Workshop - Towards Addressing Major Gaps in the Global Methane Budget
California Institute of Technology
Tuesday, May 23, 2017

“Esoteric (Others) Sources!?”

Frank Keppler

…and the ORCAS…

Well known processes of methane formation on Earth

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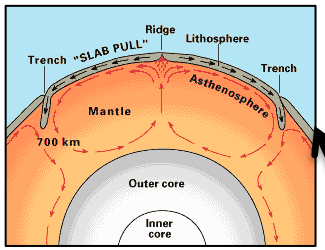
Methanogenesis – traditional ("non-esoteric")



geological

biomass burning
fossil sources
energy production

abiotic

industry

$$n\,CO + (2n+1)\,H_2 \rightleftharpoons C_nH_{2n+2} + n\,H_2O$$

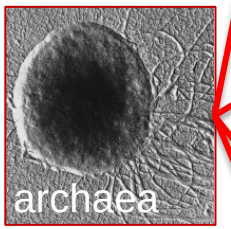
Fischer-Tropsch-process

biotic

Prokaryotes

anoxic

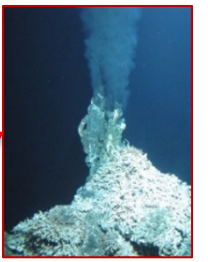
microbial



$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

$CH_3COOH \longrightarrow CH_4 + CO_2$

rice paddies,
mires, lakes,
wetlands,
landfills …



oceans

guts of
ruminants
or termites

Other methane sources

- Novel sources
- Novel processes
- The potential physiological role of methane in organisms?
- Source strengths - global upscaling?

The role of vegetation in global cycling of methane?

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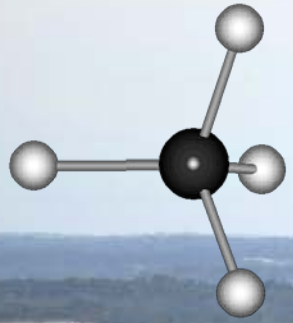
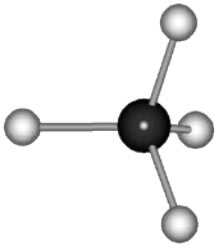


So far not considered by the IPCC reports and most global budgets studies

A view is seen from the Amazon Tall Tower Observatory (ATTO) in the middle of the Amazon January 8, 2015. REUTERS/Bruno Kelly

Very first observations…



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The earliest laboratory study reporting an emission of CH_4 from leaves was conducted…

…in the late 1950's at the Academy of Sciences of Georgia (Tbilisi) on emissions of volatile organic compounds (VOCs) from leaves of willow and poplar tress (Sanadze and Dolidze, 1960).

Доклады Академии наук СССР

(Reports of Academy of Sciences of USSR)
1960, Vol 134, № 1, pages 214-216

Physiology of plants

G.A. Sanadze and G. M. Dolidze

About Chemical Nature of Volatile Emissions Released by Leaves of Some Plants

First observations of methane formed anaerobically in living trees

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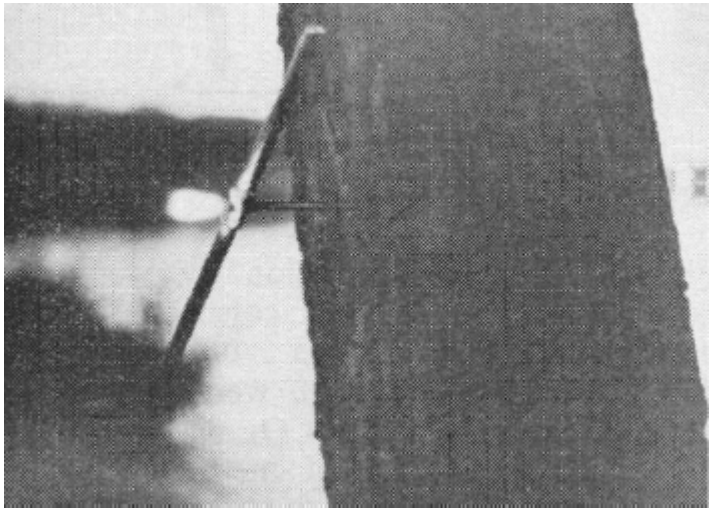
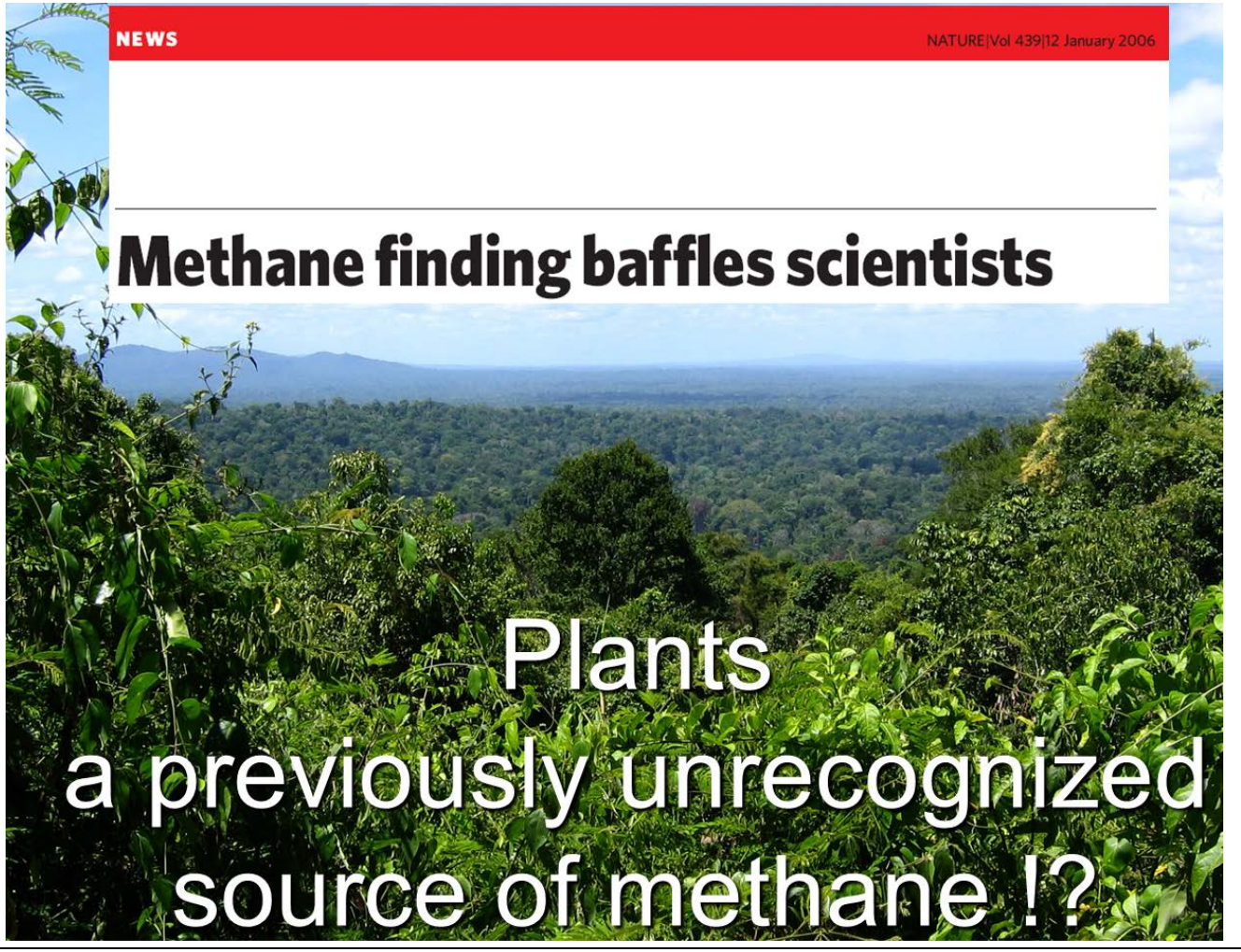
Methane Formation in Living Trees: A Microbial Origin
J. G. Zeikus & J. C. Ward, *Science* 1974



Ignited methane gas released from the tree through a increment borer
Figure taken from Zeikus & Ward, Science 1974

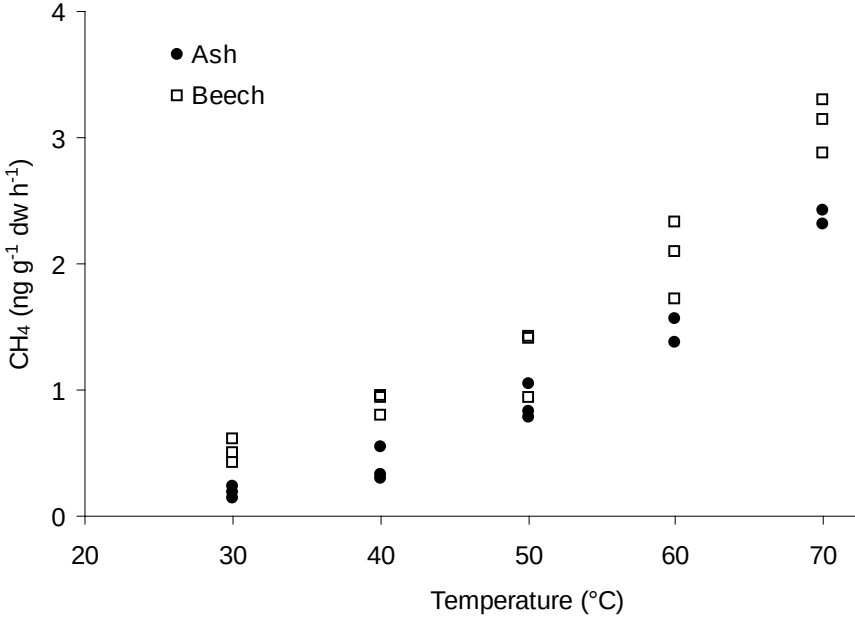
Some years later….in 2006…



Keppler et al., Nature, 2006

Methane emission from dried leaves (without microbial contribution)

Ash (*Fraxinus excelsior*)
Beech (*Fagus sylvatica*)

