

Abstract

Methane is a potent greenhouse gas that has contributed approximately 20% of the enhanced radiative forcing since pre-industrial times. Despite its importance to Earth's climate, the global methane budget source terms are poorly constrained. Methane concentrations in the surface waters of most of the world's oceans are 5-75% supersaturated with respect to atmospheric methane concentrations, implying both a local *in situ* methane source and a net flux from the ocean to the atmosphere. However, marine methane production is thought to occur only in strictly anaerobic environments. Because the surface ocean is also saturated with respect to atmospheric oxygen, the as yet unexplained methane supersaturation has been termed the "oceanic methane paradox". We provide evidence for a previously unrecognized pathway for methane production in the sea. This pathway involves production of methane via the decomposition of methylphosphonate (MPn) as a phosphorus source for growth. The diazotroph, *Trichodesmium*, is one organism capable of growth and methane production via methylphosphonate metabolism. As such, this aerobic methane pathway is predicted to be climate sensitive and responsive to changes in water column stratification and nutrient limitation.

Atmospheric Methane

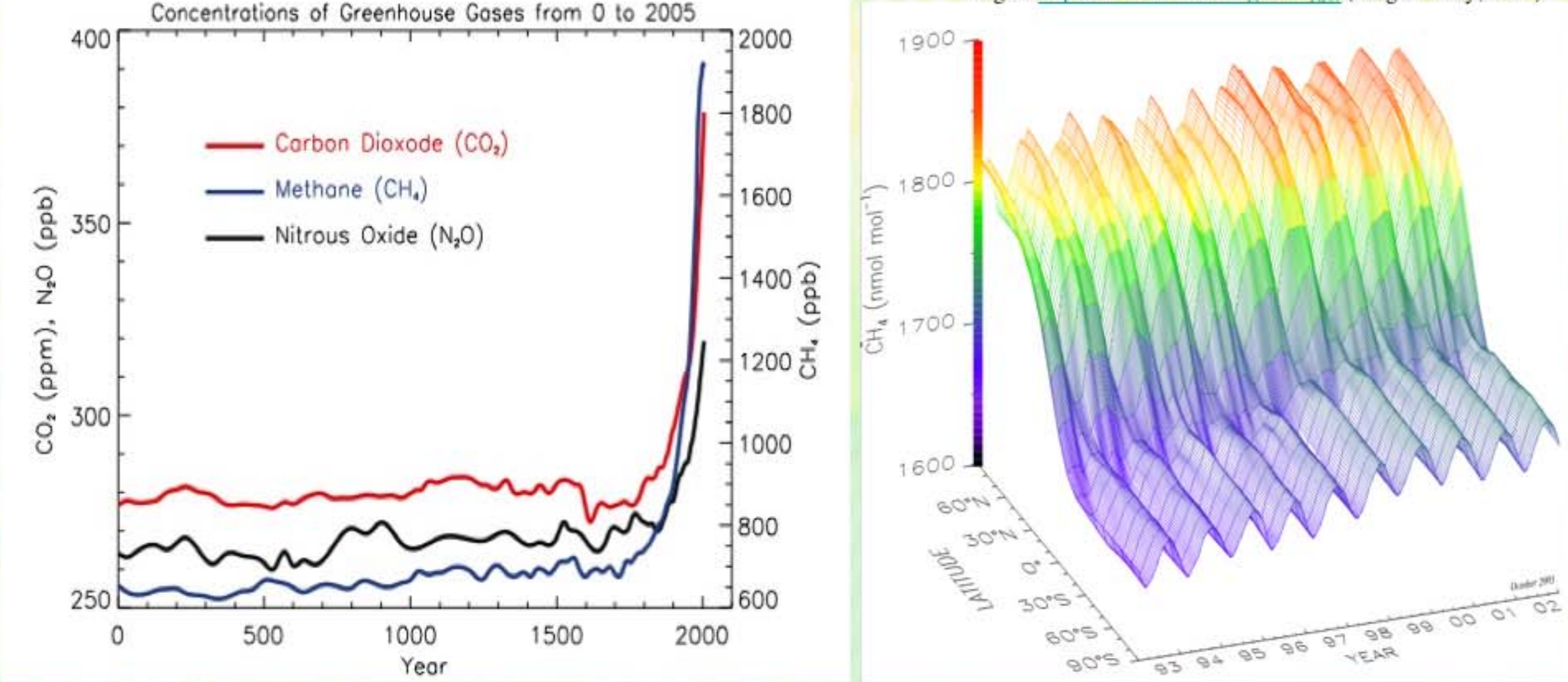


Figure 1: **Left:** Methane concentrations have increased exponentially since pre-industrial times. **Right:** The atmospheric methane burden continues to increase at ~1% per year. Slight changes in the sources and sinks can drastically affect methane concentrations in the atmosphere.

