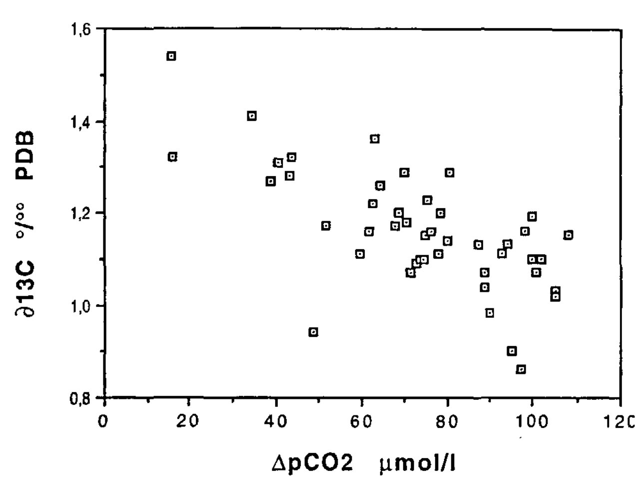

Figure 3

Relationship between $\partial^{13}C$ of ΣCO_2 and ΔpCO_2 in surface ocean waters from the Equatorial Pacific.

Relation $\partial^{13}C$ du ΣCO_2 -ΔpCO_2 dans les eaux de surface du Pacifique le long de l'équateur.

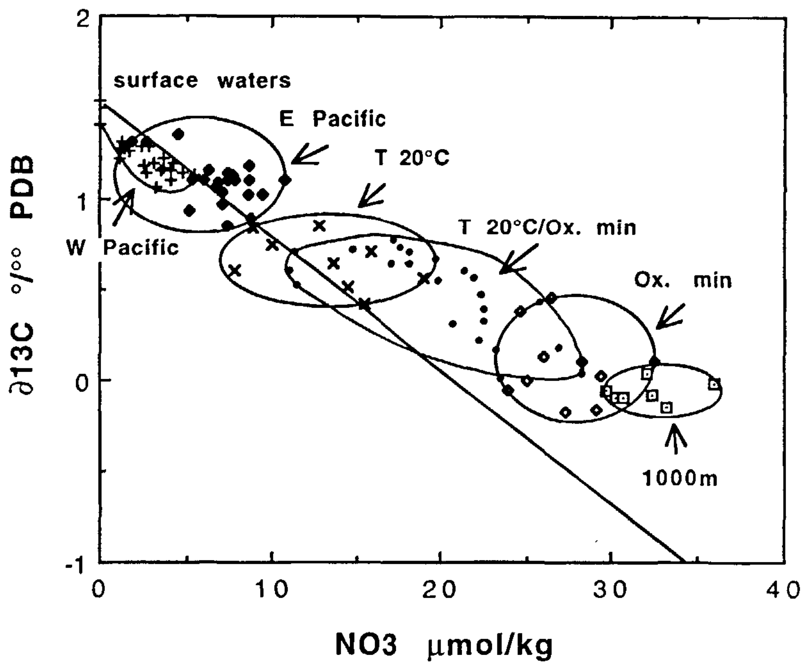

Figure 4

Relationship between $\partial^{13}C$ of ΣCO_2 and NO_3 in the ocean waters from the Equatorial Pacific. The line represents the evolution followed by surface waters to which products of organic matter remineralization are added.

Relation $\partial^{13}C$ du ΣCO_2 - NO_3 dans les eaux de surface du Pacifique le long de l'équateur. La droite représente l'évolution suivie par les eaux de surface auxquelles sont ajoutés les produits de la reminéralisation de la matière organique.

The West Pacific surface waters are well grouped along this line while the central and East Pacific surface waters are shifted to $\partial^{13}C$ values which are higher than those expected for a simple mixing between oligotrophic waters and eutrophic waters. The $\partial^{13}C$-deviation of about +0.4‰ from the production-remineralization line is thus attributed to the CO_2-outgassing effect in the Central and East Pacific where upwelling is active.