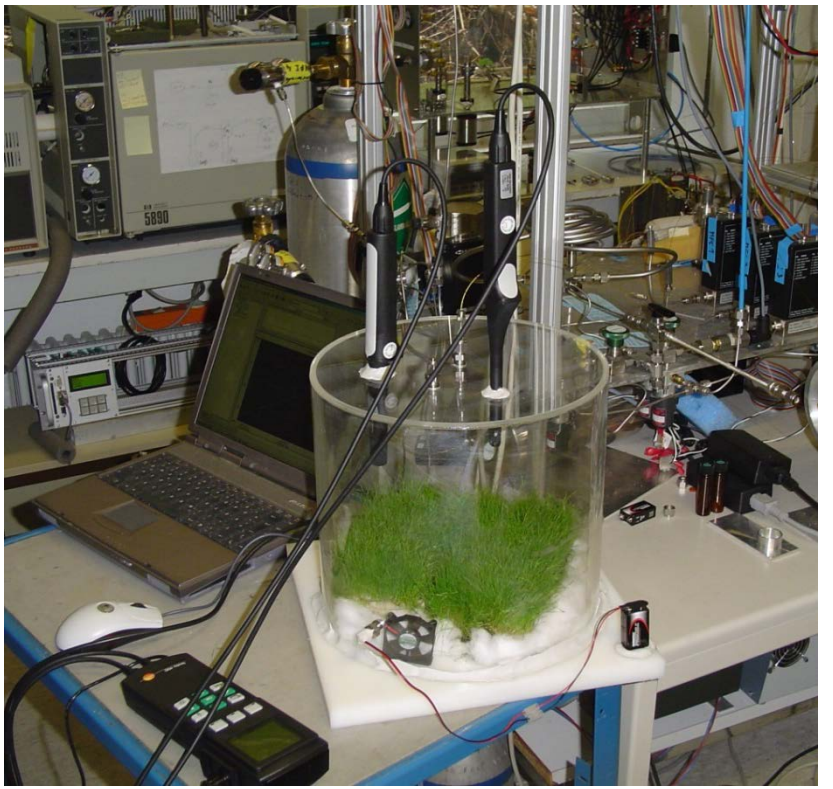


Typical emission rates at 30°C: 0.2 to 3 ng g(dw)$^{-1}$ h^{-1}

Keppler et al., Nature, 2006

Emissions of methane from intact living plants:

10-100 higher (under laboratory conditions)



Grass *(Lolium perenne)*

9 plant species including C3 and C4, grown hydroponically or on soil

Typical emission rates 12-370 ng $g(dw)^{-1}$ h^{-1})

Keppler et al., Nature, 2006

First approach of global upscaling

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not possible!

63 to 243 Tg (million tons) per year
methane emitted by vegetation
(living and dead plants)
???

Most should come from tropical forests, savannas and grasslands

Keppler et al., Nature, 2006

→ **85 Tg CH_4 yr^{-1}** as a more plausible limit

Houweling et al., Geophys. Res. Lett, 2006

...controversial discussion between scientists…

...controversial discussion between scientists...

New Phytologist

Research

Rapid report

No evidence for substantial aerobic methane emission by terrestrial plants: a ^{13}C-labelling approach

Dueck et al., New Phytologist, 2007

Global Change Biology (2008) **14**, 1–6, doi: 10.1111/j.1365-2486.2008.01607.x

RAPID COMMUNICATION

Missing methane emissions from leaves of terrestrial plants

Beerling et al., Global Change Biology, 2008

...controversial discussion between scientists continued…

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Science News – November 28, 2007

Methane-making plants in the Inner Mongolian steppe

Although a new study confirms previous findings that plants make methane, this ability may be limited to shrubs.

When, nearly 2 years ago, a study first suggested that plants emit methane, scientists received the news with a flurry of excitement, a dash of skepticism, and hasty speculations on plants' contribution to global warming. A new study published in *ES&T* (DOI: 10.1021/es071224l) is the first to confirm that plants do indeed make this potent greenhouse gas. But it also finds that the methane-making ability varies among types of plants and, at least in the grasslands of Inner Mongolia, is limited to woody shrubs.

Zhi-Ping Wang

Two-thirds of shrubs but no herbs in the Inner Mongolian grasslands emit methane.

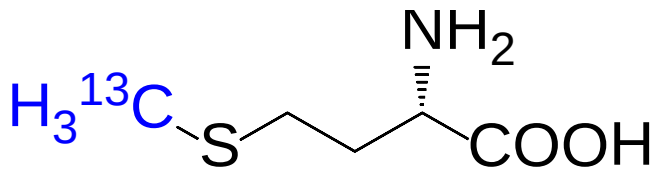
Aerobic Methane Emission from Plants in the Inner Mongolia Steppe

ZHI-PING WANG,*,†,‡ XING-GUO HAN,† G. GEOFF WANG,‡ YANG SONG,† AND JAY GULLEDGE§,||

Physical injury stimulates aerobic methane emissions from plants

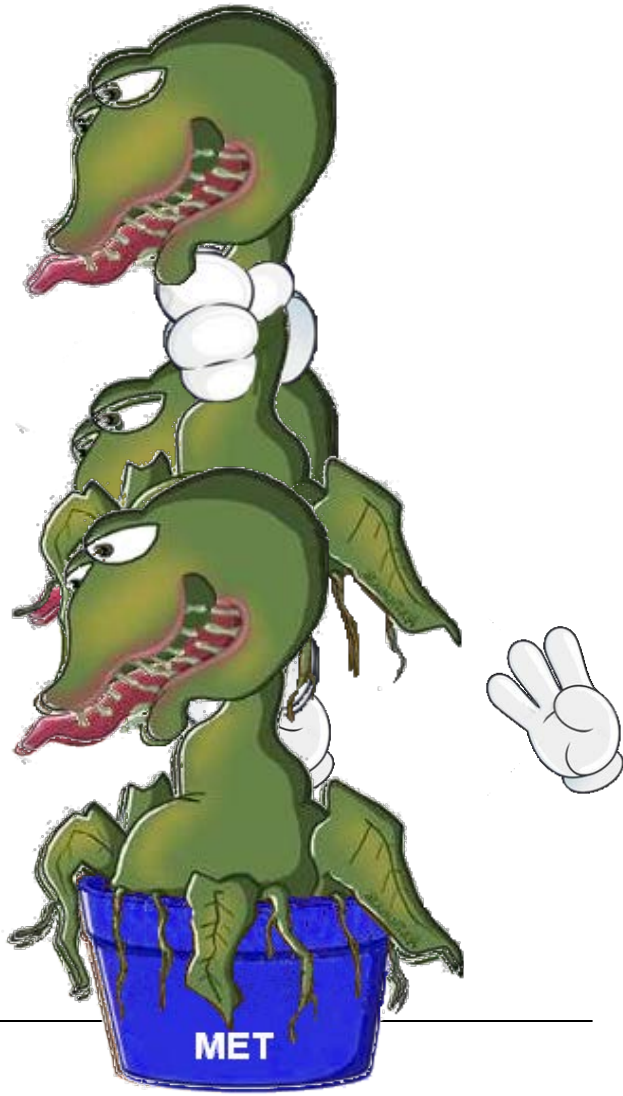
Wang et al., 2009, 2010, 2011

Feeding methionine with ^{13}C labelled methyl group to lavender plants (*Lavendula angustifolia*)



methionine (amino acid)

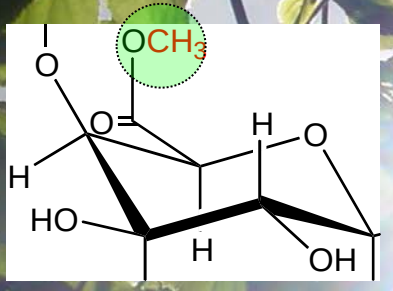
CH_4

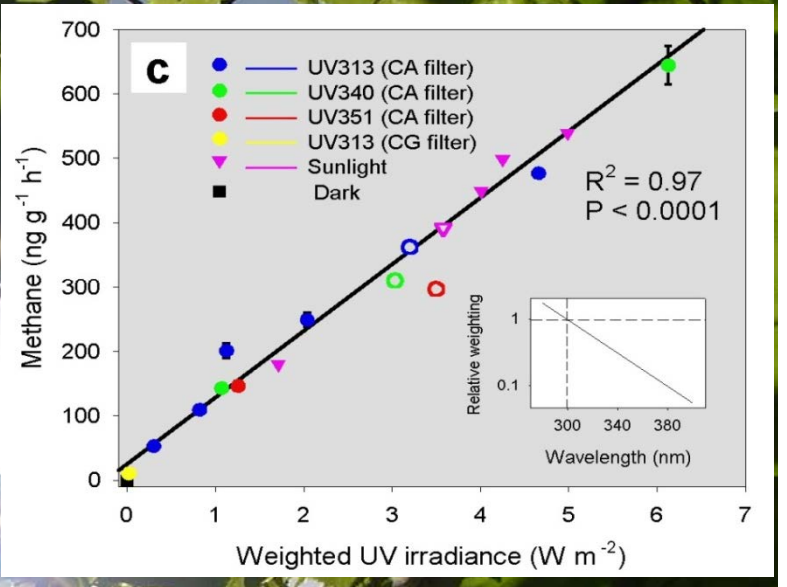


Althoff et al., Nature Communications, 2014

Lenhart et al., Biogeosciences, 2015

Effect of UV-B radiation on plant pectin





UV-light increases methane emission from pectin and dry plant matter

Vigano et al., Biogeosciences, 2008

McLeod et al., New Phytologist, 2008 and Messenger et al., PCE, 2009

reported emission rates were in the range of **1 to 650ng g(dw)$^{-1}$ h^{-1}**

Keppler et al., New Phytologist, 2008

Methane from plants (after 10 years)

More than 60 experimental studies confirmed non-archaeal methane emissions from dead and living vegetation

!

Global emissions from plants are most likely smaller than the initial upscaling approach

!

Recently, *Carmichael et al.* (2014) estimated a range of global emissions from plants (including several aspects) in the range of 32 to 143 Tg yr^{-1}

!