Source Terms and Production

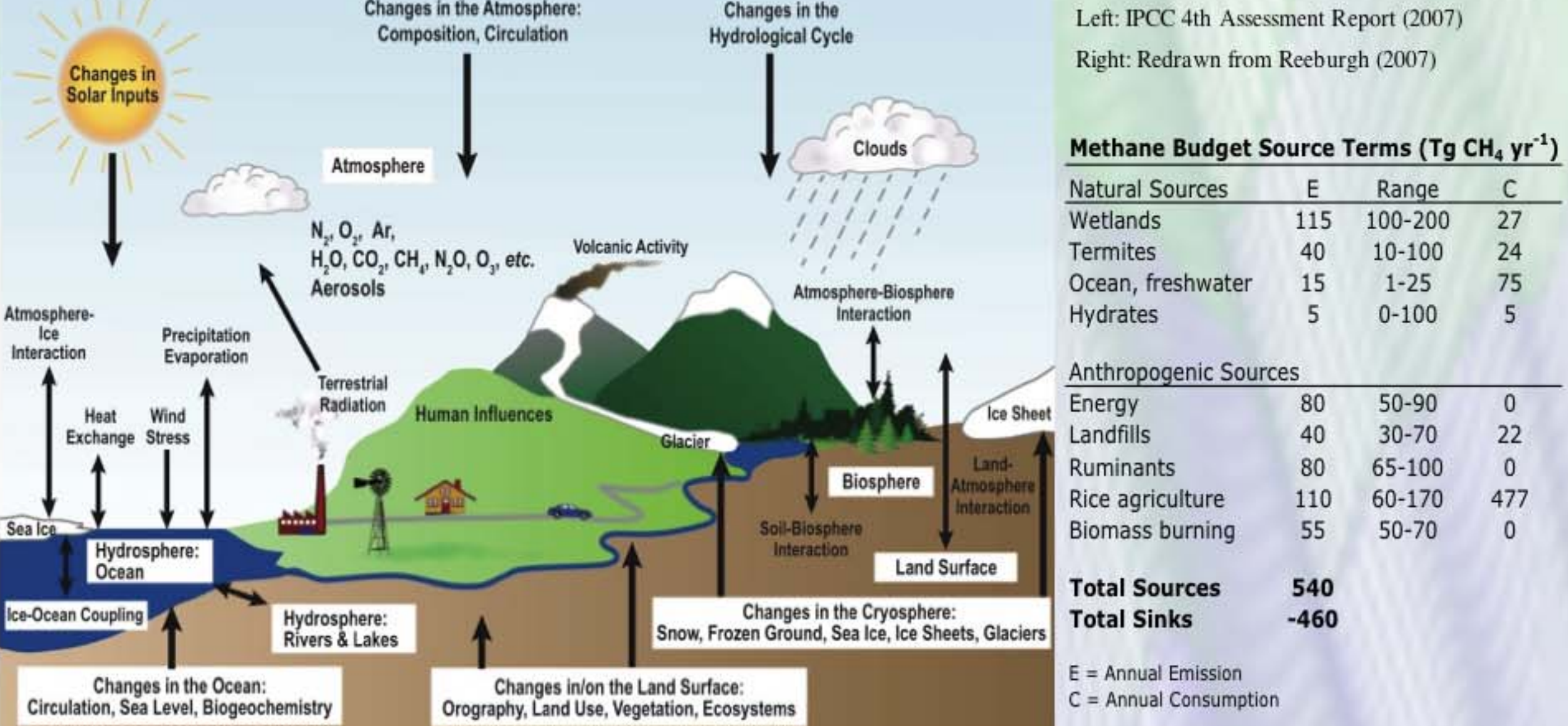
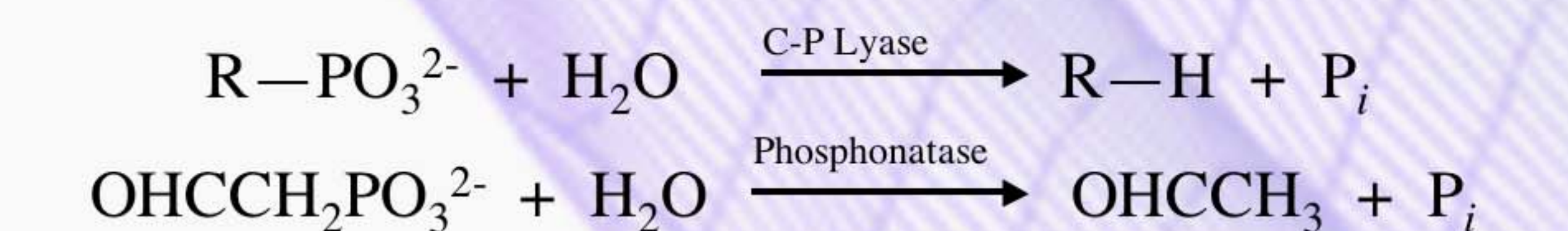


