Production and transport of methane in oceanic particulate organic matter

David M. Karl* & Bronte D. Tilbrook†

* School of Ocean and Earth Science and Technology, Department of Oceanography, University of Hawaii, Honolulu, Hawaii 96822, USA
† CSIRO, Division of Oceanography, Hobart, Tasmania 7001, Australia

METHANE **is an important component of the global carbon cycle[1] and a potent greenhouse gas[2,3]. Surface ocean waters are typically supersaturated with dissolved methane relative to atmospheric equilibrium, presumably as a result of *in situ* microbial methane production[4–8]. Because methanogenic bacteria are strict anaerobes[9] and surface ocean waters are highly oxygenated, the observation of methane supersaturation has been termed the 'oceanic methane paradox'[10]. Although methanogenic bacteria have been isolated from oceanic particulate matter, faecal pellets and zooplankton[11–14], no data are available on *in situ* rates of methane formation in these microenvironments. During a series of experiments in the North Pacific ocean, we have identified a previously unrecognized component of the oceanic methane cycle. We find that methane is associated with sinking particles, presumably as a dissolved constituent of the interstitial fluids of particulate biogenic materials, which exchanges with the water column as particles sink. This phenomenon provides a mechanism for the active transport in the water column of an otherwise passive, dissolved species. The particle-to-seawater methane flux that we measure is sufficient to replace all of the methane present in the upper water column in about 50 days and to produce the characteristic methane supersaturations in less than a month. We suggest that particulate production and transport may also be relevant to the redistribution and cycling of other bioreactive compounds in the marine environment.**

Experiments were performed at five North Pacific ocean stations during cruises of the Vertical Transport and Exchange (VERTEX) and Asian Dust Inputs to the Oceans (ADIOS) research programmes. Two coastal (both at 35.8° N, 122.6° W), one transition (33.3° N, 139.1° W) and two oceanic (35.1° N, 128.2° W and 26° N, 155° W) sites were occupied during this study. Water samples were collected in 10-litre Niskin bottles using standard CTD-rosette (conductivity–temperature–depth) procedures. Subsamples were analysed for dissolved methane concentrations[15], and for a variety of biogeochemical parameters some of which are presented elsewhere[16,17]. Sinking particles were collected using MULTITRAP arrays[18], with replicate cylindrical (length 60 cm, inside diameter 7 cm) sediment traps positioned at five or six discrete depths between 50 and 1,500 m depending on the site. Before deployment, each trap was filled with an autoclaved brine solution consisting of 27.1 g NaCl, 11.4 g $MgCl_2 \cdot 6H_2O$ and 0.74 g KCl per litre of filtered (0.22 μm) surface sea water to provide a final salinity approximately equal to twice that of the surrounding sea water. The brine is used to minimize diffusive loss of collected solutes and to prevent flushing of the traps during recovery. Replicate trap treatments were prepared with the addition of either buffered formaldehyde (0.1 M final concentration) or $HgCl_2$ (0.5 mM final concentration) to inhibit bacterial activity. From these experimental treatments we could distinguish between methane that entered the traps in association with the sinking particles (plus preservative) from methane production which might occur in the traps after particle collection (minus preservative). All sediment traps were deployed with 335-μm Nitex screens positioned at the base of the baffles. This effectively eliminated contamination by macrozooplankton which, if present, would have seriously compromised the experimental design and data interpretations. This screening procedure is known to cause an approximately 65% decrease in particle collection efficiency[19] and, obviously, selects against large particles that are more likely to contain diffusion-limited anaerobic microhabitats. Consequently, our data on particle-associated methane in the ocean should be taken as a conservative estimate for total transport by this mechanism. The downward flux of 'particulate' methane at each specific reference level in the ocean (expressed in units of nmol m^{-2} d^{-1}) was calculated from data on the methane concentration in the sediment-trap brine solution (nmol), the cross-sectional area of the sediment trap (0.0039 m^2) and the deployment period (d).