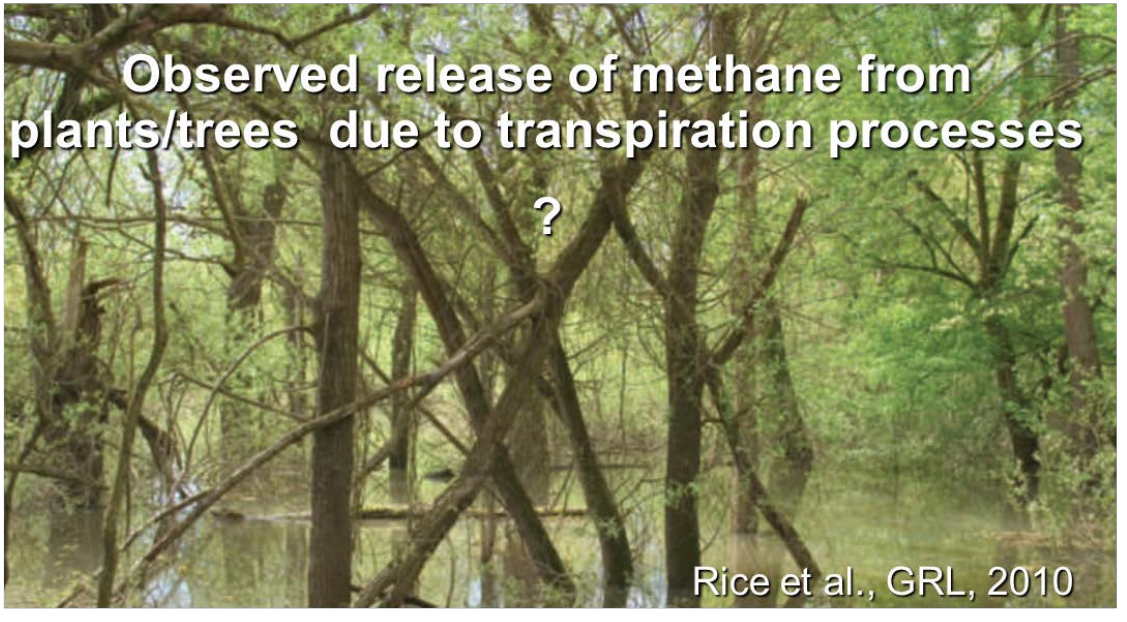
Methane transport through plants…

PROCEEDINGS OF THE ROYAL SOCIETY B

Proc. R. Soc. B
doi:10.1098/rspb.2008.1731

Emission of methane from plants

R. E. R. Nisbet[1,*], R. Fisher[2], R. H. Nimmo[1], D. S. Bendall[1], P. M. Crill[3], A. V. Gallego-Sala[4], E. R. C. Hornibrook[4], E. Lopez-Juez[5], D. Lowry[2], P. B. R. Nisbet[2,6], E. F. Shuckburgh[7], S. Sriskantharajah[2], C. J. Howe[1] and E. G. Nisbet[2]



Methane anaerobically produced in soil and transmitted to the atmosphere by trees

➡ Results were scaled globally for flooded forest regions and estimated to be 60 ± 20 Tg year^{-1}

Other methane sources

The role of trees/plants in CH_4 cycling …very recent studies

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Methane emissions from the trunks of living trees on upland soils
Wang, Z.-P. et al. (2016). New Phytol. 211, 429-439.

SCIENTIFIC REPORTS

OPEN

Pinus sylvestris as a missing source of nitrous oxide and methane in boreal forest

Received: 10 September 2015
Accepted: 07 March 2016

Katerina Machacova[1], Jaana Bäck[3], Anni Vanhatalo[3], Elisa Halmeenmäki[2], Pasi Kolari[2], Ivan Mammarella[2], Jukka Pumpanen[4], Manuel Acosta[1], Otmar Urban[1] & Mari Pihlatie[2,5]

microbial wood decay?

plants *per se*?

transport/transmission?

New Phytologist — Research

Rapid report

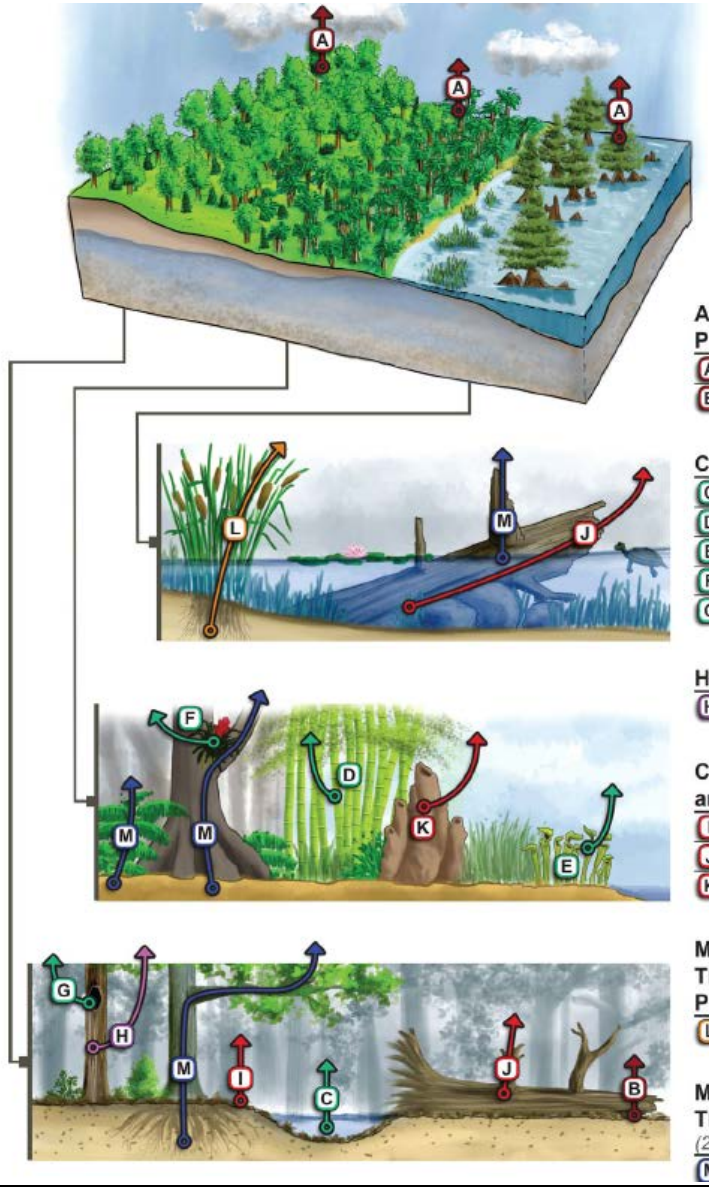
Temperate forest methane sink diminished by tree emissions

Authors for correspondence: Scott Pitz[1,2] and J. Patrick Megonigal[2]

2017

Potential CH_4 emissions from vegetation

from Carmichael et al. 2014



Aerobic Methane Production *(8 - 60)*
- A Live Trees and/or Leaves
- B Leaf Litter

Cryptic Wetlands *(1)*
- C Bole Depression
- D Bamboo Internodes
- E Pitcher Plant
- F Tank Bromeliad
- G Tree Hole

Heartwood Rot *(2-3)*
- H Live Trees

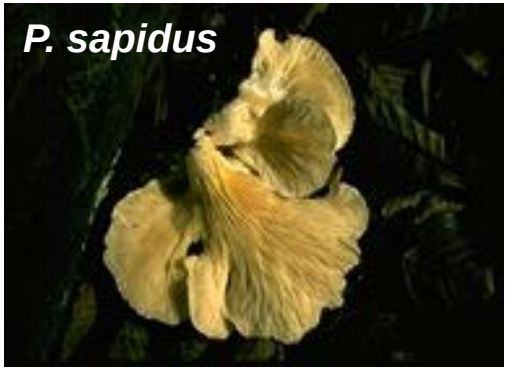
Coarse Woody Debris and Litter *(19)*
- I Leaf Litter and/or Twigs
- J Snags
- K Termites

Methane Transport Through Herbaceous Plants
- L Herbaceous Vegetation

Methane Transport Through Woody Plants *(2-60)*
- M Trees

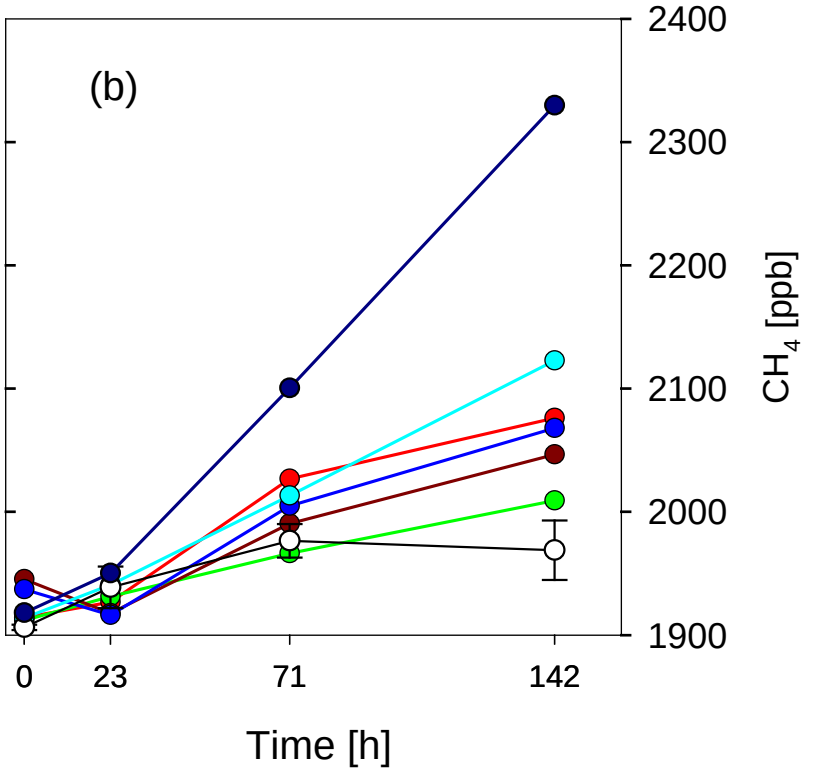
32 to 143 Tg yr^{-1}

Methane formation by fungi (Basidiomycota)



Lenhart et al., Nature Communications, 2012

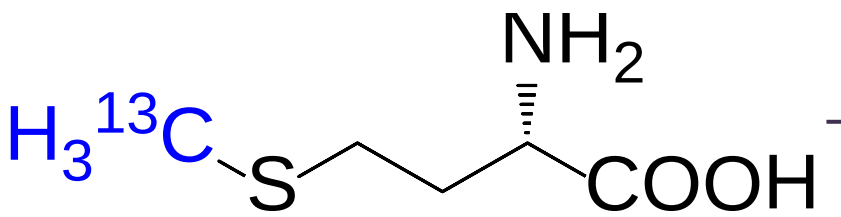
Methane formation by fungi (Basidiomycota)



Lenhart et al., Nature Communications, 2012

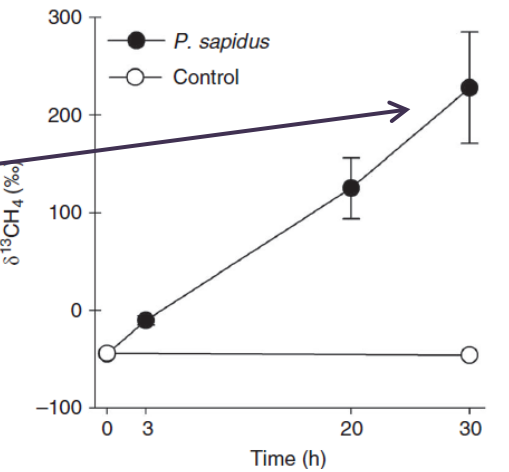
Methionine as a precursor of methane in fungi

Methionine



Feeding methionine with ^{13}C labelled methyl group

=> **H_3C**- group **is** a **CH_4** precursor!



