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REEVALUATION OF THE OCEANIC FLUX OF METHANE : UNCERTAINTIES AND LONG TERM VARIATIONS

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ABSTRACT

Recently published data enable a better evaluation of the methane flux injected into the atmosphere from the ocean surface. Only 3.5 Mt per year are ascribed to the open ocean. However emissions from particularly methane rich areas could be considerably more important.

The open ocean source, being practically proportional to the supersaturation of the surface sea waters, should vary with the atmospheric mixing ratio. Therefore, the open ocean could rapidly become a sink for an atmospheric mixing ratio of the order of 2.25 ppmv. In contrast, the oceanic source was significantly more important during the last glacial maximum, at 15,000 B.P., reaching up to 50 % of the total source. This strongly supports the existence, both during ice ages and today, of intense shallow submarine sources and / or gas seepages.

1. INTRODUCTION

Whereas numerous workers have attempted to evaluate the continental sources of methane, its oceanic source is still poorly documented. Only Ehhalt (1974), using pionneer measurements by Lamontagne et al (1973), mentioned in its methane budget an oceanic source of 4.7 to 20.7 Tg a^{-1} (open ocean 4-6.7 ; shelf 0.7-14). This early evaluation was subsequently used by several authors without careful re-examination (Khalil and Rasmussen, 1983 ; Cicerone and Oremland, 1988). More recently, the model of Fung et al. (1991), once again, used Ehhalt's values but without "carrying out 3D simulations for scenarios of several methane sources and sinks that are extremly poorly known ... These include oceans ...".

2. OCEANIC FLUX EVALUATION

Very few measurements of methane concentration are available from near-surface seawaters, which would enable a true oceanic flux evaluation. To our knowlege, only 93 near-surface values can be taken into account. These are listed in Table 1 and summarized in figure 1. They include unpublished measurements by Bonsang et al. (1991, personal communication). As shown in Table 1 (bracketed data), a large number of measurements were made in the Gulf of Mexico, which is heavily contaminated by oil and natural gas, as well as in special areas such as coastal shallow waters and areas of high biological activity such as the Black Sea. Focusing only on open ocean samples (n = 62), we estimate a mean methane concentration of about 56 * 10^{-9} liter of gas STP per liter of sea water (standard deviation 18 * 10^{-9} l / l).

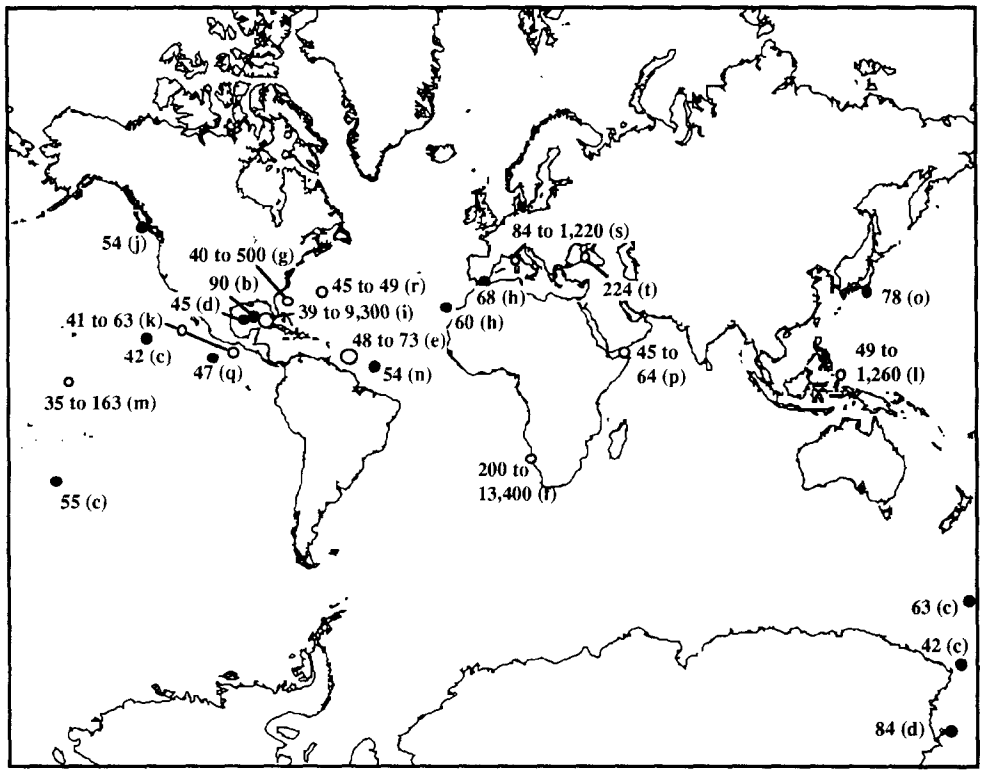

Figure 1. Methane concentrations in surface seawaters, expressed in 10^{-9} liter of gas STP per liter of seawater. References are listed in Table 1.Dots indicate the site of the measurement ; open circles correspond to a series of measurements. The letter correponds to the reference (Table 1).