The anthropogenic CO_2 uptake by surface ocean waters

The only available $\partial^{13}C$ measurements of ΣCO_2 in surface waters in the Equatorial Pacific are those provided by the Hudson expedition in 1970 which crossed the equator on a meridional section along 150°W (Kroopnick *et al.*, 1977). The $\partial^{13}C$ values of surface water ΣCO_2 measured by Kroopnick during this cruise, showed $\partial^{13}C$ values increasing from 1.7‰ at the equator to 2.3‰ at 15°S. A similar trend was observed from a sub-meridional transect between 140°and 150°W during the Alize 2 cruise, with $\partial^{13}C$ values increasing from 1.16‰ at the equator to 1.56‰ at 15°S (Tab. 3). The overall ^{13}C depletion in ocean surface ΣCO_2 after this 20 years period may be explained by the anthropogenic input of ^{13}C-depleted CO_2; it represents a gradual $\partial^{13}C$ decrease by 0.025‰ yr^{-1}, a value which agrees well with that of 0.020‰ yr^{-1} found by Quay *et al.*, (1992) in other locations of the Pacific Ocean for the same time interval.

The vertical $\partial^{13}C$ distribution

It is generally admitted that the biological productivity of the Equatorial Pacific decreases westward (Chavez and Barber, 1987; Dugdale *et al.*, 1992; Dandonneau, 1992), but during the Alize 2 cruise, no longitudinal gradient of the chlorophyll-*a* concentration was detected. The vertical distribution of the whole chemical tracers indicates that the thermocline is a major dynamic boundary and that it corresponds to very sharp gradients of all chemical parameters. The depth of the upper thermocline which coincides with the isotherm 20°C increases from about 45 m at 95°W to 180 m at 165°E.

The distribution of $\partial^{13}C$ at depth through the Pacific Ocean

The concentration of the oxygen minimum increased westward from 0.3 ml l^{-1} at 95°W to 1.2 ml l^{-1} at 165°E. Similarly, the $\partial^{13}C$ values of ΣCO_2 at the oxygen minimum level change from –0.17‰ at 95°W to 0.35‰ at 165°E, confirm that the highest regeneration rates in the water column were located in the East Pacific (Fig. 5).

The $\partial^{13}C$ depth variations from the surface down to 1000 m along the equator, shows clearly the input of ^{13}C-depleted CO_2 by ascending deeper waters. Waters with $\partial^{13}C$ value of ≈ 0‰ are lying at about 250-350 metres in the East Pacific and at 1000 metres in the West Pacific. This pattern fits remarkably well with the variations with depth of dissolved oxygen and nutrient concentrations (Reverdin *et al.*, 1991).

The $\partial^{13}C$ -nitrate relationship at depth

The $\partial^{13}C$-(NO_3) pairs corresponding to the upper thermocline level, follow the linear trend of organic matter oxidation (Fig. 4). Below this level, the $\partial^{13}C$-(NO_3) pairs are generally grouped outside this trend with significant relative enrichments in ^{13}C and (NO_3). This means that in waters below the oxygen minimum, the anthropogenic CO_2 contamination is very weak. Furthermore, the $\partial^{13}C$ and (NO_3) variations occur mostly between the upper thermocline and the oxygen minimum levels. These levels may thus be considered as major geochemical boundaries which delineate a water layer where most of the organic matter remineralization occurs.