Lenhart et al., Nature Communications, 2012

CH_4 and N_2O from cryptogamic covers

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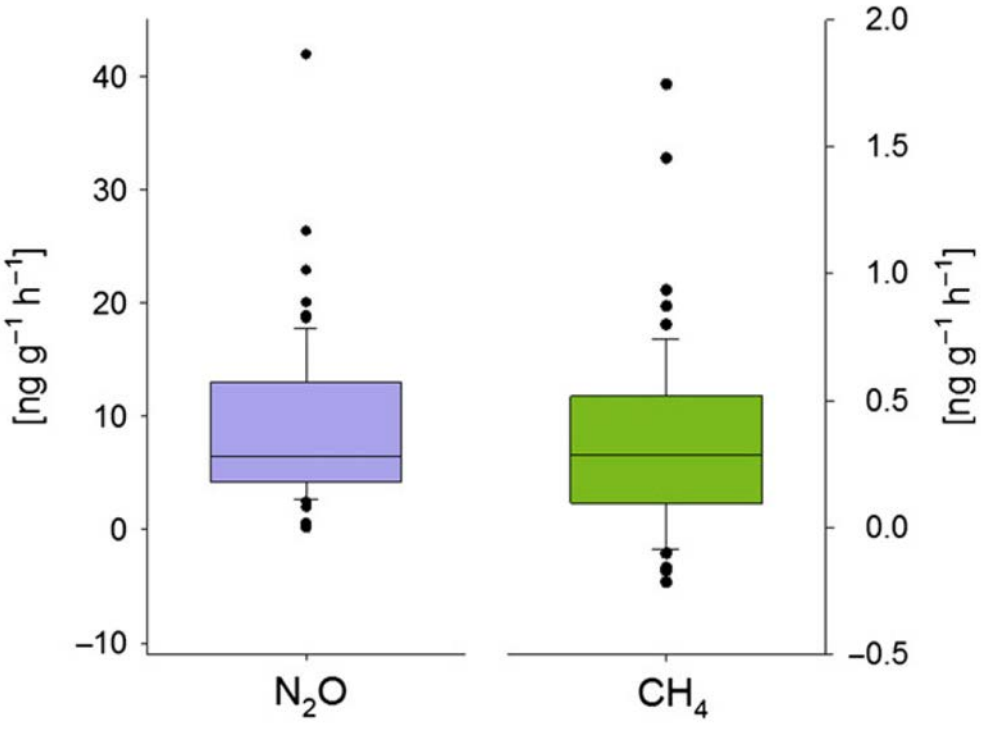
68 samples from different climatic regions:
lichens and mosses grown on trees, rocks, soil

CH_4, N_2O and CO_2 emissions from 68 cryptogamic samples



Best estimates*:

N_2O: 7,92 ng g^{-1} h^{-1}

CH_4: 0,28 ng g^{-1} h^{-1}

CO_2: 0,42 mg g^{-1} h^{-1}

*geometric mean

significant on a global scale

N_2O:CO_2-ratio: 0,000016

CH_4:CO_2-ratio: 0,0000007

minor on a global scale

Lenhart et al., Glob. Change Biol., 2015

CH_4 sources in the plant-soil system

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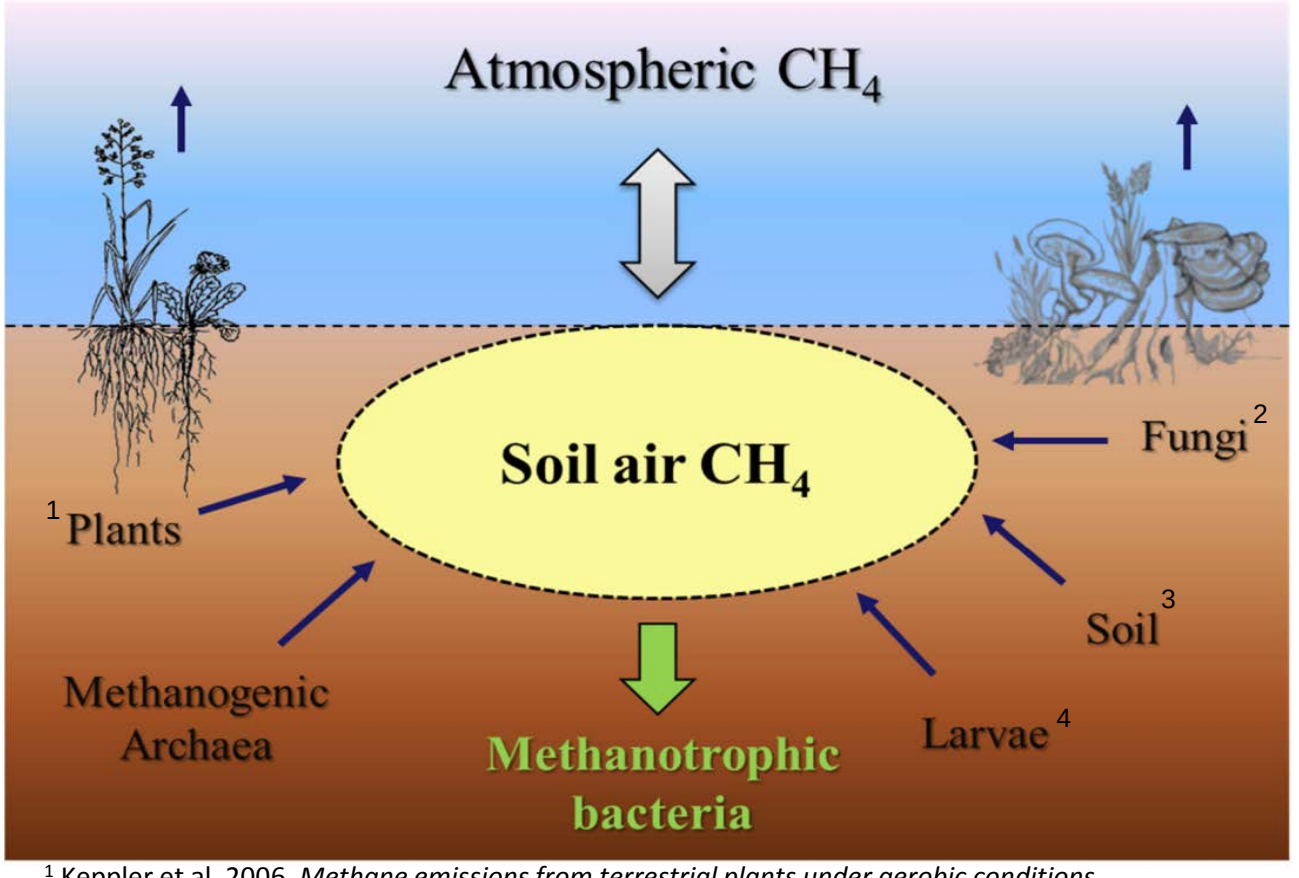
Microbial CH_4 **consumption** and CH_4 **production** from various sources



difficult to study in the field !

[1] Keppler et al. 2006, *Methane emissions from terrestrial plants under aerobic conditions*
[2] Lenhart et al. 2012, *Evidence for methane production by saprotrophic fungi*
[3] Jugold et al. 2012, *Non-microbial methane formation in oxic soils*
[4] Hackstein and Stumm 1994, *Methane production in terrestrial arthropods*