Results indicate that large amounts of methane accumulate in the sediment traps during deployments in both coastal and oceanic habitats (Table 1). The primary conclusion from these field experiments is that dissolved methane is a common constituent of the interstitial fluids of sinking particles in the ocean and that methane partitions into the trap solution phase following particle collection. Adsorption of methane to, and subsequent desorption from, solid-phase particulate constituents cannot be ruled out as another mechanism of transport but seems less likely. A comparison of preserved (formaldehyde or $HgCl_2$) with unpreserved control treatments supports our conclusion that methane is associated with the particles when they entered the traps, and is not an artefact of post-collection organic matter decomposition (Table 1).

The observed methane fluxes were largest in the near-surface waters and decreased with increasing water depth (Table 1 and

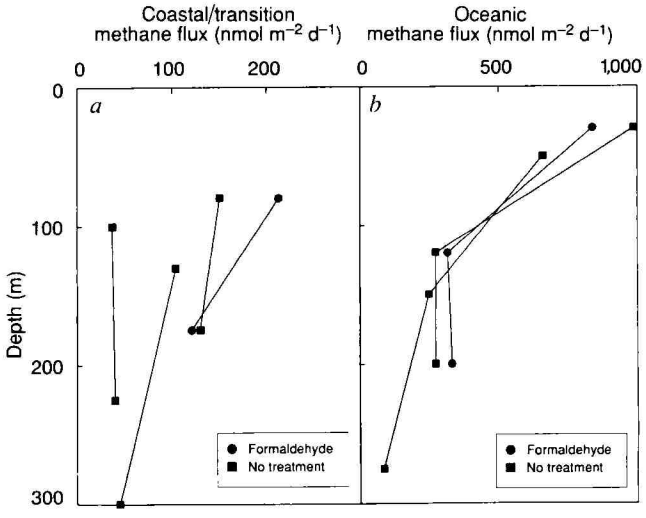


FIG. 1 Methane fluxes as a function of depth, for coastal/transition regions (*a*) and oceanic habitats (*b*). The data shown are for paired sediment traps deployed with or without formaldehyde (0.1 M final concentration) as a preservative. The exact station locations are given in Table 1. Both the magnitude of the methane fluxes and the flux divergence are greater in the oceanic regions.

TABLE 1 Representative coastal and oceanic downward 'particulate' methane and particulate carbon fluxes for the north Pacific ocean

Location, date and depth (m)	Deployment period (d)	Preservative added	Trap methane accumulation* (nmol per trap)	'Particulate' methane flux (nmol m^{-2} d^{-1})	Particulate carbon flux (mmol C m^{-2} d^{-1})	Carbon-specific methane flux (nmol CH_4 $mmol^{-1}$ C)
Coastal (35.8° N, 122.6° W; June 84)	13					
100		None	1.9	36.9	4.1	9
225		None	2.1	40.2	2.1	19
Coastal (35.8° N, 122.6° W; May 85)	12					
80		Formaldehyde	11.2, 8.9†	214	5.7 (±0.6)	38
		$HgCl_2$	7.9	169	—	—
		None	7.1 (±1.4)‡	151 (±31)	4.8(±1.3)	31
175		Formaldehyde	5.6, 5.8	122	3.0 (±0.2)	41
		$HgCl_2$	7.0	149	—	—
		None	6.1 (±0.2)	131 (±5)	2.3 (±0.6)	57
Transition (35.1° N, 128.2° W; June 84)	22					
130		None	9.0	105	1.51	70
300		None	3.9	45.6	0.51	89
Oceanic (33.3° N, 139.1° W; June 84)	22					
50		None	56.6	660	—	—
150		None	21.4	250	0.99	252
275		None	7.3	85.2	0.65	131
Oceanic (26° N, 155° W; April 86)	3.1					
30		Formaldehyde	10.1	836	1.19	703
		None	11.9	984	—	—
120		Formaldehyde	3.8	315	1.59	198
		None	3.3	272	—	—
200		Formaldehyde	4.0	331	0.75	441
		None	3.3	271	—	—

* Total methane accumulations were corrected for the time zero system blank, which was determined either by measuring methane concentrations in the trap solutions just before deployment, or by measuring methane concentrations in traps deployed on the same *in situ* array but at much greater depths (600–1,500 m) where the influence of surface methane production and particle-associated transport would be expected to be minimal. The latter system blank was determined to be 5.2 (s.d. ± 1.1; $n = 14$) nmol CH_4 per l of trap solution and did not vary with depth or deployment period.