Table 1. Methane concentrations in surface waters. The calculated values give the saturation concentrations of surface seawaters corresponding to the atmospheric mixing ratios, and to sea water temperatures and salinities. They were obtained by multiplying the atmospheric mixing ratio by B, the Bunsen solubility coefficient. R is the ratio of the measured to calculated dissolved gas concentrations, the latter being based on the assumption that equilibrium conditions prevail at the air - sea interface.

Area	Reference	atmos. CH_4 * ppmv	seawater CH_4 nl/l	B** ml/l	calcul. CH_4 nl/l	R
	a. Lamontagne et al (1973)					
W. tropical N. Atlantic		1.40	40			1.30
E. tropical N. Pacific			47			1.30
Norwegian-Greenland Sea			64			1.40
Greenland Ice Pack			86			1.30
Sargasso Sea			43			1.30
Caribbean Sea			43			1.40
Gulf of Mexico			53			1.60
Mediterranean sea			53			1.30
E. Medit. Sea			50			1.30
Arabian Sea			52			1.70
Red Sea			48			1.70
Black Sea			79			1.80
Cariaco Trench			49			1.50
	b. Brooks et al (1974)					
28°32N - 93°24W	May 74	1.46	90	26.6	39	2.32
Pacific	c. Lamontagne et al (1974)					
20°N - 129°W	Nov. - Dec. 72	1.42	42	28.0	40	1.05
30°S - 163°W		1.42	55	31.0	44	1.25
60°S - 177°E		1.42	63	43.1	61	1.03
70°S - 175°E		1.42	42	43.7	62	0.68
	d. Sackett and Brooks (1975)					
23°46N - 96°58W (0)	Jan. 72	1.42	45	24.8	35	1.28
23°46N - 92°39'W	June 71	1.41	45	24.8	35	1.29
77°10S - 172°06E (0m)	Feb. 72	1.42	84	49.0	70	1.21
28°11N - 92°41W (0m)	Oct. 73	1.45	50	24.3	35	1.42
W. subtropical N. Atl.	e. Scranton and Brewer (1977)					
19°02N - 65°59W (1m)	Feb. 75	1.47	56	24.8		1.75
18°59N - 61°16W (1m)			53	24.9		1.64
18°59N -58°41W (1m)			70	25.0		2.15
18°59N - 52°28W (6m)			48	25.0		1.48
19°22 N - 50°48W (10m)			54	25.4		1.65
16°10 N - 56°13W (5m)			48	24.9		1.49
15°17 N - 58°50W (5m)			53	24.2		1.67
12°44'N - 60°39 W (4m)			73	24.3		2.31
Walwis Bay (S.W. Africa)	f. Scranton and Farrington (1977)					
23°S - 12/14°E	Dec. 75	1.47	[13400]	30.8	45	295.87
		1.47	[200]	30.2	44	4.51
	g. Brooks (1979)					
transect from Mississipi Delta	Nov. 77	1.51	[500]	28.8	43	11.51
to N.W.Caribbean Sea		1.51	[40]	28.8	43	0.92
	h. Traganza et al (1979)					
Gibraltar Straits (0m)	June 77	1.52	68	29.2	44	1.53
Capo Verde (0m)		1.52	60	26.5	40	1.49

Table 1. Continued.