Figure 2: **Left:** Methane plays a major role in all global systems. It is mainly produced by methanogens. It is also produced thermogenically by the reduction of carbon dioxide at very high temperatures. The ultimate sinks for methane are the atmosphere and to a lesser extent, soil. **Right:** The source terms in the methane budget are poorly constrained and each constituent source term may differ by a factor of two or more.

Phosphonates

- Phosphonates are a poorly understood class of organic compounds characterized by a direct carbon-phosphorus (C-P) bond. Despite their potential to contribute to cellular growth, the role of phosphonates in the marine environment remains elusive.
- Various gram-negative bacteria have been shown to utilize MPn as a sole source of phosphorus. Utilization of MPn by these microorganisms results in the stoichiometric production of methane. Thus, MPn could be an important nutrient source to support the growth of microorganisms in P-limited ecosystems, and biological utilization of MPn may be directly linked to global methane fluxes.



Oceanic Methane Paradox

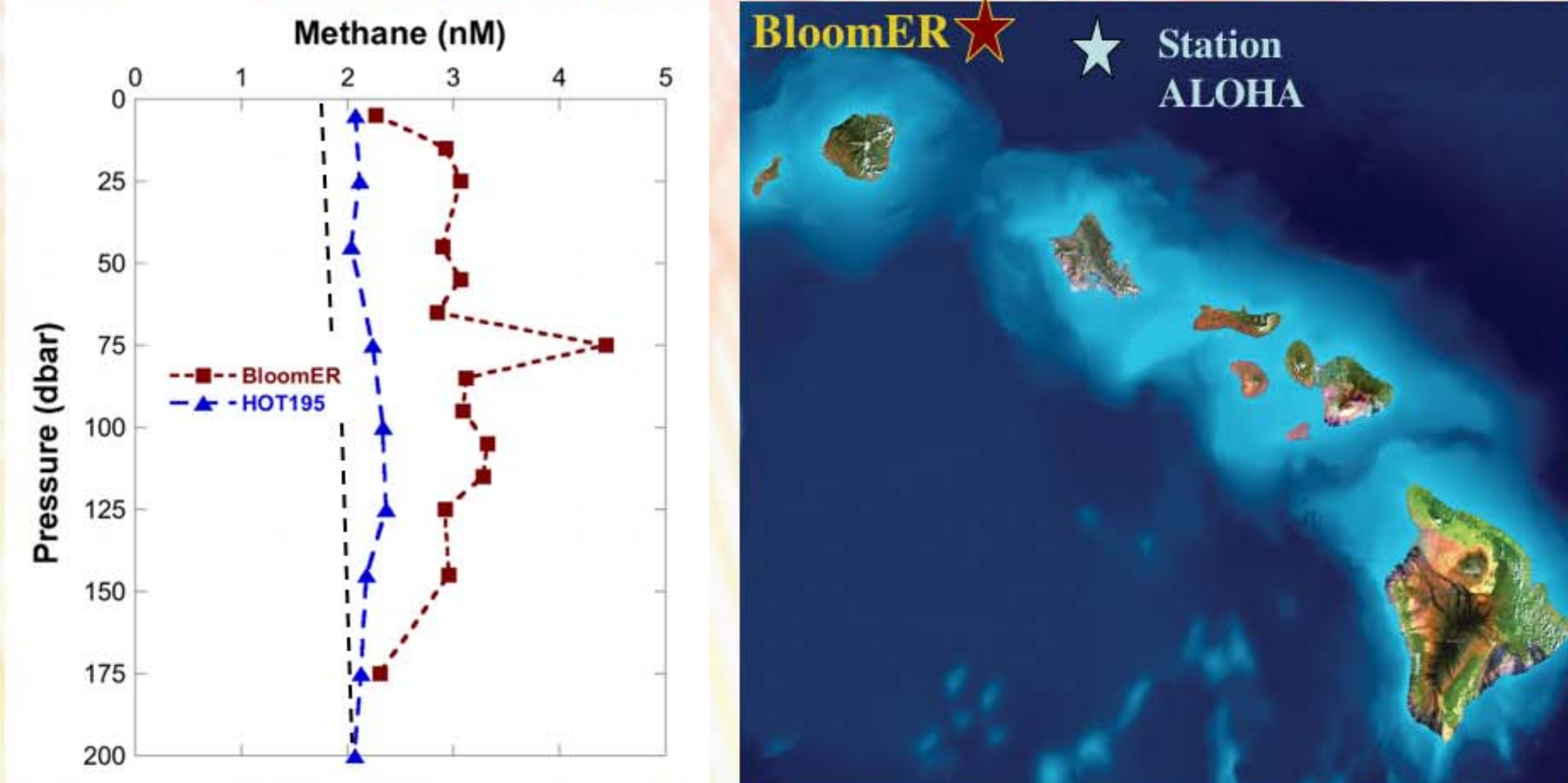


Figure 3: Methane is supersaturated in most of the world's surface ocean waters. Because the surface is well oxygenated and methane production is thought to occur in strictly anaerobic environments, this supersaturation has been termed the "oceanic methane paradox". **Left:** Depth profiles show that methane concentrations and flux to the atmosphere can vary greatly over small space and time scales. During a possible *Trichodesmium* bloom, methane concentrations were up to 150% greater than previously observed. **Right:** ALOHA 22°45' N, 158° W (September 2007) and BloomER 23° N, 159° W (August 2007)

Hypotheses

- Aerobic degradation of methylphosphonate is an important source of methane in the North Pacific Subtropical Gyre (NPSG).
- Intensification of phosphorus cycling and nitrogen fixation in the NPSG has stimulated an increase in the production/consumption of alternative dissolved organic phosphorus (DOP) such as phosphonates.
- Trichodesmium* will degrade MPn without C or N enrichment and produce methane, but production will be down-regulated by the addition of P_i .