† Values are from duplicated sediment traps deployed at a common depth.

‡ Mean ±1 s.d. of the mean for triplicate sediment traps deployed at a common depth.

Fig. 1). These data suggest a euphotic zone particulate methane source, an observation which is consistent with empirical models for the flux of total organic matter[16,20]. Preservative-containing sediment traps deployed in both coastal and oceanic regions at depths greater than approximately 500 m failed to accumulate methane. These results suggest that the methane production process is probably a surface ocean phenomenon. Bacterial methane oxidizers are known to inhabit the upper water column[21], and they may be a major sink for the particle-associated methane. Gas exchange with the atmosphere may also be an important sink for methane, especially in areas with large surface ocean supersaturations or deep surface ocean mixed-layers.

Both the magnitude of the observed methane enrichments and the depth-dependent flux patterns varied considerably among the study areas. The estimated methane fluxes in the coastal environments were lower than the open ocean stations, in spite of the much greater flux of particulate carbon inshore (Table 1). The calculated 'carbon-specific methane fluxes' for all regions investigated varied by nearly two orders of magnitude among sites with highest values in the open ocean habitats. Subsequent sediment-trap experiments conducted in surface waters of both coastal (Gerlache strait) and oceanic (Bransfield strait) regions of Antarctica during December 1986–January 1987 (ref. 22), failed to detect any particle-associated methane in spite of an order of magnitude range in particulate carbon fluxes (up to 30 mmol C m^{-2} d^{-1}). Therefore, we must conclude that the processes controlling the surface water methane production and flux are geographically variable and probably result from an unique mechanism of particle formation rather than from particle formation *per se*.

As particles sink, the depth-dependent loss of methane is also greater for the oceanic stations (Fig. 1). Methane may be lost from the particle fluids by diffusion, net oxidation or particle disaggregation. From our data we cannot distinguish among these potential sinks, but we currently favour the diffusive loss pathway. If we assume a value of 200 nmol CH_4 $mmol^{-1}$ C to be a representative estimate of the carbon-specific methane production rate for open ocean habitants (Table 1), then the daily net production of methane in the upper 200 m of the water column by this mechanism could approach 0.01 mmol m^{-2}. This estimate must be considered to be conservative because we have not included the likely possibility of particle recycling (that is, production and destruction) within the surface ocean that could also release additional methane. However even this minimum estimate for the production of methane is sufficient to replace all the methane in the upper ocean in approximately 50 days. The methane supersaturations typically observed in the open ocean (~20%, relative to atmospheric equilibrium) could easily be produced in less than one month. Consequently, this hypothesized particle-to-water column flux of methane could be the primary pathway for methane formation in the upper water column.

We hypothesize that methane is formed in zooplankton guts and enters the sinking particle field through the process of faecal pellet formation. The geographical variations seen in total and carbon-specific methane fluxes can be explained either by regional differences in zooplankton species or, more likely, by metabolic differences attributable to food availability. In the food-poor oceanic habitats, the length of time required for gut passage is increased and anaerobic decomposition is more likely to occur than under food-replete grazing conditions[23]. The structural integrity of the faecal pellets is likewise affected by feeding rates, favouring the formation of pellets more likely to be mechanically disrupted under periods of food limitation. The ecological predictions of a higher carbon-specific methane content and greater particle-to-water column flux in oligotrophic marine habitats are both supported by our field observations. The decrease in methane production at all locations with increasing water depth is believed to be a reflection of the more general phenomenon of decreased particle production processes[16] and metabolic activity[24] observed elsewhere, but this does not rule out the existence of deep production of methane by this or similar mechanisms.

Our present finding that sinking particles can maintain an interstitial fluid composition that may be different from the surrounding sea water suggests that other dissolved compounds and elements may also have pathways of production and transport analogous to those described here for methane. Among these

are other potentially deleterious greenhouse gases such as nitrous oxide and dimethyl sulphide. Furthermore, buoyant rising particles[25,26] may also effect a flux of dissolved materials to the ocean's surface and thus serve to accelerate the ocean-to-atmosphere transfer of certain gaseous constituents. □

Received 31 August 1993; accepted 7 March 1994.

