

OCEANOGRAPHY

Making methane

Most of the world's surface oceans are oversaturated with respect to atmospheric methane and emit large quantities of this greenhouse gas. Aerobic decomposition of phosphorus-containing organic compounds may be responsible.

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Without greenhouse gases such as methane the Earth would be a frozen wasteland¹. But in the context of global climate change, the rising atmospheric methane concentrations observed in recent decades have become a cause for concern. In order to predict future concentrations of atmospheric methane, scientists have gone to great lengths to understand the global methane budget — including the unenviable task of measuring gaseous methane emissions from cattle². One focus of these investigations has been the oceans, a supplier of vast quantities of methane to the atmosphere³. Why methane concentrations in the oxygen-rich surface waters of most of the world's oceans are so high has remained a puzzle, as methane production is thought to occur in strictly anaerobic environments. Contrary to these expectations, on page 473 of this issue, Karl and colleagues⁴ suggest that the net efflux of methane from ocean to atmosphere is driven by aerobic methane production, fuelled by the microbial breakdown of phosphorus-containing compounds called phosphonates.

Phosphonates are organic compounds characterized by a direct carbon–phosphorous bond, unlike the more complex carbon–oxygen–phosphorous linkages found in most phosphorus-containing biomolecules. Although ubiquitous in marine organisms, phosphonates typically comprise only a very small percentage of total marine phosphorus. In fact, biochemical pathways that cycle phosphonates in the ocean are highly unusual, and may be relicts of ancient metabolic processes⁵. When provided with a selection of phosphorus-containing compounds, most microorganisms will preferentially use other types of organic phosphorus over phosphonate. But

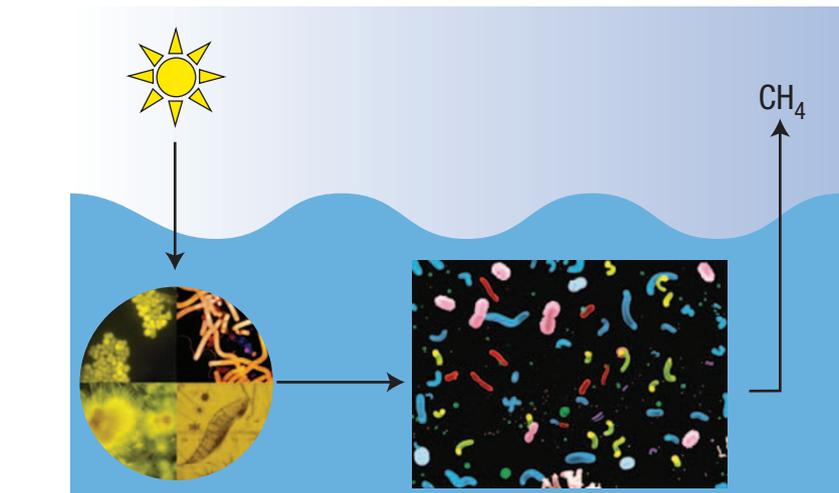


Figure 1 Methane production in the upper ocean. Sunlight fuels the growth of photosynthetic organisms, which support the growth of marine biota (represented by circle). Upon decomposition, photosynthetic and non-photosynthetic biota feed into the oceanic phosphonate pool. Aerobic bacteria (represented by rectangular box) use methylphosphonate — a particular type of phosphonate — to grow, producing methane (CH_4) as a by-product.

microbes do not always have access to a rich and varied buffet of phosphorus-containing compounds. In nutrient-poor regions of the ocean, for example, it seems likely that microorganisms rely on phosphonates for their phosphorus supply. Indeed, recent research has shown that nitrogen fixers, a particular class of organisms that live in nutrient-poor ocean environments and convert atmospheric nitrogen into biologically usable forms, have the ability to use phosphonates⁶.

The physiological capacity to produce methane using phosphonates is present in some bacteria⁷. Phosphonates could therefore explain why methane concentrations in the surface ocean vastly exceeding levels predicted by basic biological and chemical principles. The fact that the escape of this methane into the atmosphere fails to restore equilibrium suggests continual replenishment from a local source. This source could be conventional anaerobic methanogenesis in oxygen-depleted microhabitats, such as the guts of animals or the insides of

particles suspended in the sea water, or unconventional methanogenesis via some unrecognized pathway which is compatible with the oxic ocean surface^{8,9}.