Results

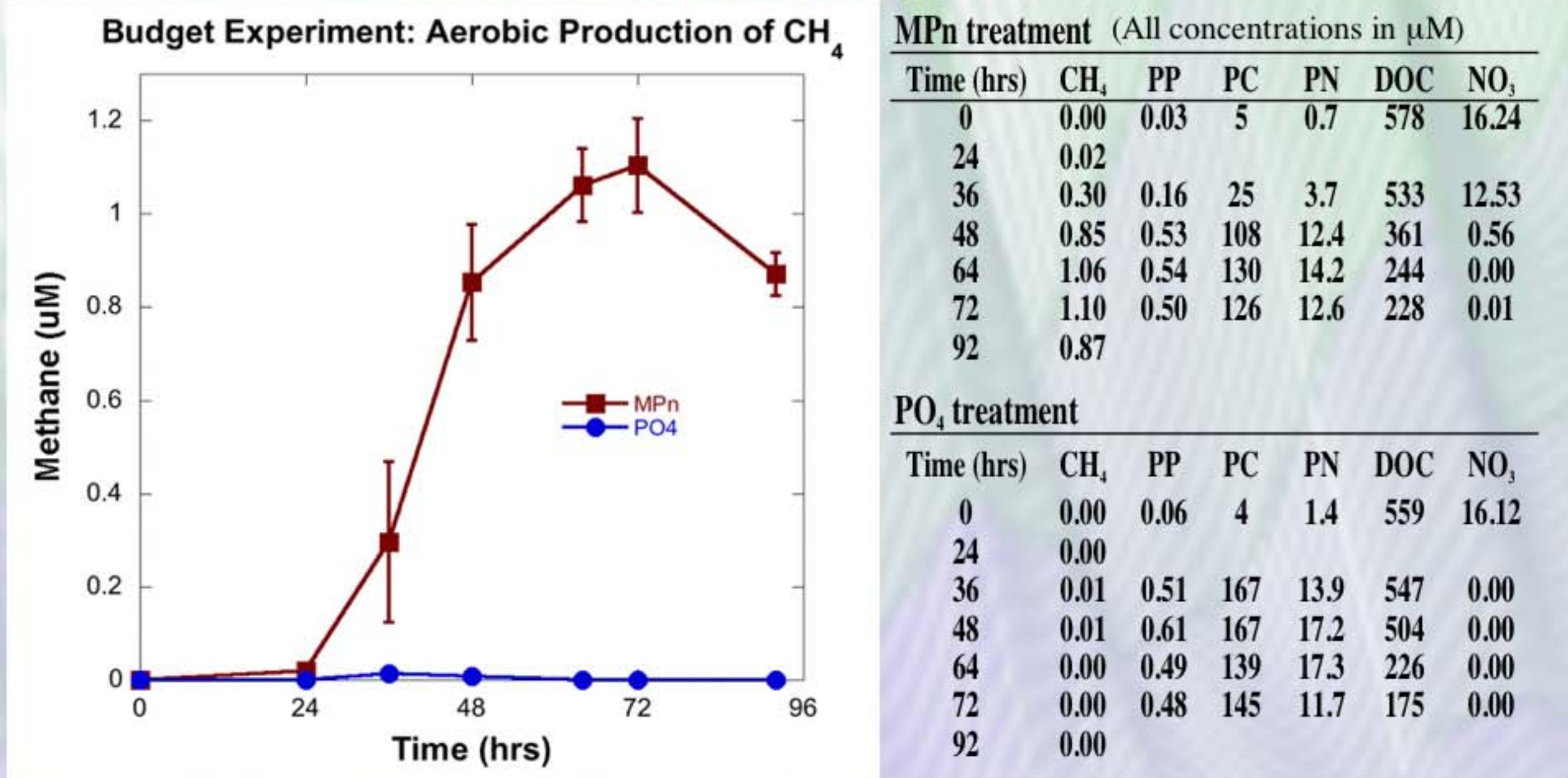


Figure 4: Results indicate the MPn is rapidly consumed under aerobic conditions and the rate of methane accumulation can be tracked through particulate matter that accumulates as biomass. No methane was produced in PO_4 incubations, nor was it produced in filtered seawater amended with MPn.