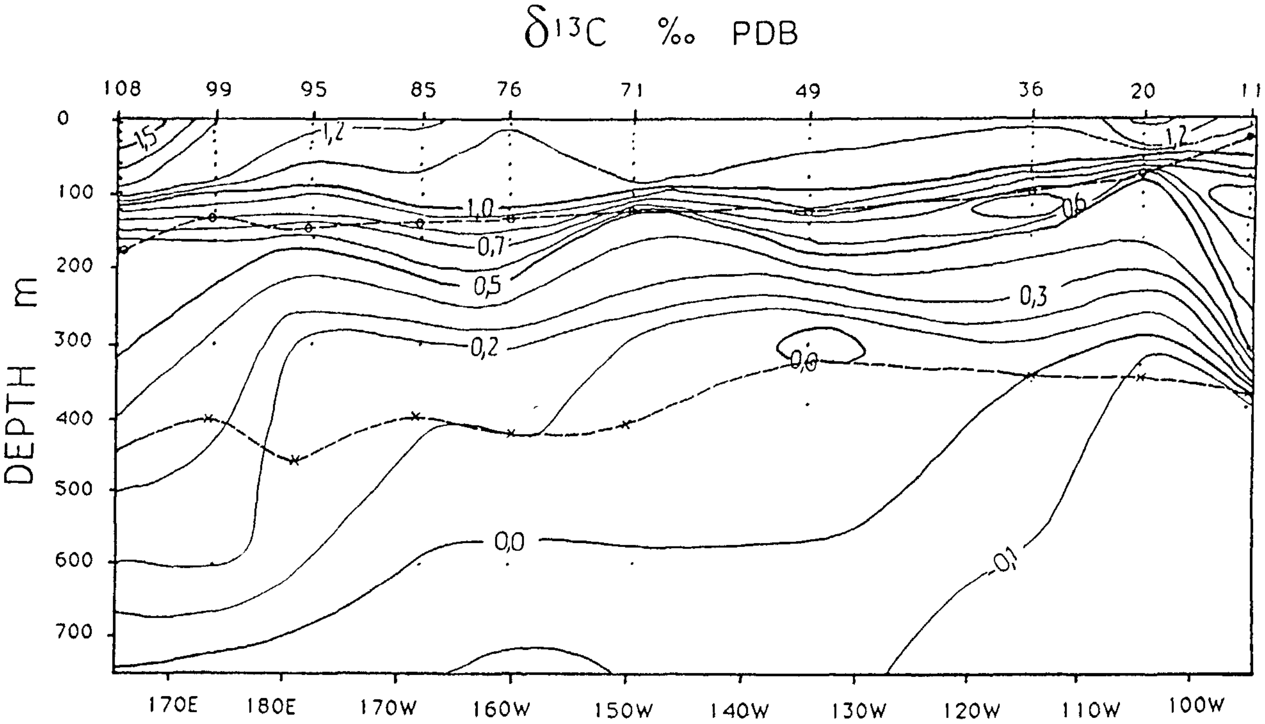

Figure 5

Equatorial distribution of $\partial^{13}C$ values of ΣCO_2 at depth in the Pacific Ocean. The upper and lower dashed lines represent respectively the isotherm 20°C (upper thermocline) and the oxygen minimum level.

Distribution verticale des valeurs de $\partial^{13}C$ du ΣCO_2 des eaux du Pacifique le long de l'équateur. Les lignes en pointillés représentent l'isotherme 20°C (thermocline supérieure) et le niveau du minimum d'oxygène.

The carbon isotope budget in the water column

For a better understanding of the zonal $\partial^{13}C$ variations in the water column, we have calculated the depth-integrated $\partial^{13}C$ values for the ten equatorial profiles. These values represent the integrated areas from 0 m to 940 m comprised between the $\partial^{13}C$ depth profiles and the vertical line which corresponds to the $\partial^{13}C$ value of the deeper water; they would give the global ^{13}C balance in the 0-940 m layer related to the production-regeneration plus outgassing budget at each station.

The 0-940 m integrated $\partial^{13}C$ values are low in the East Pacific, increase progressively westward and are doubled in the Western Pacific (Tab. 4). This means that in the East Pacific the amounts of CO_2 coming from organic matter regeneration are at least twice more important than in the West Pacific .