Oceanic methane: sources and sinks → potential role of marine vegetation

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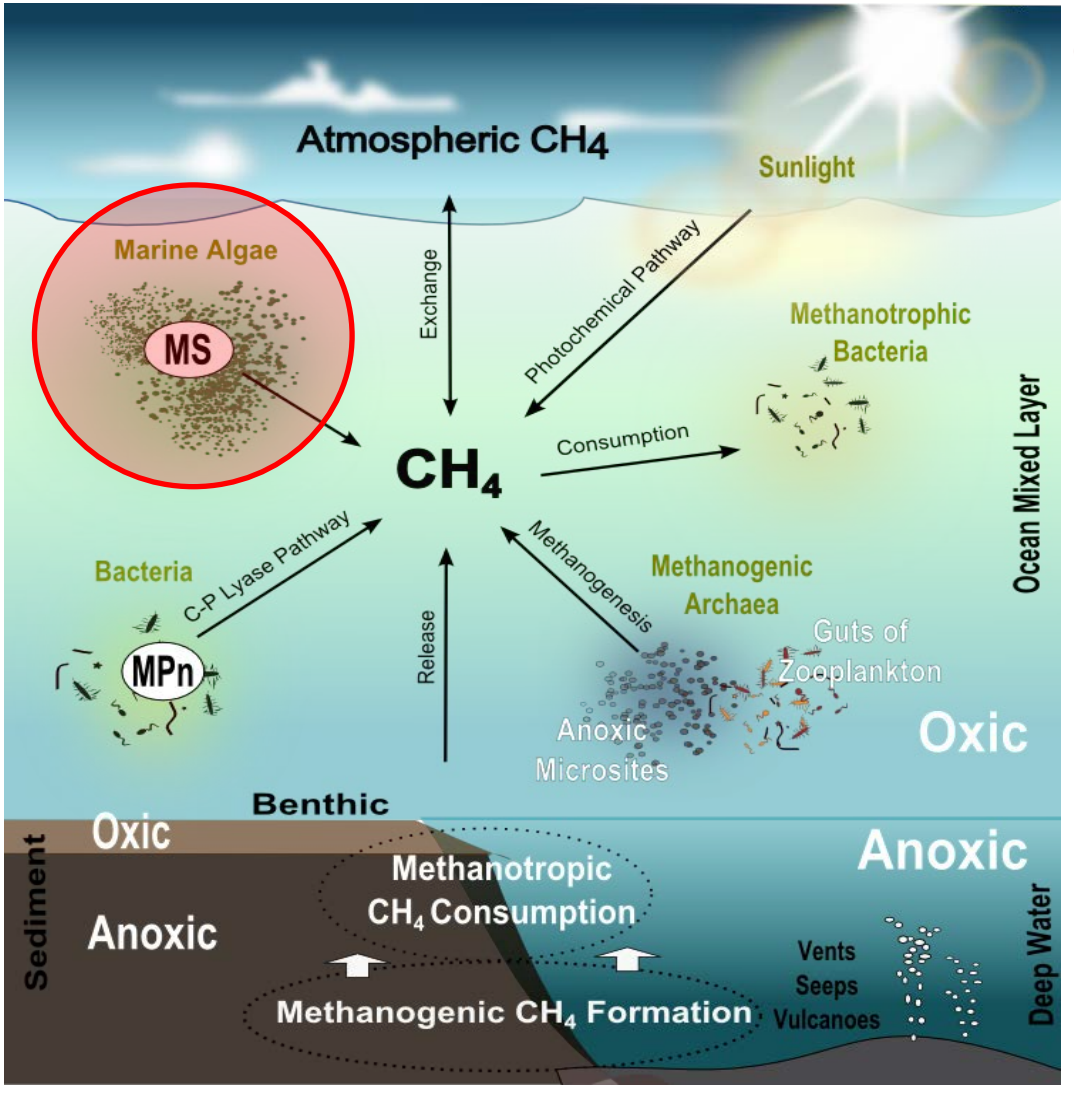
marine Vegetation

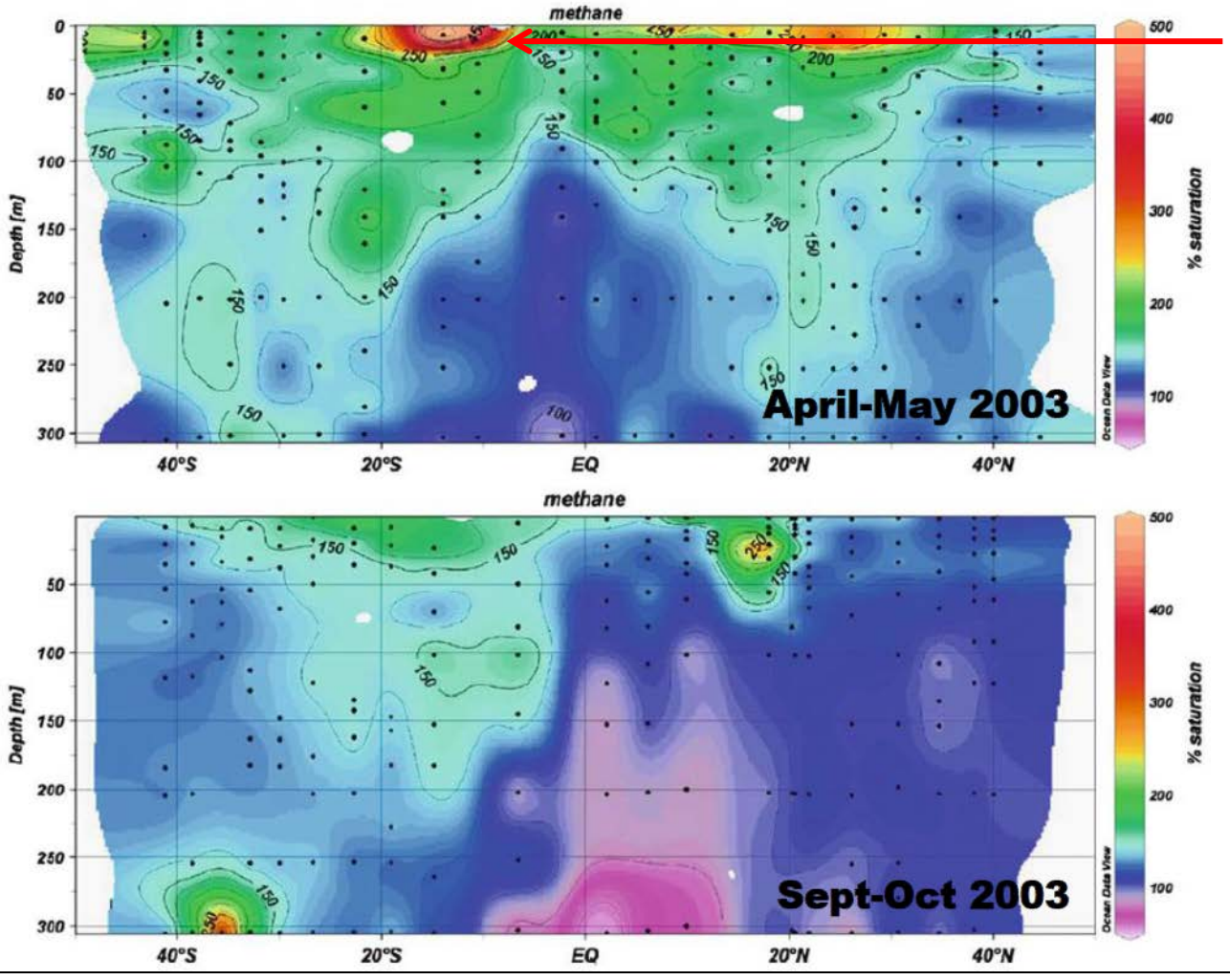


Other methane sources

The ocean methane paradox

Methane oversaturation in the upper water column e.g. in the Atlantic Ocean

Why?



Other methane sources

Forster et al., 2009

Methane formation from algae
Emiliania huxleyi (coccolithophore)

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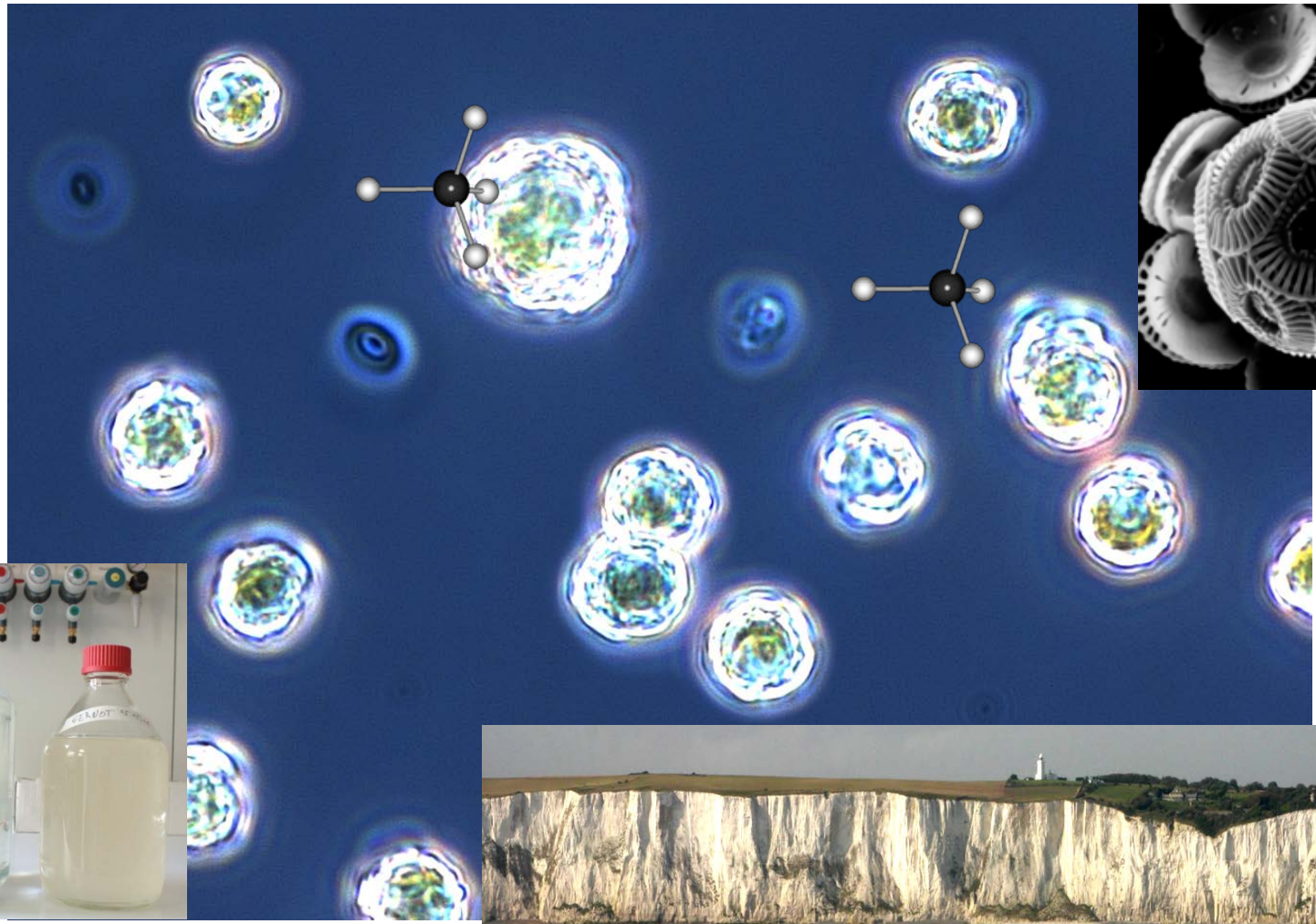

