



Phosphate oxygen isotope evidence for methylphosphonate sources of methane and dissolved inorganic phosphate

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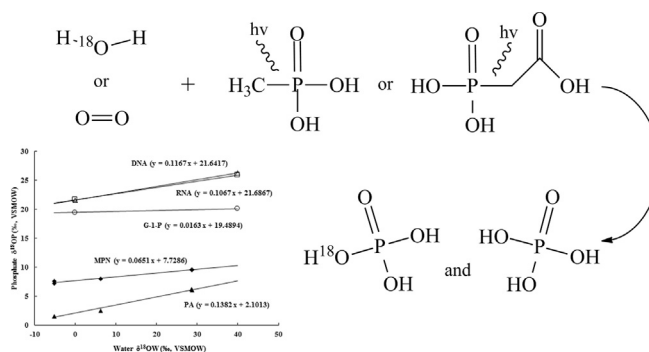
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HIGHLIGHTS

- Photo-degradation of MPn, a likely mechanism of methane release to the atmosphere.
- Multi-labeled water isotope probing approach was used to probe the C–P bond cleavage.
- Both ambient water and atmospheric O₂ involved during photo-degradation of MPn and PA.

GRAPHICAL ABSTRACT



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ABSTRACT

The ocean is an important source of methane, however, the sources of oceanic methane and mechanisms of its release to the atmosphere have only recently begun to be understood. Recent studies have identified methylphosphonate (MPn) as a previously unknown and likely source of methane in the aerobic ocean (Karl et al., 2008), as well as shown the biosynthesis of methylphosphonic acid to be a widespread trait in marine microbes (Metcalf et al., 2012). The mechanisms and reaction pathways from MPn to free methane, however, have not been well studied. Here we present results of laboratory studies on the photo-degradation of MPn, a likely mechanism of methane release to the atmosphere and phosphate release to the surface oceans. Phosphonoacetic acid was also studied as an additional model compound for comparison. We used the multi-labeled water isotope probing (MLWIP) approach, involving ¹⁸O-labeled waters to probe the photolytic mechanism of C–P bond cleavage in phosphates through analysis of P released from MPn as PO₄. These studies identified distinct reaction pathways involving phosphates compared with other common organophosphorus compounds (e.g., phosphoesters), as well as suggest the involvement of both ambient water and atmospheric oxygen in C–P bond cleavage. There is only a small amount of water oxygen incorporated into product PO₄ after cleavage of the C–P bond in MPn, suggesting atmospheric O₂ or radicals formed from O₂ under Ultra Violet Radiation (UVR), as the primary source of O that replaces C in the C–P bond of MPn. Model calculations suggest that the δ¹⁸O_P signature of phosphate released via UV-degradation of phosphates is largely (75%) inherited from the original phosphate substrate. This opens up the possibility of tracing and differentiating specific phosphate sources of dissolved phosphate from other

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organophosphorus (Porg) sources (e.g., phosphoesters) used in primary production, as well as for tracing specific MPn sources of atmospheric methane.

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1. Introduction

Methane is a potent greenhouse gas, its sources and sinks and emission from the oceans, play a key role in understanding the flow of carbon within the biosphere (Lamontagne et al., 1973; Metcalf et al., 2012; Quay et al., 1999; Reeburgh, 2007). Moreover, the methane cycle involves numerous important geologic reservoirs and phenomena including marine sediments, cold seeps, mud volcanoes, hydrothermal vents and methane clathrate deposits (Quay et al., 1999; Reeburgh, 2007). The surface ocean is generally supersaturated (5–75%) with methane, which indicates a net flux of methane from the oceans (Lamontagne et al., 1973; Rudd and Taylor, 1980; Scranton and Brewer, 1977; Tilbrook and Karl, 1995), however the mechanism of oceanic methane production is not well understood. Karl et al. (2008) hypothesized that methylphosphonate (MPn) metabolism is a major pathway of the production of methane in aerobic environments, based on incubation experiments where methane was emitted following the addition of MPn to natural microbial consortia in seawater. Aerobic methane accounts for a significant fraction (4%) of the global methane budget (Karl et al., 2008). In the uppermost euphotic zone of the ocean, UVR is also likely to play a role in the degradation of MPn and the release of methane to the atmosphere. Additionally, there is a potential for dissolved inorganic phosphate (PO_4 or Pi) release to surface waters via UV-induced phosphate degradation that has not been characterized. Metcalf et al. (2012) identified a specific marine archaeon, *Nitrosopumilusmaritimus*, that is capable of producing cell-associated methylphosphonate, and also found that biosynthesis of methylphosphonic acid is a widespread trait in marine microbes.