1. Martens, C. S. in *Microbial Growth on C_1 Compounds* (eds Crawford, R. L. & Hanson, R. S.) 276–281 (Am. Soc. for Microbiology, Washington DC, 1984).
2. Tyler, S. C. in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes* (eds Rogers, J. E. & Whitman, W. B.) 7–38 (Am. Soc. for Microbiology, Washington DC, 1991).
3. Cicerone, R. J. & Oremland, R. S. *Global Biogeochem. Cycles* **2,** 299–327 (1988).
4. Brooks, J. M., Reid, D. F. & Bernard, B. B. *J. geophys. Res.* **86,** 11029–11040 (1981).
5. Burke, R. A. Jr, Reid, D. F., Brooks, J. M. & Lavoie, D. M. *Limnol. Oceanogr.* **28,** 19–32 (1983).
6. Lamontagne, R. A., Swinnerton, J. W., Linnenbom, V. J. & Smith, W. D. *J. geophys. Res.* **78,** 5317–5324 (1973).
7. Scranton, M. I. & Brewer, P. G. *Deep-Sea Res.* **24,** 127–138 (1977).
8. Traganza, E. D., Swinnerton, J. W. & Cheek, C. H. *Deep-Sea Res.* **26,** 1237–1245 (1979).
9. Boone, D. R. in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes* (eds Rogers, J. E. & Whitman, W. B.) 57–70 (Am. Soc. for Microbiology, Washington DC, 1991).
10. Kiene, R. P. in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes* (eds Rogers, J. E. & Whitman, W. B.) 111–146 (Am. Soc. for Microbiology, Washington DC, 1991).
11. Bianchi, M., Marty, D., Teyssie, J.-L. & Fowler, S. W. *Mar. Ecol. Prog. Ser.* **88,** 55–60 (1992).
12. Sieburth, J. McN. in *Microbes in the Sea* (ed. Sleigh, M. A.) 11–38 (Ser. in Mar. Sci., Ellis Horwood, Chichester, 1987).
13. Oremland, R. S. *Limnol. Oceanogr.* **24,** 1136–1141 (1979).
14. Marty, D. G. *Limnol. Oceanogr.* **38,** 452–456 (1993).
15. Swinnerton, J. W. & Linnenbom, V. J. *J. Gas Chromatogr.* **5,** 570–573 (1967).
16. Martin, J. H., Knauer, G. A., Karl, D. M. & Broenkow, W. W. *Deep-Sea Res.* **34,** 267–285 (1986).
17. Laws, E. A., DiTullio, G. R., Betzer, P. R., Karl, D. M. & Carder, K. L. *Deep-Sea Res.* **36,** 103–120 (1989).
18. Knauer, G. A., Martin, J. H. & Bruland, K. W. *Deep-Sea Res.* **26,** 97–108 (1979).
19. Karl, D. M. & Knauer, G. A. *Oceanogr. Mag.* **2,** 32–35 (1989).
20. Pace, M. L., Knauer, G. A., Karl, D. M. & Martin, J. H. *Nature* **325,** 803–804 (1987).
21. Sieburth, J. McN. *et al. Curr. Microbiol.* **14,** 285–293 (1987).
22. Karl, D. M., Tilbrook, B. D. & Tien, G. *Deep-Sea Res.* **38,** 1097–1126 (1991).
23. Dagg, M. J. & Walser, W. E. Jr, *Limnol. Oceanogr.* **31,** 1066–1071 (1986).
24. Karl, D. M. & Knauer, G. A. *Deep-Sea Res.* **31,** 221–243 (1984).
25. Smith, K. L. Jr, Williams, P. M. & Druffel, E. R. M. *Nature* **337,** 724–726 (1989).
26. Grimalt, J. O., Simoneit, B. R. T., Gomez-Belinchon, J. I., Fischer, K. & Dymond, J. *Nature* **345,** 147–150 (1990).

ACKNOWLEDGEMENTS. This paper represents contribution 3540 from the School of Ocean and Earth Science and Technology.