Emiliania huxleyi
Cultivation under sterile conditions

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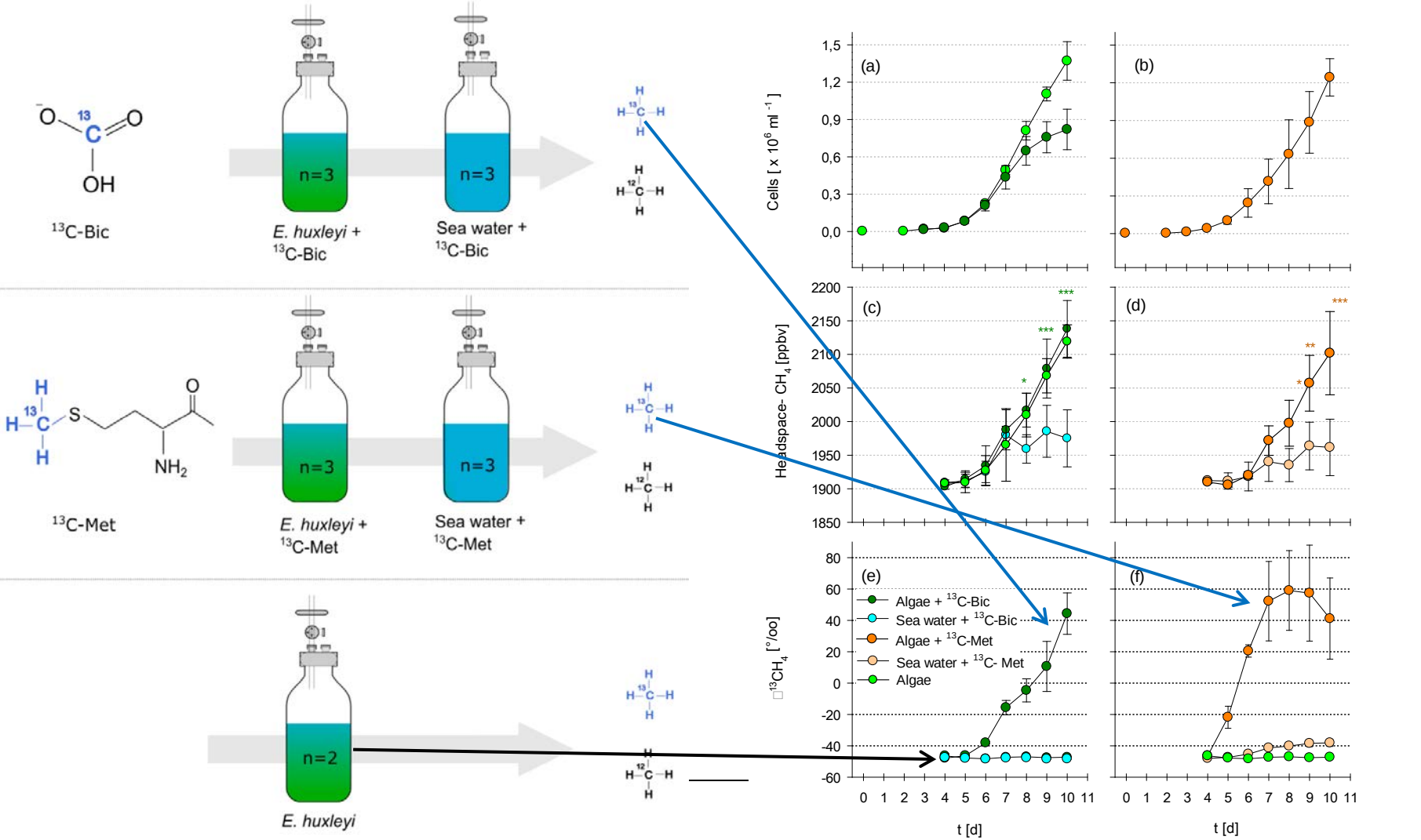
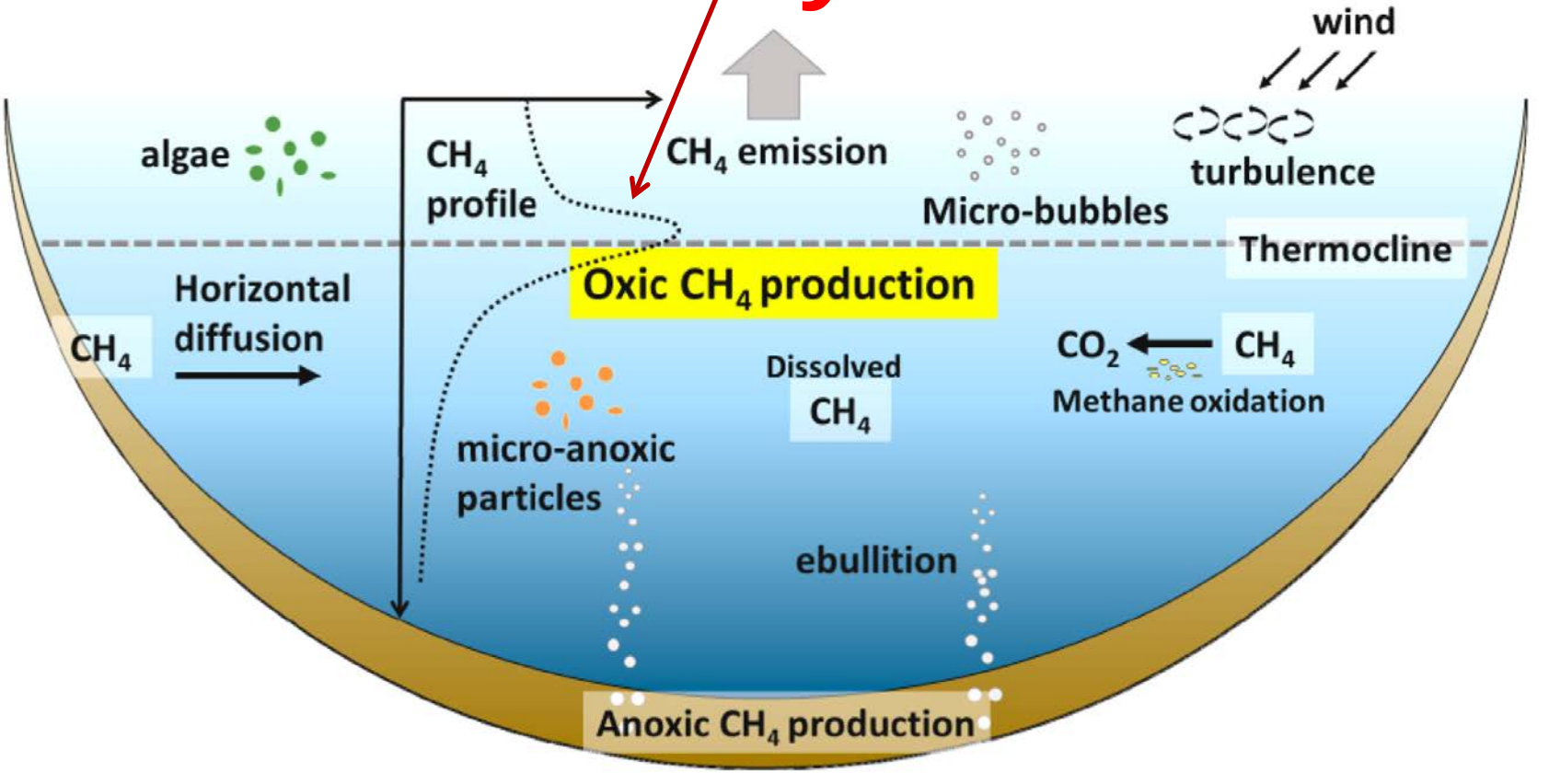
Lenhart et al., Biogeosciences, 2016



Methane oversaturation in oxic lake waters

Why?



Tang et al., ES&T, 2016

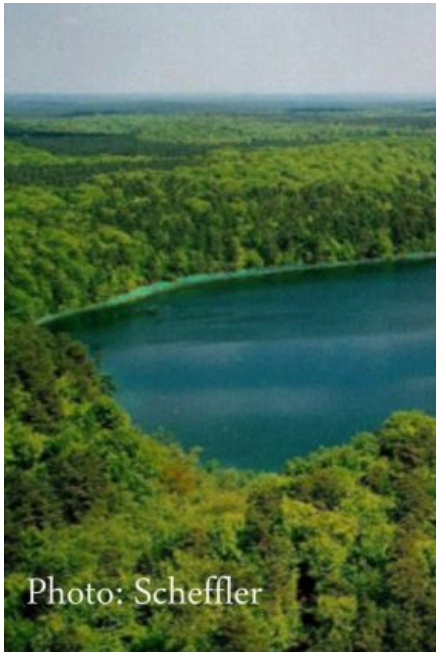
Methane oversaturation in oxic lake waters
Example: Lake Stechlin, Germany

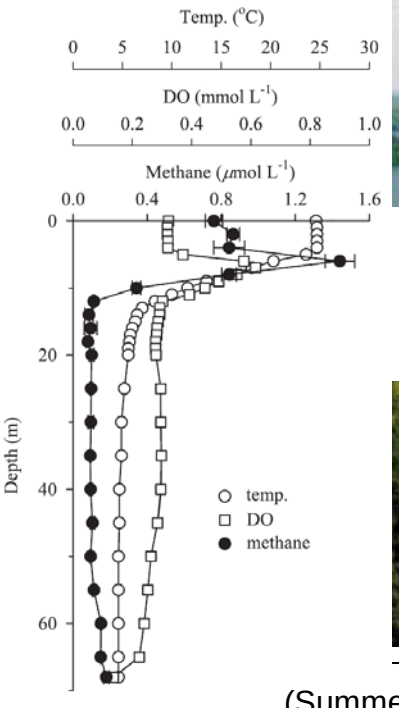
Limnol. Oceanogr., 59(1), 2014, 275–284

doi:10.4319/lo.2014.59.1.0275

Paradox reconsidered: Methane oversaturation in well-oxygenated lake waters

Kam W. Tang,[1,2,*] Daniel F. McGinnis,[3,4] Katharina Frindte,[4] Volker Brüchert,[5] and Hans-Peter Grossart[4,6]