MPn is the most structurally-simple phosphate (Fig. 1a) and may be both a precursor to the more complex phosphate molecules and a partial degradation product thereof (Ilikchyan, 2009). In *Escherichia coli*, *Pseudomonas* and many other bacteria, MPn can be used as a sole source of phosphorus (P) during aerobic growth (Cook et al., 1978; Kononova and Nesmeyanova, 2002; White and Metcalf, 2007). Phosphonoacetic acid (PA) is also characterized by a carbon phosphorus (C—P) bond and relatively simple structure (Fig. 1b). It is used as an anti-viral agent and its congener 2-hydroxylphosphonoacetic acid is widely used as a scale and corrosion inhibitor in power plants and oil refill water systems. Thus, PA may have a significant environmental impact in selected systems (e.g., power plant runoff, waste discharge sites). Other anthropogenically-produced phosphates (e.g., the widely used herbicide glyphosate or Roundup™) are used in a wide range of applications and are discharged into the environment, imparting toxicity to aquatic biota and soil, as well as in marine environments and sediments (Paytan et al., 2003).

In aquatic systems, dissolved organic phosphate degradation occurs within the water column (Karl et al., 2008; Paytan and McLaughlin, 2007), thus, solar UV irradiation could play an important role in MPn degradation, especially at shallow depths. UV photons usually interact with reactant molecules to form radical species that stimulate attack on the phosphate C—P bond (Rusu and Yates, 2000), but the detailed mechanism for cleavage of the C—P bond still remains elusive (Xu et al., 2011). The multi-labeled water stable isotope probing (MLWIP) studies (e.g. Li et al., 2016; Liang and Blake, 2009) performed here, provide new insights into the C—P bond cleavage mechanism. A better understanding of C—P bond cleavage mechanisms under different conditions will help predict reactions of MPn in models of degradation and transport of MPn in natural environments.

In this study, we present results of experiments performed on the photo-degradation of MPn using multiple ^{18}O -labeled waters to probe the mechanism and kinetics of C—P bond cleavage and measurement of the oxygen isotopic composition of Pi ($\delta^{18}\text{O}_\text{P}$) released from MPn. We also studied PA as a model compound for comparison, with the goal of evaluating $\delta^{18}\text{O}_\text{P}$ as a tracer for phosphate sources and cycling in the environment. Additionally, we developed a simple model to calculate the O-isotope composition of the original phosphate source compound. Data presented here is an expansion of our previously published work on the UV degradation of phosphates, which focused primarily on the herbicide glyphosate (Sandy et al., 2013). The MLWIP approach used here to probe the C—P bond cleavage mechanism, has been widely applied by our group over the past decade and recently followed by others (Paudel et al., 2015; Sun et al., 2017; Wu et al., 2015) to study reaction pathways and P-cycling processes, and to provide insight into the enzymatic, microbial, photolytic and abiotic reaction mechanisms of several P compounds including: orthophosphate, pyrophosphate, phosphomonoesters, phosphodiester and phosphates.

2. Materials and methods

MPn and PA (Fig. 1) were obtained from Sigma-Aldrich and used to make experimental solutions which comprised phosphate dissolved in three different Pi-free ^{18}O -labeled waters.

2.1. Aqueous solution of MPn and PA with ^{18}O -labeled waters

Aqueous solutions of MPn and PA with concentrations selected to release between 50 and 150 μmol of Pi upon complete degradation, were prepared in 0.2 μm -filter sterilized Pi-free ^{18}O -labeled waters with measured O-isotope compositions ($\delta^{18}\text{O}_\text{W}$) of -5.1 , -5.2 , 6.1 and 28.6 , 28.7% (VSMOW). Low (400 W) and high (1200 W) intensity UV

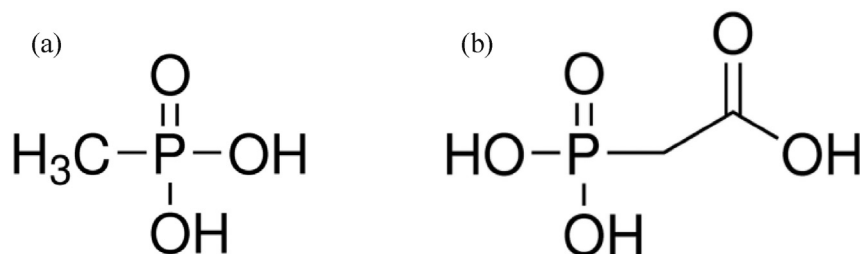


Fig. 1. Structural representation of (a) methylphosphonate (MPn) and (b) phosphonoacetic acid (PA).

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