Area	Reference	atmos. CH_4 * ppmv	seawater CH_4 nl/l	B** ml/l	calcul. CH_4 nl/l	R
Gulf of Mexico	i. Brooks et al (1981)					
27°34N-96°07W (0m)	1977	1.50	[83]	27.2	41	2.03
27°17N-95°45W (0m)		1.50	[81]	26.4	40	2.05
27°17N-92°57W (0m)		1.50	[57]	27.2	41	1.40
27°01N-91°16W (0m)		1.50	[56]	26.2	39	1.43
27°33N-90°07W (0m)		1.50	[54]	26.6	40	1.35
28°03N-89°50W (0m)		1.50	[1100]	27.8	42	26.40
28°30N-89°41W (0m)		1.50	[9300]	27.4	41	226.11
28°09N-91°06W (0m)		1.50	[209]	27.3	41	5.10
27°55N-93°06W (0m)		1.50	[70]	27.8	42	1.68
27°28N-94°28W (0m)		1.52	[39]	23.7	36	1.08
27°28N-94°44W (0m)		1.52	[47]	23.7	36	1.30
27°12N-94°28W (0m)		1.52	[49]	23.7	36	1.36
27°20N-94°36W (0m)		1.52	[46]	23.6	36	1.28
28°05N-89°22W (0m)		1.52	[48]	23.6	36	1.34
N-E Pacific	j. Lilley et al (1982)					
48°36N - 123°30W (0m))	June 78	1.52	54	26.9	41	1.31
	Aug. 78	1.52	54	26.9	41	1.31
E tropical N Pacific	k. Burke et al (1983)					
25°N - 118°W (0m)	April 1979	1.54	52	29.0	45	1.17
22°N - 118°W (1m)		1.54	41	28.2	43	0.95
18°N - 118°W (1m)		1.54	63	26.2	40	1.56
15°N - 115°W (1m)		1.54	57	25.4	39	1.46
13°N - 111°W (1m)		1.54	50	24.4	38	1.33
9°N - 107°W (0m)		1.54	41	24.2	37	1.10
7°N - 97°W (0m)		1.54	49	24.1	37	1.32
8°N - 97°W (1m)		1.54	56	24.3	37	1.50
Pacific (Celebes Basin)	l. Belviso et al (1987)					
5°22N - 123°27E (5m)	Nov. - Dec. 84	1.62	[1260]	27.0	44	28.79
5°00N - 125°12E (5m)		1.62	[287]	27.0	44	6.56
5°23N - 126°01E (5m)		1.62	[155]	27.0	44	3.54
5°18N - 125°52E (210m)		1.62	[56]	27.0	44	1.27
6°07N - 126°36E (5m)		1.62	[49]	27.0	44	1.12
6°27N - 127°39E (5m)		1.62	[325]	27.0	44	7.42
N.W. Pacific	m. Gamo et al (1987)					
18°54N - 155°14 W (72 m)	Sept. 85	1.64	78	25.6	42	1.86
18°54N - 155°16W (99 m)		1.64	163	26.4	43	3.76
18°47N - 155°33W (0)		1.64	35	24.9	41	0.86
18°47N - 155°33W (10)		1.64	38	24.9	41	0.93
Mid-Atlantic Ridge	n. Charlou et al (1988)					
12°24'N - 44°05'W (10m)	Feb.- March 85	1.69	56	25.6	43	1.29
13°47'N - 44°59 W (12m)		1.69	54	25.6	43	1.25
14°05N - 45°01 W (10m)		1.69	42	25.6	43	0.97
N.W. Pacific	o. Gamo et al (1988)					
34°59'N - 139°13 E (2m)	Feb. 88	1.67	78	21.7	36	2.15
Gulf of Aden	p. Jean-Baptiste et al (1990)					
11°52N -43°15E (6m)	June 87	1.67	61	22.4	37	1.63
12°04N - 43°54E (7m)		1.67	64	22.4	37	1.71
13°35N - 47°51E (17m)		1.67	45	22.5	37	1.20
12°43N - 48°44E (9m)		1.67	58	22.5	37	1.55
13°07N - 49°32E (4m)		1.67	53	22.5	37	1.41
13°15 N - 50°17E (54m)		1.67	59	22.5	37	1.57

Table 1. Continued

Area	Reference	atmos. CH_4 * ppmv	seawater CH_4 nl/l	B** ml/l	calcul. CH_4 nl/l	R
Est Pacific	q. Charlou et al (1991)					
12°49N-103°56W (10m)	Dec. 86	1.66	48	23.7	39	1.22
12°55N-103°59W (3m)		1.66	47	24.3	40	1.16
12°49N-104°29W (51m)		1.66	43	23.5	39	1.10
S.E. Sargasso Sea	r. Jones (1991)					
27°N - 73°W (0m)	June 86	1.66	49	27.9	46	1.07
27°N - 73°W (0m)	Sept. 86	1.66	45	27.9	46	0.97
27°N - 73°W (0m)	June 87	1.67	45	27.9	47	0.96
N.W. Mediterranean Sea	s. Bonsang et al (perso. comm.)					
43°36N-7°29E (5m)	Oct. 89	1.71	[230]	28.2	48	4.77
43°36N-7°29E (35m)		1.71	[117]	30.4	52	2.25
43°36N-7°29E (5m)	May 90	1.73	[84]	26.9	46	1.81
43°36N-7°29E (15m)		1.73	[168]	29.0	50	3.35
43°36N-7°29E (0m)	May 90	1.73	[1220]	26.9	46	26.25
43°36N-7°29E (15m)		1.73	[118]	29.0	50	2.35
Black Sea	t. Reeburgh et al (1991)					
43°05N-34°00E (0m)	June 88	1.69	[224]	29.0	49	4.57