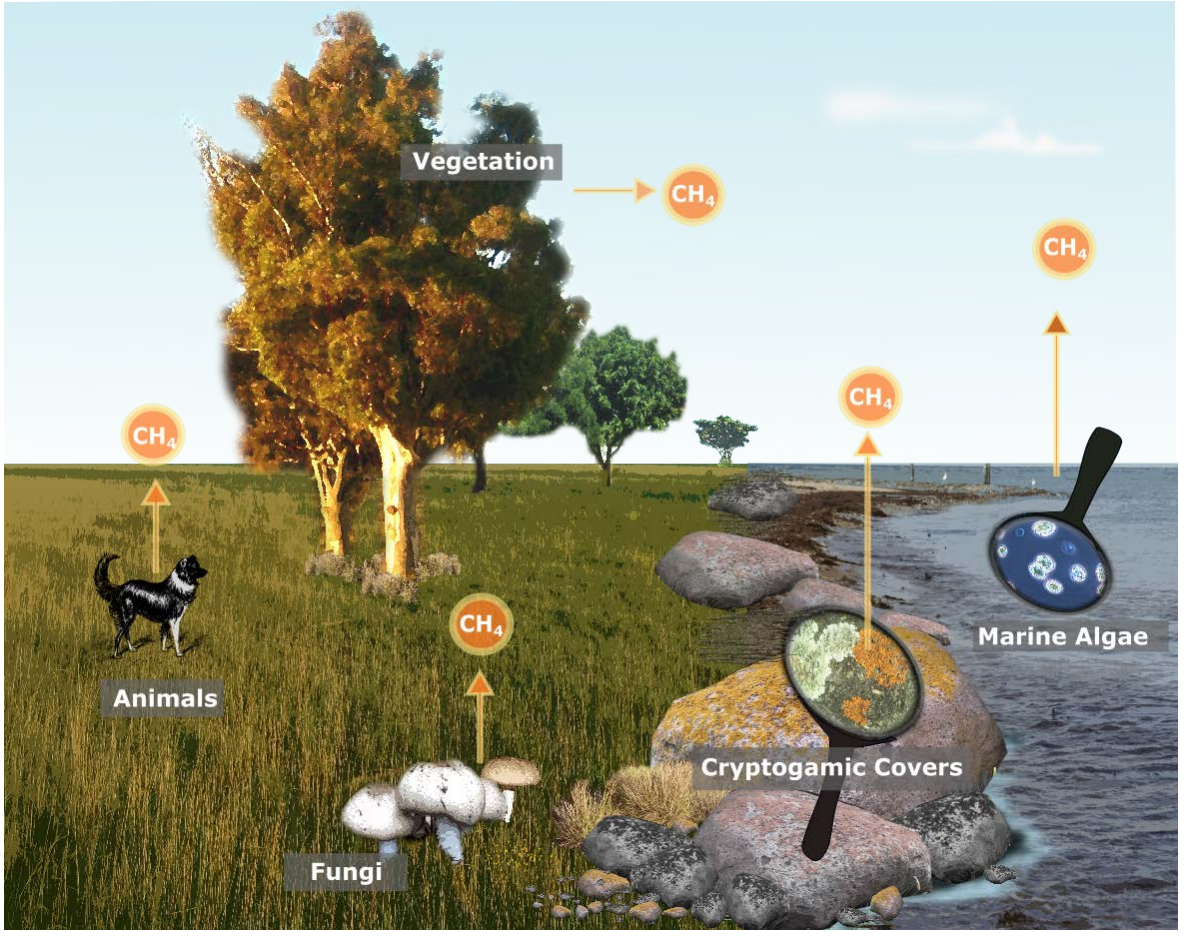


Why?

(Summer, July 21 and 22, 2010)

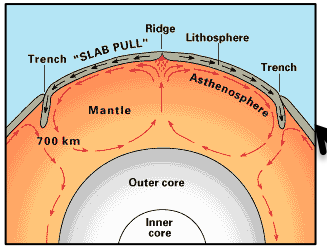
Summary of novel terrestrial and aquatic methane sources:

“aerobic, non-microbial, non-archaeal…???”



Althoff et al. 2014; Boros & Keppler, 2017; Bruhn et al. 2012; Carmichael et al. 2014; Keppler et al. 2006, 2009; Klintzsch 2015; Lenhart et al. 2012, 2015, 2016; Liu et al. 2015; Machacova et al. 2016; Wang et al. 2013, 2016

Methanogenesis (traditional) 2017



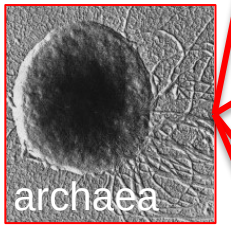
chemical

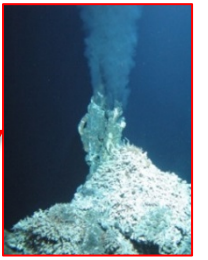
non-archaeal
aerobic/oxidative

Eukaryotes

microbial
anoxic

Prokaryotes



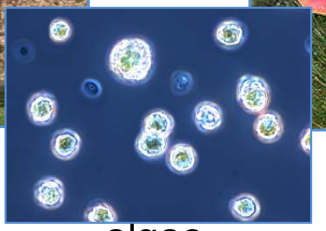


dead
plants

soils

plants

lichens



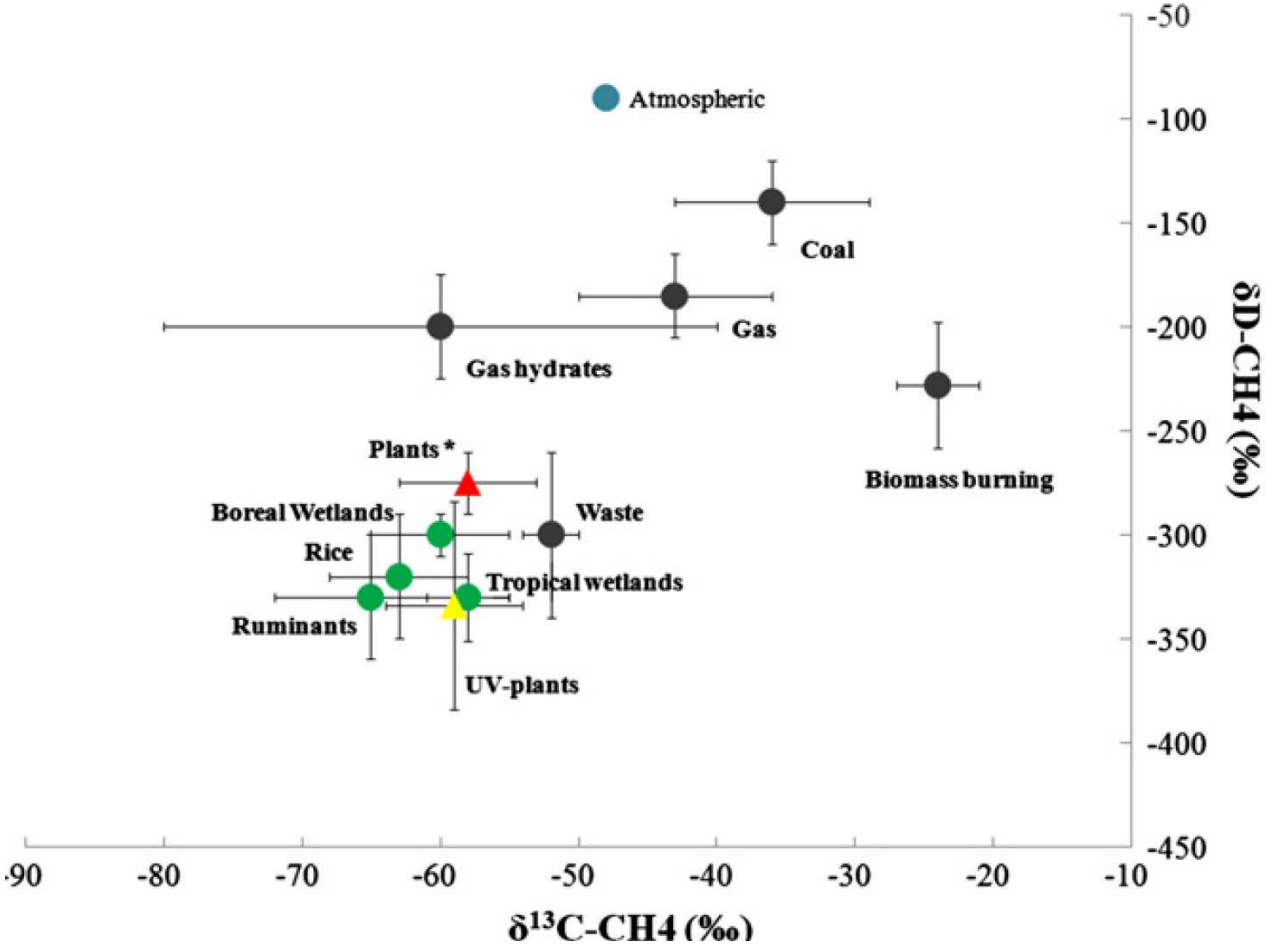
algae

fungi

Stable isotope values of CH_4 from plants

In a similar range as what is known for microbial formation

(isotopic composition from other novel sources are not known so far)



Other methane sources

Vigano et al., Atmos. Environment, 2009

Pathways of methane formation in aerobic environments?

