

A DIURNAL CYCLE IN NEAR-SURFACE ATMOSPHERIC METHANE CONCENTRATION FROM MICROSEEPAGE AS CONSTRAINED BY TLS AND TGO J.E. Moores^{1,2}, P.L. King², C.L. Smith¹, G.M. Marinez³, C. Newman⁴, S. Guzewich⁵, P.-Y. Meslin⁶, S. Atreya³, C. Webster⁷, P. Mahaffy⁵ and A.C. Schuerger⁸,
¹Centre for Research in Earth and Space Science, York University, Toronto, ON M3J 1P3 Canada (jmoores@yorku.ca), ²Research School of Earth Sciences, Australian National University, Canberra, ACT, Australia, ³University of Michigan, Ann Arbor, MI USA, ⁴Aeolis Research, Pasadena, CA USA, ⁵NASA-Goddard Spaceflight Center, Greenbelt, MD, USA ⁶Université Paul Sabatier, Toulouse, France, ⁷NASA-Jet Propulsion Laboratory, Pasadena, CA, USA, ⁸Department of Plant Pathology, University of Florida, FL, USA.

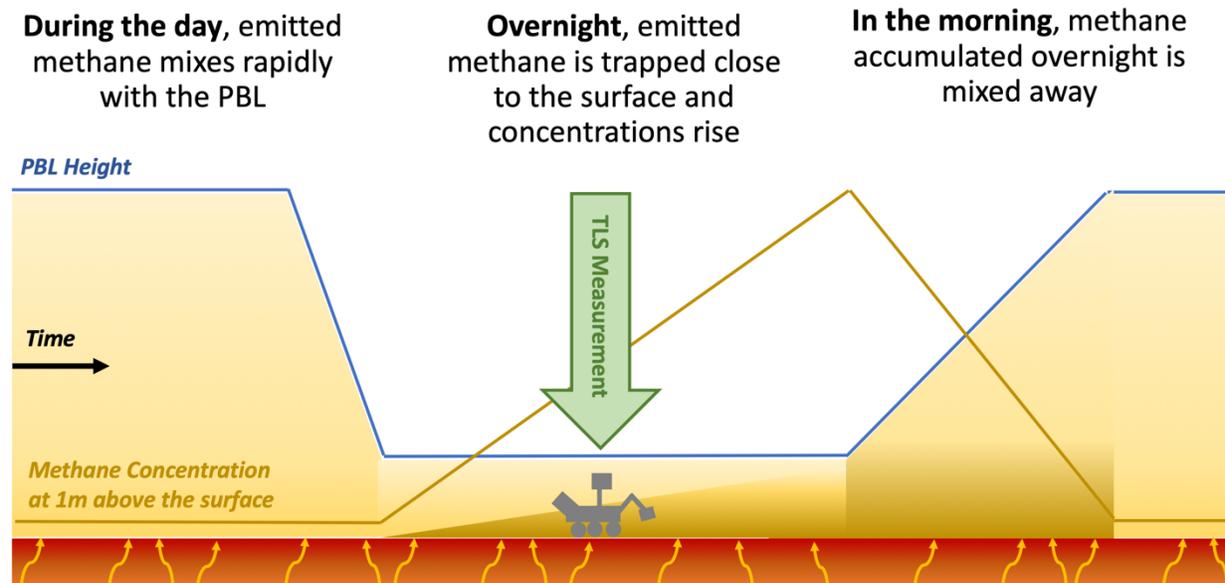
Introduction: Methane is a trace gas of intense interest on Mars. On the Earth, methane is produced primarily through biological processes. However, on Mars, there are several abiotic production mechanisms including water-rock reactions, subsurface thermal decomposition [1] and UV-photolysis of exogenous organic carbon [2] which can be important due to the relatively small quantity of methane observed in the atmosphere in periodic plumes [3,4,5] and seeping into the atmosphere through the subsurface [6,7]. Small amounts of seasonally-varying methane have been observed near the surface (within the lower Planetary Boundary Layer or PBL) [6] throughout the year but this varying background is not seen in the middle and upper atmosphere [8] suggesting a significant gradient.

Ultimately, if the concentrations of methane measured near the surface are representative of daytime values, this gradient is inconsistent with the known photochemistry and dynamics of the Martian atmosphere [8,9] which finds that methane should have an atmospheric lifetime of approximately 300 years and should mix thoroughly within months. This

suggests that any methane present in the atmosphere should accumulate, be well-mixed and should therefore be observable for centuries. Indeed, under reasonable assumptions for daytime mixing described by Korablev et al. [8], emission of CH₄ with a daily average of 410 pptv as detected by the Curiosity rover in Gale crater [6] would produce a visible signal of CH₄ in the upper atmosphere within a few decades that would be detectable by the Trace Gas Orbiter (TGO) [8].

The case for a diurnal variation: The measurements of methane concentration near the martian surface are acquired in the middle of the night [6] when atmospheric conditions are stable and mixing is suppressed by several orders of magnitude. As such, if methane concentrations exhibit a strong diurnal variation near the surface, fluxes into the upper atmosphere may be significantly smaller than anticipated since very little absolute methane must be released at night in order to generate relatively large concentrations (see Figure 1) in the near-surface air.