* Khalil and Rasmussen (1990) ; ** Yamamoto et al (1976)

It may be also observed in Table 1 that almost all superficial seawaters in the open ocean are supersaturated relative to the atmospheric methane mixing ratio. The frequency distribution in Figure 2 shows that the most frequent supersaturation value is of the order of 1.3.

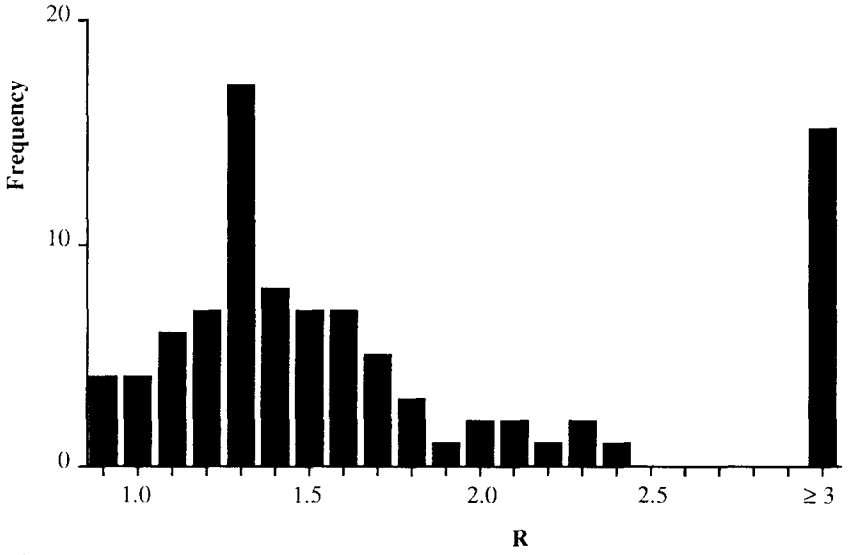

Figure 2. Frequency distribution of methane supersaturation of surface waters. R is the ratio of the measured to calculated dissolved gas concentration. * : supersaturation from 3 to 296

Therefore, as expected, open ocean surface waters should be a source of methane to the atmosphere. Owing to the relatively constant supersaturation of the sea surface, a flux calculation may be tentatively undertaken using the average piston velocity (PV) calculated for CO_2 sea-air exchange, which is of the order of 13 cm hr^{-1} (Etcheto et al., 1991; Heiman and Monfray, 1991). This value has to be slightly corrected for the Schmidt numbers (Sc) for CO_2 and CH_4 according to Kanakidou (1988) :

$$[PV]_{CH_4} / [PV]_{CO_2} = [Sc_{CH_4} / Sc_{CO_2}]^{-1/2} = [553 / 610]^{-1/2} = 0.95$$

With this correction, the open ocean methane flux is :

$$\Phi_{\text{open ocean}} = [\,56 - 56/1.3\,] * 10^{-9} * 10^{3} * [13 * 10^{-2} * 0.95] * 8{,}760 * 3.6\,10^{14} * 16/22.4$$

l / l l / m^3 m / hr hr /a m^2 g / l(gas)

$$= 3.6 * 10^{12}\ g\ a^{-1}$$

We next examine methane emissions from coastal areas that represent about 7 % of the ocean total surface. As mentioned previously, their methane content is generally considerably higher than in the open ocean (Scranton and Farrington, 1977). Assuming a mean seawater concentration of methane of 200 nl of gas per liter (see Table 1), and a piston velocity of the order of 26 cm hr^{-1} (instead of 13, because of breaking waves), we find:

$$\Phi_{\text{coastal}} = \Phi_{\text{open ocean}} * 0.07 * [(200-56/1.3) / (56-56/1.3)] * 26 / 13$$

$$= 6.1 * 10^{12}\ g\ a^{-1}$$

The total oceanic flux of methane could therefore be about $10 * 10^{12}$ g a^{-1}