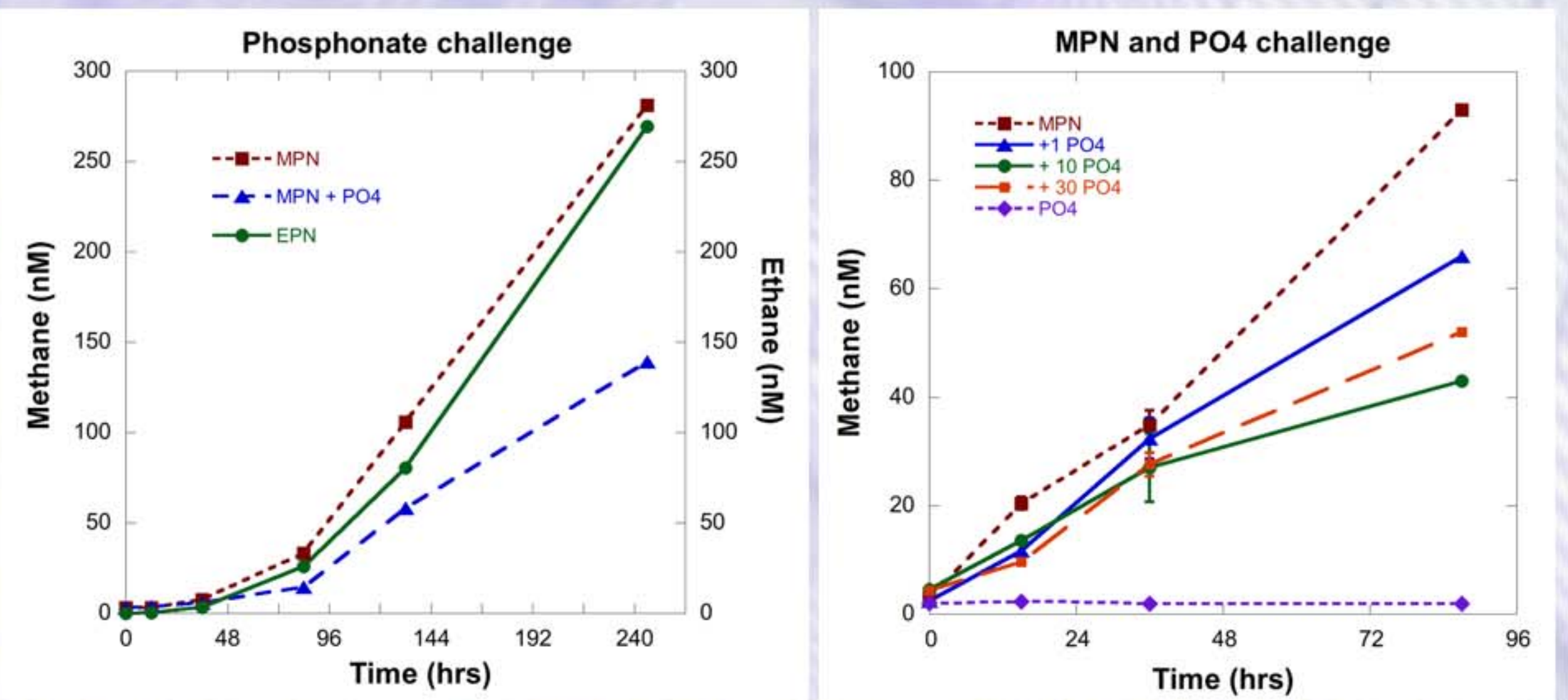


Figure 5: Phosphonate gene expression has been reported in the N. Atlantic Ocean and in laboratory cultures by the diazotroph, *Trichodesmium*. We incubated cultures of *Trichodesmium* IMS-101 amended with phosphonate as the sole source of phosphorus. **Left:** Cultures that were spiked with MPn started producing methane within the first 12 hours of incubation. Likewise, cultures that were spiked with ethylphosphonate (EPn) rapidly produced ethane. **Right:** While P_i did not inhibit MPn utilization, there was decreasing methane production with increasing amounts of P_i added.