During the day, the near surface mixed layer, termed the Planetary Boundary Layer or PBL extends



The atmosphere should show a diurnal pattern to constant methane microseepage if background concentrations are near Zero

to several km in height [10] whereas at night, the mixed layer is restricted to only a few meters of the surface. Thus, very little absolute methane is required to produce 410 pptv at 1 m during this time.

Indeed, if methane is emitted into the martian atmosphere through microseepage, as anticipated [1] and as well modelled [7], it would naturally create a variation like that shown in Figure 1 with concentrations building up in a small layer near the surface overnight and then mixed and diluted in the morning with several km of air down to a concentration of only a few pptv.

Methods and Results: In this context, the TGO results [8] impose a powerful constraint on CH₄ in Mars's atmosphere. By indicating that methane is largely absent from the bulk of the martian atmosphere at most times and in most places, it becomes possible to use the Curiosity rover Tunable Laser Spectrometer (TLS) measurements of overnight methane concentration [6] to derive fluxes of this gas out of the subsurface. These are calculated to vary by season [11] from $5.2 \times 10^{-11} \text{ kg m}^{-2} \text{ sol}^{-1}$ ($1.8 \times 10^{-5} \text{ tonnes km}^{-2} \text{ year}^{-1}$) to $16 \times 10^{-11} \text{ kg m}^{-2} \text{ sol}^{-1}$ ($5.7 \times 10^{-5} \text{ tonnes km}^{-2} \text{ year}^{-1}$), similar to the values derived by [7]. These values are over an order of magnitude smaller than those calculated by [8] using the typical day-time mixing timescale of 1 sol [e.g. 12].

The lower limit of 50 pptv established by TGO on the bulk atmosphere [8] may be expressed as a maximum input into the martian atmosphere of $\sim 2.4 \text{ kg sol}^{-1}$ assuming a lifetime of 300 years. Taking the average of the derived flux values of $\sim 1 \times 10^{-10} \text{ kg m}^{-2} \text{ sol}^{-1}$, a total surface area of $2.4 \times 10^{10} \text{ m}^2$ or $2.4 \times 10^4 \text{ km}^2$ may be emitting methane at rates comparable to the environment in which MSL has been operating. All of Gale need not emit methane as the same lack of mixing which prevents vertical dispersal of methane during the day would also prevent horizontal dilution. Indeed, as MSL has begun its ascent of Mt Sharp, the concentration of methane overnight has fallen by half [6].

Amplification of a fast destruction mechanism:

If a fast destruction mechanism exists, especially one in the lower atmosphere involving dust, such as the sequestration mechanism proposed by [13], it would be amplified by the diurnal process described here. During the day, our calculations show that the eddy diffusivity, which measures the vigor of the atmospheric mixing process, is sufficiently high such that each gas molecule will encounter a dust grain on the order of once per second. Overnight, diffusivity may fall as low as the molecular diffusion limit, which is itself consistent with turbulent kinetic energy considerations [10]. This results in typical encounter time-

scales of weeks, suggesting only a few percent of gas molecules will have even one encounter with a grain during the overnight period.

As such, if gas-solid interactions with dust, such as [13] are important, these will happen much more frequently during the day, resulting in not only a dilution, but also a more rapid sequestration/destruction of this material. Overnight, the sequestration/destruction would be slowed by orders of magnitude, allowing the methane seepage to be observed by a near-surface detector (i.e. TLS on Curiosity). The net effect of this amplification, outside of the plumes, would make a larger micro-seepage flux from the subsurface mimic the same atmospheric concentrations as the currently observed small fluxes. This would help explain why martian subsurface fluxes appear to be exceptionally small compared to terrestrial seepage rates [1].

A need for more surface data: No upcoming surface spacecraft to Mars have plans to observe methane with the same (or better) sensitivity as the TLS instrument onboard MSL. However, the difference between the TGO and TLS results indicate that significant interesting chemistry may occur near the surface with methane being both diluted and sequestered/destroyed as it rises, challenging orbital measurements. As such, to understand what is happening, more measurements near the surface are needed over the diurnal cycle and across different geologies.

Yet, understanding the geographic distribution and temporal variation in methane producing regions remains key to understand what locations on Mars host underground processes which create and release methane. It would appear that such measurements can only be effectively observed by spacecraft able to sample the lower few meters of the martian atmosphere during the stable overnight period.

References: [1] Oehler and Etiope, 2017 *Astrobiology* [2] Schuerger et al., 2012 *JGR-Planets* [3] Webster et al., 2015 *Science* [4] Mumma et al., 2009 *Science* [5] Giuranna et al., 2019, *Nature Geosci.* [6] Webster et al., 2018 *Science* [7] Moores et al., 2019 *Nature Geosci.* [8] Korablev et al., 2019 *Nature* [9] Atreya et al., 2007 *P&SS* [10] Newman et al., 2017 *Icarus* [11] Moores et al., 2019, submitted [12] Moores et al., 2016, *ASR* [13] Jensen et al., 2014, *Icarus*