It is interesting that this last figure does not differ appreciably from most of the values used in preceding methane budgets, including the figure adopted by Fung et al (1991). This ocean flux, being almost 2 % of the total source of methane, is therefore negligible at the present time. However, it was shown by Hovland et al. (1991) that a considerable flux of methane is also emitted from shallow submarine sources such as gas seepages. Large bubbles of this gas would be able rapidly to reach the ocean surface, without being oxidized nor consumed by methanotrophic bacteria. According to these authors, this flux could be as high as $72 * 10^{12}$ g a^{-1}, and could therefore contribute significantly to the total methane budget. Moreover, as pointed out by these authors, this methane is likely to be depleted in ^{14}C, which could account for the isotopic measurements of Lowe et al. (1988) and Whalen et al. (1989). Nevertheless, this evaluation is still not supported by sufficient experimental data.

3. FLUX VARIATIONS EXPECTED IN THE FUTURE

It is clear that the methane enrichment of surface sea waters due to gas seepage from the ocean bottom does not depend on the expected changes in the atmospheric mixing ratio. In the same way, as long as oceanic circulation and biological productivity are unchanged, methane emissions from coastal areas should be practically constant. In contrast, the methane flux from the open ocean is driven by the supersaturation coefficient of the surface sea water, that is the difference between the air and water partial pressures. Assuming that the superficial water concentrations remain approximately constant, even though the atmospheric mixing ratio increases, the supersaturation will decrease in the future, as suggested by Cicerone and Oremland (1988). The linear variation of the oceanic flux versus the atmospheric mixing ratio is shown in Figure 3. For a value of about 2.25 ppmv, the oceanic source would be cancelled ; for higher mixing ratios, the ocean becomes a methane sink instead of a source.

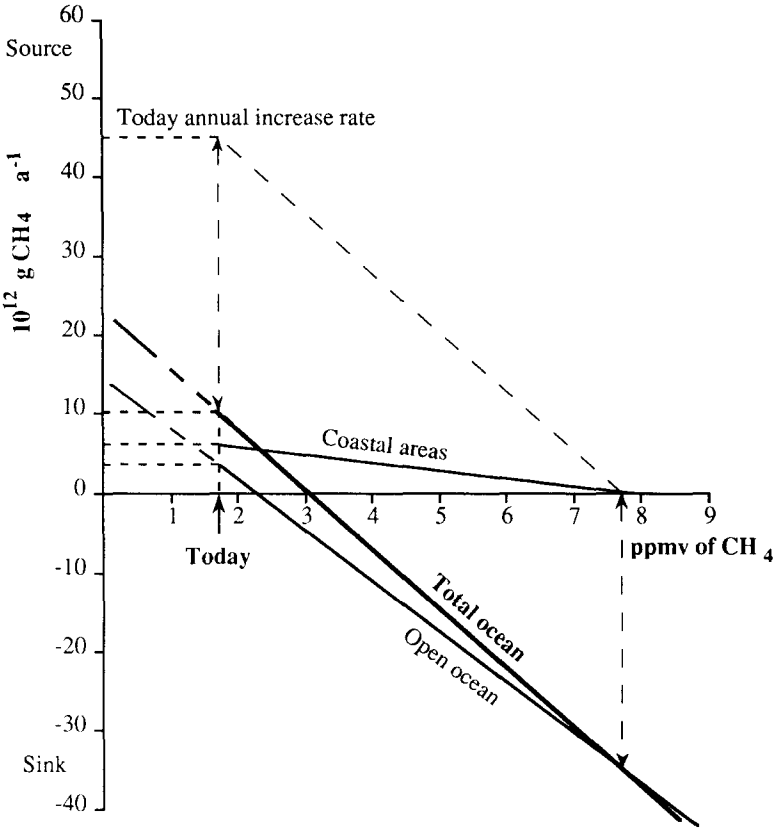

Figure 3. Variation of the methane oceanic sink versus atmospheric mixing ratio

If the preceding hypotheses were valid, and all the methane sources except the open ocean kept their present values, corresponding to the present rate of increase of about 45 * 10^{12} g a^{-1}, as the methane mixing ratio reaches about 8 ppmv the oceanic sink could compensate for the anthropogenic source, resulting in a spontaneous stabilization of the atmospheric reservoir (at an unrealistic level).