Karl *et al.* show that microbial breakdown of phosphonates can produce methane in aerobic marine environments, providing evidence for unconventional methanogenesis. They use a series of seawater incubation experiments to demonstrate that marine bacteria are capable of using methylphosphonate (MPn), the simplest form of phosphonate, as their sole source of phosphorus. They show that this aerobic decomposition converts MPn to methane at a one-to-one ratio. The decomposition of MPn, and thus the production of methane, was less efficient in the presence of inorganic phosphorus, and more efficient in the presence of increased concentrations of nitrate. Karl *et al.* suggest that even a small fraction of organic phosphorus cycling through methylphosphonate would be more than enough to sustain methane supersaturation in the upper oceans.

The connections between methane cycling and nitrogen and phosphorus availability could have significant climatic implications⁴. Nitrogen and phosphorus play a key role in determining the growth of marine organisms at the bottom of the food chain, and the availability of these nutrients in the upper ocean is largely controlled by the upwelling of nutrient-rich waters from the deep ocean. Mixing between surface and deep-ocean layers is predicted to decrease as a result of greenhouse-gas induced global warming, making nutrient limitations more likely in surface waters. According to Karl and colleagues, this increased nutrient limitation could promote the use of phosphonates by marine microbes, and thus methane production, in a warmer world.

Whether methane production driven by phosphonate decomposition

can fully account for methane supersaturation in the surface of the world's oceans depends on the supply of low-molecular-weight phosphonate compounds, such as methylphosphonates, to marine organisms that can use them. Recent oceanographic studies suggest that phosphonates are indeed found in the low-molecular-weight fraction of dissolved organic matter¹⁰. This finding nicely supports the idea presented by Karl and colleagues that simple compounds like methylphosphonate constitute a potential source of phosphonates for the methane production reaction.

The methane production mechanism proposed by Karl and colleagues could, in principle, operate over vast stretches of the global ocean. But only future research can determine the contribution of this

mechanism, and the positive feedback it implies, to the evolution of global climatic change.

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CLIMATE SCIENCE

Of sun and ice



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In September 2007, Arctic sea ice extent reached a new record low that undercut the previous minimum by 24%. The loss of northern ice was so substantial that it prompted Arctic researchers to speculate whether the ice cover had been tipped over the edge to deterioration. But the precise causes for the spectacular melting of 2007 are not clear.

One proposal, investigated by Axel Schweiger and colleagues (*Geophys. Res. Lett.* **35**, L10503; 2008), suggests that a persistent high-pressure

system lingering over the Arctic region from June to August 2007 may have led to unusually low cloud cover that could have exacerbated normal summer melt and contributed to the record low. However, as is so often the case in climate studies, the story turns out to be more complex.

Satellites recorded sufficiently low cloud cover over the Arctic that summer to warrant the conditions to be considered unusual, but the blue skies did not coincide with the areas where the ice cover vanished. Instead, the summer sunshine spread

across the northernmost Arctic Ocean, where sea ice was left intact even in 2007. Ice thicknesses decreased significantly in these northernmost regions in response to the sunny weather, although direct sunlight is not very effective at warming bright surfaces like sea ice — as anyone knows who has worn a black T-shirt and white trousers in the sun. But these ice losses did not count towards the record low because they were losses in thickness rather than ice-covered area.

The total contribution of clouds to the 2007 summer reduction in sea ice extent could be a different story. The Arctic ice ocean model used in Schweiger and colleagues' study simulates ice loss where it was observed — but as a consequence of cloudier skies. Although counterintuitive, this positive effect of cloud cover on ice melt can be explained through complex interactions between cloud cover, air temperature and humidity. However, the model does not fully include these interactions, leaving a full investigation of the contribution from clouds for future studies.

Clearly, blue skies are not to blame for the 2007 record low in sea ice extent. But the Arctic's sunny summer of 2007 could still contribute to the future prospects of the ice cover. The northernmost ice may have withstood the big melt of 2007, but thinner high-Arctic sea ice will be more vulnerable to further warming.

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