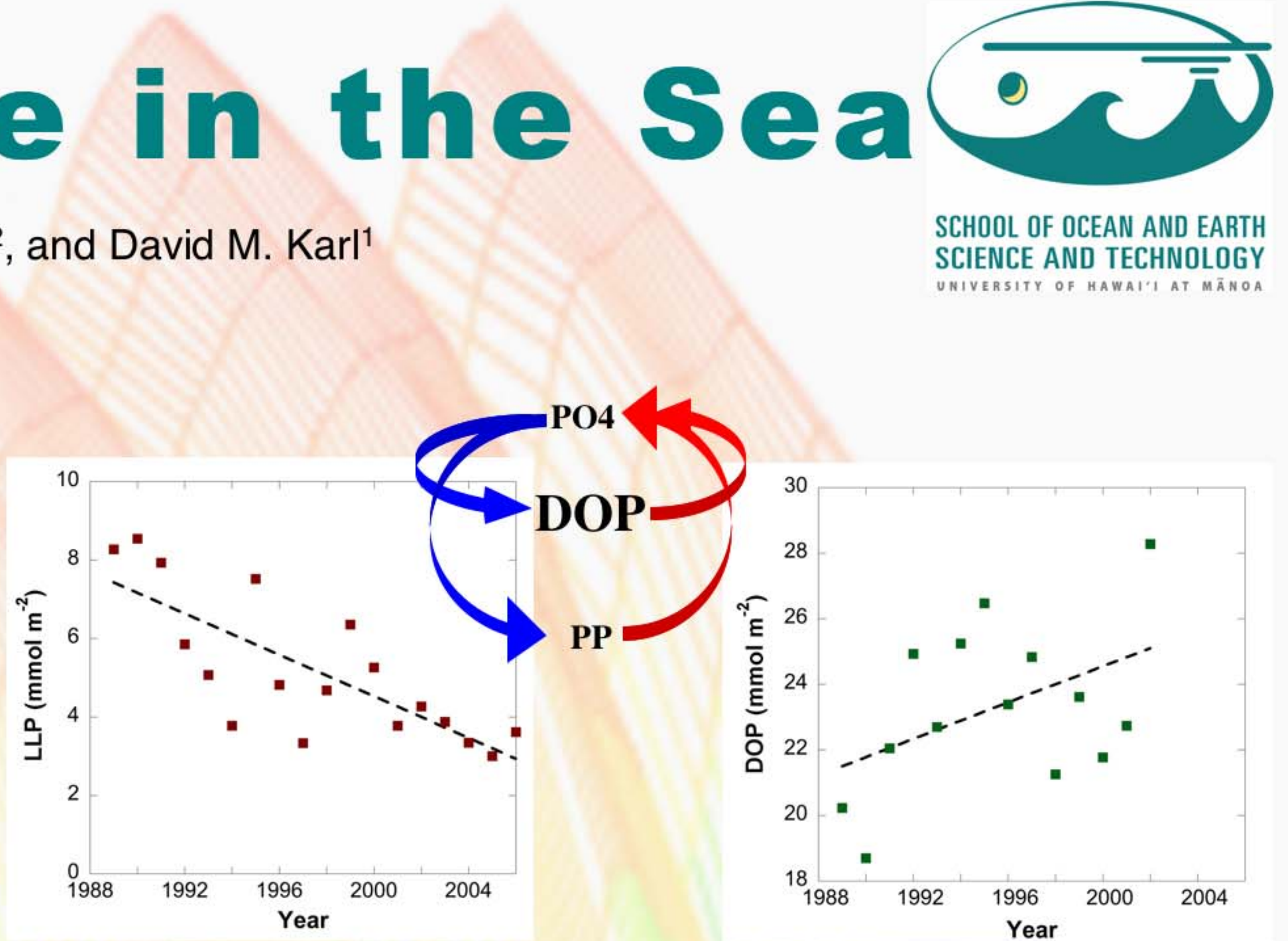


Figure 6: Depth integrated (0-100m) yearly averages of phosphorus concentrations. **Left:** Since 1988, there has been a decreasing trend in low level phosphorus (LLP) measurements. **Right:** Conversely, there is an increasing trend in dissolved organic phosphorus (DOP), which may be leveling off. This data suggests that the NPSG may have shifted to a phosphorus (P) limited system. In a P limited system, microorganisms may evolve to synthesize/consume DOP compounds such as phosphonates to gain a competitive advantage.