4. METHANE FLUX DURING THE LAST GLACIAL PERIOD

It was shown by Chappellaz et al (1990) that the atmospheric mixing ratio of methane was considerably lower during the last glacial maximum at 15,000 B.P. Ice core studies suggest a value of 0.35 ppmv. Assuming the same methane residence time in the atmosphere as today and a present source of approximately 460 * 10^{12} g a^{-1}, this mixing ratio would correspond to a total flux :

$\Phi = 460 * 10^{12} * 0.35 / 1.7 = 95 * 10^{12}$ g a^{-1}

However, as suggested by Valentin (1990) and Valentin and Crutzen (1990) from atmospheric modelling, such an evaluation should probably take into account a shorter life time for methane of 5.5 years (instead of 10.5).

The preceding flux evaluation should therefore be corrected as follows :

$$\Phi_{\text{total, glacial period}} = \frac{95 * 10^{12}}{5.5 / 10.5} = 180 * 10^{12} \text{ g a}^{-1}$$

This last value is in agreement with the value of $150 * 10^{12}$ g a^{-1} of Nisbet (1990).

A simple extrapolation of the relationship between the oceanic flux and the atmospheric pool would lead, from Figure 3, to an oceanic flux of $20 * 10^{12}$ g a^{-1}. However, this value must be corrected for two opposing effects. First of all, at this time sea level was about 100 m lower than today. Consequently, the surface of the coastal areas was practically zero, and we should only consider the flux from degassing in the open ocean. The sea surface temperature was not significantly lower than today, especially in the tropical zones (COHMAP, 1988). On the other hand, there is evidence that the wind velocity was significantly higher (COHMAP, 1988), leading to an average piston velocity of the order of 20 cm hr^{-1} instead of 13 cm hr^{-1}. We can therefore calculate an oceanic flux of :

$$\Phi_{\text{open ocean, glacial period}} = 3.6\ 10^{12} * \frac{56 - \left[\frac{56}{1.3} * \frac{0.35}{1.7}\right]}{56 - \frac{56}{1.3}} * \frac{20}{13}$$

$$= 20 * 10^{12} \text{ g a}^{-1}$$

The flux from the open ocean was then at least 10 % of the total flux to the atmosphere instead of 2 % today.

In the absence of anthropogenic sources, the continental glacial emission of $160 * 10^{12}$ g a^{-1} should be mainly ascribed to the soils of rain forests and natural wetlands. This is significantly higher than the evaluations by Matthews and Fung (1987) and Aselmann and Crutzen (1989) of 110 and $80 * 10^{12}$ g a^{-1}, respectively at the present time. At present, wetlands and bogs in northern forests between 50° and 70° N contribute about 60 % of the total emission from natural wetlands (Matthews and Fung, 1987). Taking into account the low temperatures at continental surfaces, and consequently the lower than present emission rates, the preceding flux evaluations would imply the existence, during glacial periods, of wetland areas about three times larger than now. This seems to be in complete disagreement with most of the data and simulation models, which show that the climate of glacial periods was particularly dry (Guiot et al., 1989 ; Bonnefille et al., 1990). Moreover most of the region between 50° and 70°N was under ice or in the zone of permafrost. Globally the wetland emission of methane may have been much reduced during glacial times, perhaps around $40 * 10^{12}$ g a^{-1} (Nisbet, 1990). We are therefore led to conclude that the oceanic methane source was much higher than 10 %. The difference could be attributed to these shallow submarine sources and gas seepages proposed by Hovland et al.(1991).

5. CONCLUSION

The fluxes of methane between the open ocean and the atmosphere are generally small in comparison with all the other sources of this gas. However, they are far from being constant. Particularly, at the present atmospheric increase rate, the modern open ocean source could become a sink in a matter of 20 years.

The origin of methane at the surface of the open ocean is still an open question. However, the very simple (and rough) hypothesis of a sea surface concentration not significantly modified by climatic changes implies that, either the surface area of wetlands was considerably larger during ice ages than generally admitted, or the oceanic source accounted for about half of the methane emissions. This strongly supports the existence, during ice ages

and therefore today, of intense shallow submarine sources and/or gas seepages, as proposed by Hovland et al. (1991). The total oceanic source of methane is therefore likely to be of the order of 50 to 60 * 10^{12} g a^{-1}, of which only 3 or 4 * 10^{12} g a^{-1} would be emitted from open ocean. This could account for the ^{14}C depletion of atmospheric methane, and partly for the rather similar variations of CH_4 and CO_2, as observed in ice cores by Chapellaz et al. (1990).

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