CONCLUSION

The dominant factor affecting the horizontal and vertical distributions of $\partial^{13}C$ in ΣCO_2 of the Equatorial Pacific waters is the physical circulation, especially the upwelling of waters originating from relatively shallow depths which spread over the East and Central Pacific ocean. During the Alize 2 cruise from 95°W to 165°E, the advection from depth of cold waters caused the temperature drop by 7°C and the $\partial^{13}C$ decrease by 0.64‰ in the surface waters. The combined effects of CO_2 evasion and of high biological productivity levels in the zone of active upwelling caused the increase of $\partial^{13}C$ values in the surface ocean waters. This increase is superimposed to the major $\partial^{13}C$ depletion due to massive CO_2 inputs from underlying waters. Therefore, in the central and eastern equatorial Pacific, it is the deep-CO_2 input from upwelled waters, depleted in ^{13}C, which mostly controls the carbon isotope variations of ΣCO_2.

The upper thermocline and the oxygen minimum level correspond to major boundaries between which a large part of the carbon remineralization occurs. Variability of the position of these levels induced by climatic and/or biological constraints would thus have direct implications on chan-

Table 4

Integrated $\partial^{13}C$ values of ΣCO_2 from 0 to 940 m calculated at ten hydrological sections from the Equatorial Pacific .

Valeurs de $\partial^{13}C$ du ΣCO_2 intégrées de 0 à 940 m pour dix stations hydrologiques du Pacifique équatorial.

N° station	integral °/°°m
11	239,1
20	215,2
36	278,6
49	230,8
71	255,6
76	352,7
85	281,0
95	337,2
99	340,5
108	496,9

ging the carbon budget and the $\partial^{13}C$ signature of the equatorial upwelling.

For a more global point of view, the $\partial^{13}C$ value of ΣCO_2 of surface ocean in this part of the Equatorial Pacific has decreased by ≈ 0.025‰ yr^{-1} during the last twenty years due to the introduction of anthropogenic CO_2 into the atmosphere by burning fossil fuels and deforestation. This result demonstrates the sensitivity of the $\partial^{13}C$ value of ΣCO_2 as a tracer to quantify the ability of the different portions of the oceans for atmospheric CO_2 absorption .

Acknowledgements

We are particularly indebted to our colleagues who have participated to the Alize 2 cruise, with a special mention to the chief scientists G. Reverdin and A. Morlière for encouraging the inclusion of this isotopic study in the Alize 2 project, a part of the TOGA programme. We thank also Y. Dandonneau and M. Rodier who made the pCO_2 and nutrients measurements and gave us facilities to use their data.

REFERENCES

Broecker W.S. and E. Maier-Raimer (1992). The influence of air and sea exchange on the carbon isotope distribution in the sea. *Global Biogeochemical Cycles*, **6**, 3, 315-320.

Broecker W.S. and T.H. Peng (1982). *Tracers in the Sea.* Lamont-Doherty Geological Observatory, Palisades, New York, 690 p.

Chavez F.P. and R.T. Barber (1987). An estimate of new production in the equatorial Pacific. *Deep Sea Research*, **35**, 5, 839-853.

Dandonneau Y. (1992). Surface chlorophyll concentration in the tropical Pacific ocean: an analysis of data collected by merchant ships from 1978 to 1989. *Journal of Geophysical Research*, **97**, C3, 3581-3591.

Deuser W.G., E.T. Degens and R.R.L. Guillard (1968). Carbon isotope relationships between plankton and sea water. *Geochimica et Cosmochimica Acta*, **32**, 657-660.

Dugdale R.C., F.P. Wilkerson, R.T. Barber and F.P. Chavez (1992). Estimating new production in the equatorial Pacific ocean at 150°W. *Journal of Geophysical Research*, **97**, 681-686.

Eldin G., A. Morlière and G. Reverdin (1992). Acoustic doppler current profiling along the Pacific equator from 95°W to 165°E. *Geophysical Research Letters*, **19**, 913-916.