Discussion

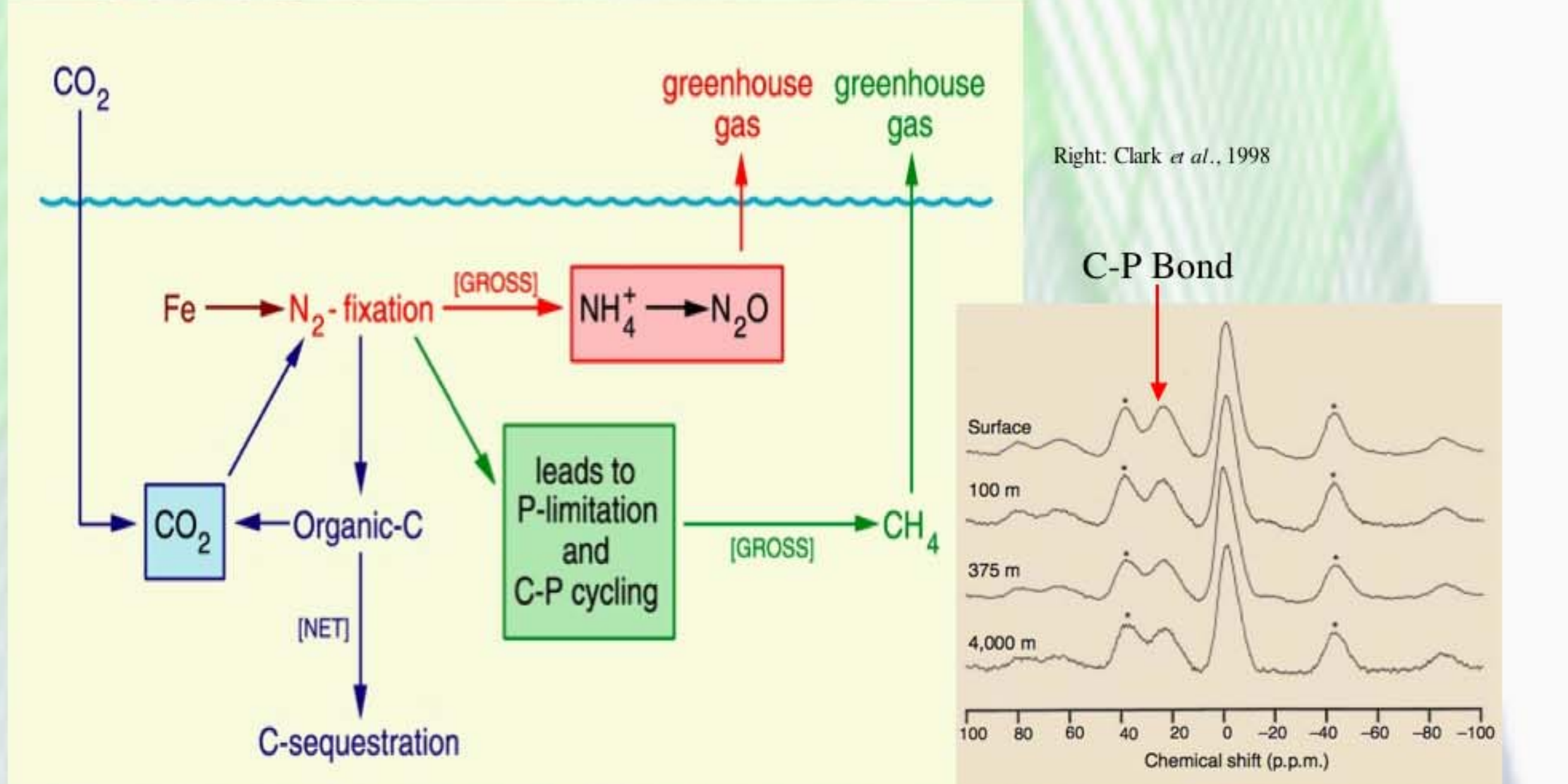


Figure 7: Our results demonstrate that phosphonate utilization may play an important role in surface ocean methane fluxes and may be the missing term in the "oceanic methane paradox". **Left:** Data from *Trichodesmium* experiments and phosphorus time series data (see above) show that MPn utilization and methane production may be climate sensitive and even induced by nitrogen fixation. **Right:** In NPSG surface waters, the high molecular weight DOP pool can contain up to 25% phosphonates. We estimate that if only 1-2% of this pool is recycled through MPn, the surface ocean methane supersaturation could be sustained.

Methods

- Seawater for most of the experiments was collected at the Hawaii Ocean Time-series (HOT) site, Station ALOHA (22°45' N, 158° W).
- Methane measurements were determined by headspace analysis, assuming a Bunsen coefficient of 0.024 for methane at 25°C and salinity 34‰, during timed incubations. Methane was quantified using a flame ionization detector (FID) gas chromatograph (GC) following adsorption onto a Porapak N column with a carrier flow rate of 25mL/min.
- Trichodesmium* experiments were performed at Oregon State University. Briefly, IMS-101 is grown in YBCII media in an environmentally controlled incubator on a 12:12 hour night:day cycle at 24°C.
- Gases were quantified using a purge column and cryogenic trap before being injected into a GC. Samples were purged with ultra-pure helium at a flow rate of 100mL/min, trapped onto Porapak Q submerged in liquid nitrogen, and then heated and injected into the GC, fitted with a Porapak N column, at a flow rate of 25mL/min.

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