Goericke R. and B. Fry (1994). Variations of marine plankton $\partial^{13}C$ with latitude, temperature and dissolved CO_2 in the world ocean. *Global Biogeochemical Cycles*, **8**, 1, 85-90.

Inoue H.Y. and Y. Sugimura (1985). Carbon isotopic fractionation during the CO_2 exchange process between air and sea water under equilibrium and kinetic conditions. *Geochimica et Cosmochimica Acta*, **49**, 2453-2460.

Inoue H.Y. and Y. Sugimura (1992). Variations and distributions of CO_2 in and over the equatorial Pacific during the period from the 1986/88 El Niño event to the 1988/89 La Niña event. *Tellus*, **44B**, 1-22.

Keeling C.D. (1992). Global observations of atmospheric CO_2. *in* : NATO Advanced Study Institute on the Global Carbon Cycle. (unpublished report)

Kroopnick P.M. (1985). The distribution of ^{13}C of ΣCO_2 in the world ocean. *Deep Sea Research*, **32**, 1, 57-84.

Kroopnick P., S.V. Margolis and C.S. Wong (1977). $\partial^{13}C$ variations in marine carbonate sediments as indicators of the CO_2 balance between the atmosphere and oceans. *in*: The Fate of Fossil Fuel CO_2 in the Oceans (Eds. N.R. Andersen and A. Malahoff), Plenum, New-York, p. 295-321.

Lefèvre N. and Y. Dandonneau (1992). CO_2 fluxes in the equatorial Pacific in January-March 1991. *Geophysical Research Letters*, **19**, 22, 2223-2226.

Lefèvre N., C. Andrié, Y. Dandonneau, G. Reverdin and M. Rodier (1994). New production constrained by air-sea exchange, temperature effects, the CO_2 distribution in the equatorial Pacific in January-March 1991. *Journal of Geophysical Research*, **99**, C6, 12639-12654.

Mook W.G., J.C. Bommerson and W.H. Staverman (1974). Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planetary Science Letters*, **22**, 169-176.

Murnane R.J. and J.L. Sarmiento (1993). On the relative importance of biology and air-sea exchange for surface ocean $\partial^{13}C$ *in*: 4th International Conference CO_2, World Meteorological Organization Global Atmospheric Watch (Carquairanne, France, 13-17 September 1993), 208-211.

Philander G.S. (1990). *El Niño, La Niña and the Southern Oscillation.* Academic Press, San Diego, California, 289 p.

Quay P.D., B. Tilbrook and C.S. Wong (1992). Oceanic uptake of fossil fuel CO_2 : carbon-13 evidence. *Science*, **256**, 74-78.

Rau G.H., R.E. Sweeney and I.R. Kaplan (1982). Plankton $^{13}C/^{12}C$ ratio changes with latitude: differences between northern and southern oceans. *Deep Sea Research*, **29**, 1035-1039.

Rau G.H., T. Takahashi and D.J.D. Marais (1989). Latitudinal variations in plankton $\partial^{13}C$: implications for CO_2 and productivity in past oceans. *Nature*, **341**, 516-518.

Reverdin G., A. Morlière and G. Eldin (1991). *Alizé 2, campagne océanographique trans-Pacifique (janvier-mars 1991). Recueil des données.* Rapport interne LODYC 91/13 , 341 p.

Tans P.P., J.A. Berry, R.F. Keeling (1993). Oceanic $^{13}C/^{12}C$ observations : a new window on ocean CO_2 uptake. *Global Biogeochemical Cycles*, **7**, 2, 353-368.

Tans P.P., T.J. Conway and T. Nakazawa (1989). Latitudinal distribution of the sources and sinks of atmospheric carbon dioxide derived from surface observation and an atmospheric transport model. *Journal of Geophysical Research*, **94**, D4, 5151-5172.

Wyrtki K. (1981). An estimate of Equatorial Upwelling in the Pacific. *Journal of Physical Oceanography*, **11**, 1205-1214.