From https://contemplativepathways.files.wordpress.com/2012/08/cornwalls_glendurgan_lowres.jpg?w=640&h=480

Reactive oxygen species involved in CH_4 generation

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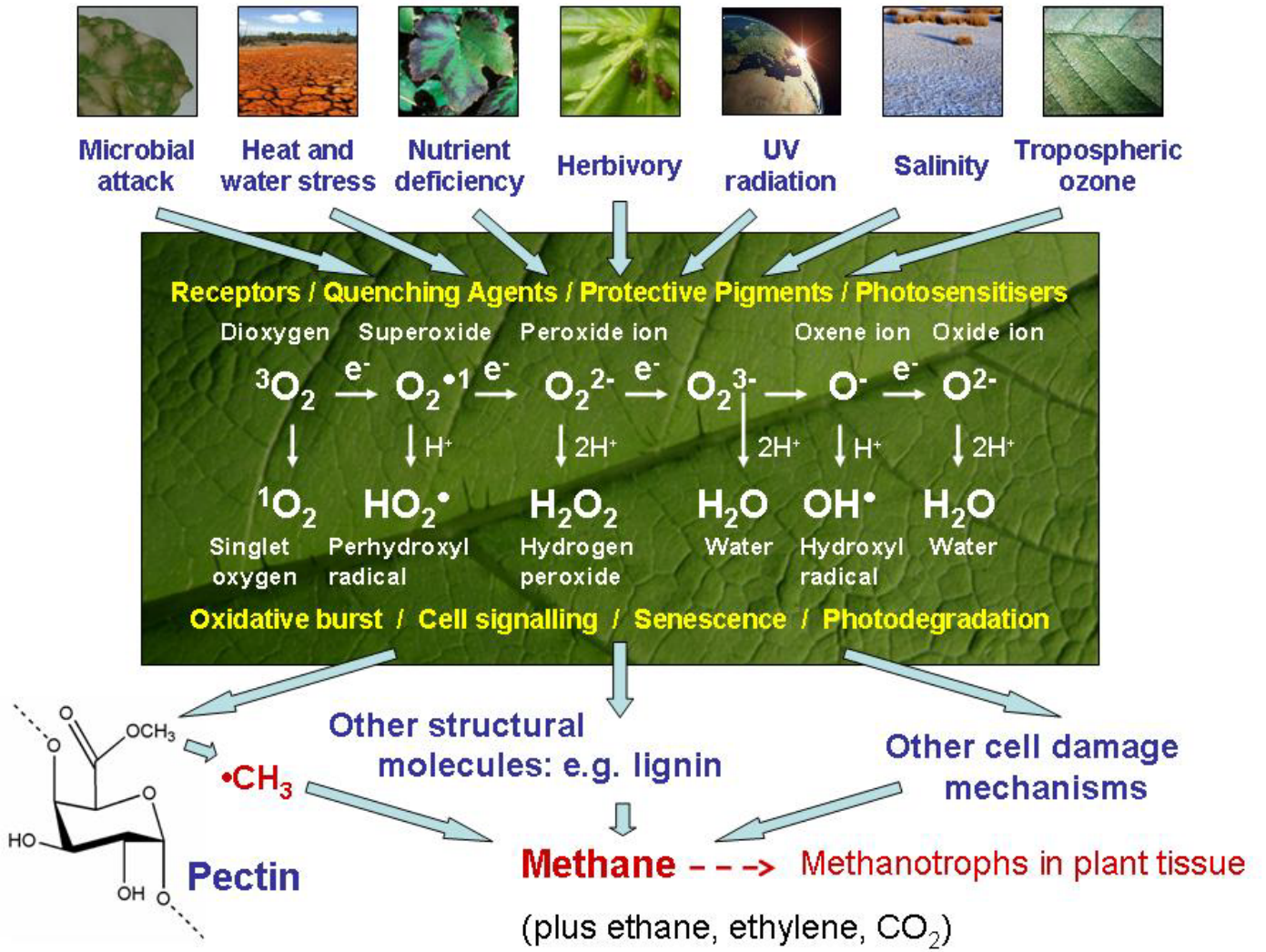

Keppler et al., Environmental Chemistry, 2009

designed by Andy McLeod

Novel chemical pathway of CH_4 formation from organosulfur compounds:

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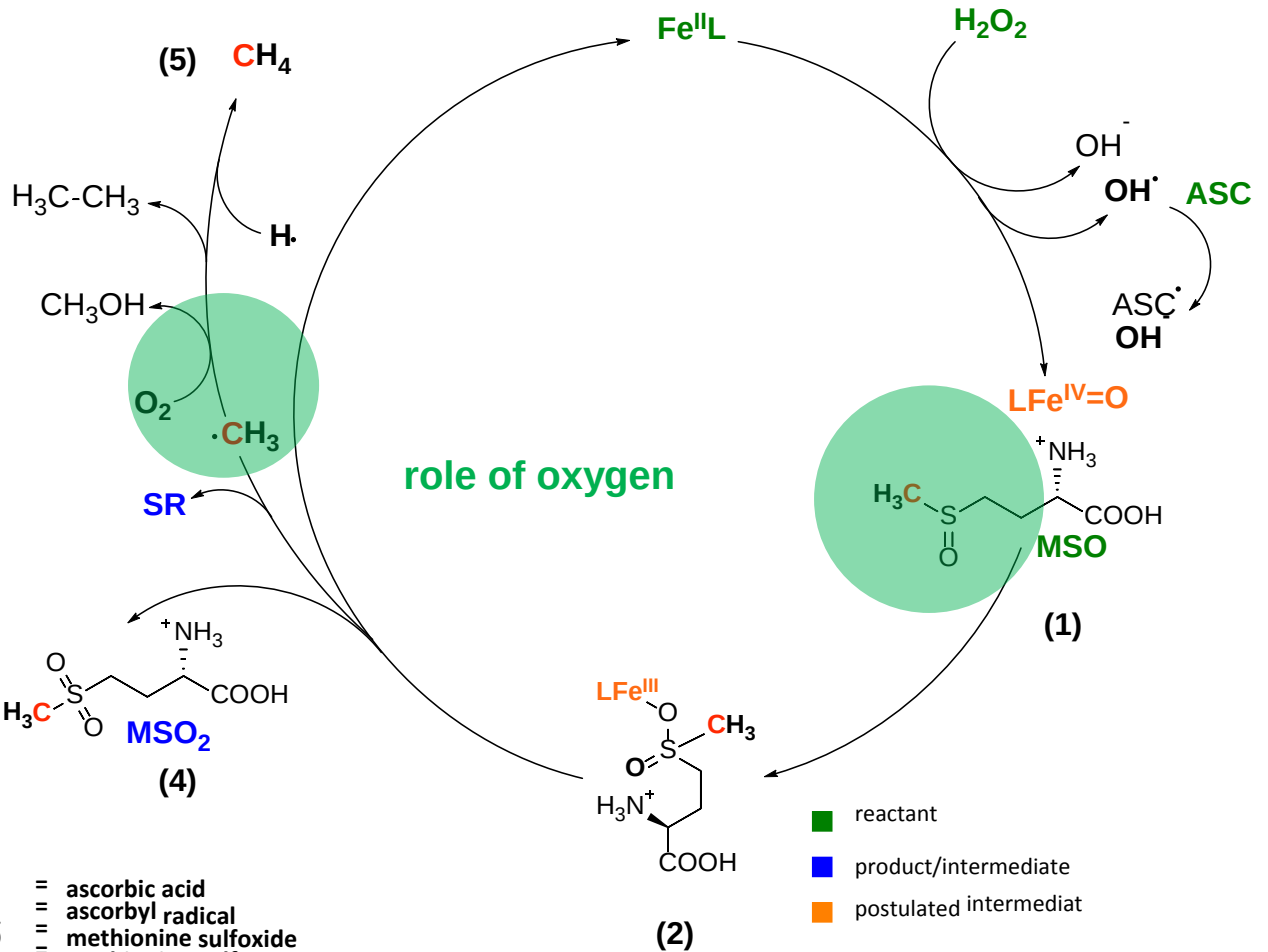
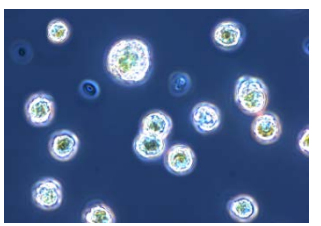
Ingredients: methionine, hydrogen peroxide, ascorbic acid and iron II





Althoff et al., Nature Communications, 2014
Benzing et al., Angewandte Chemie Int. Ed., in revision

Summary & Outlook
…for biochemists

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The physiological role of CH_4 in plants?

OPEN

Methane protects against polyethylene glycol-induced osmotic stress in maize by improving sugar and ascorbic acid metabolism

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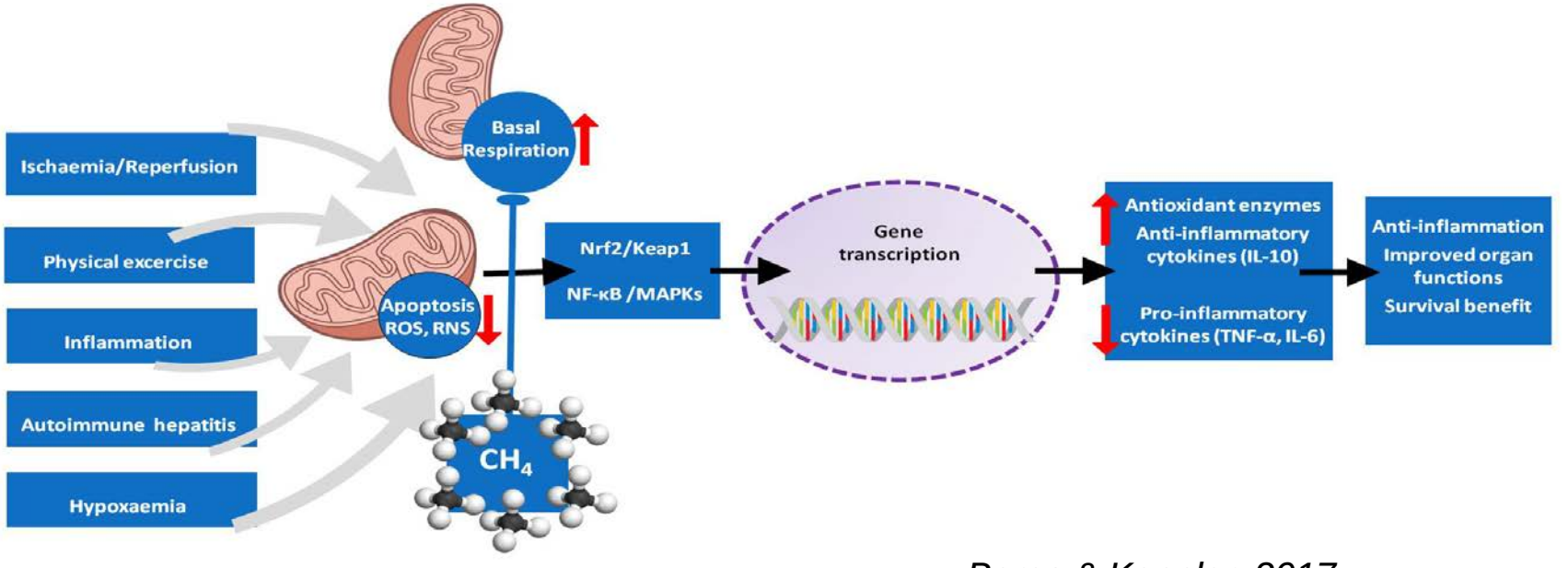
Bin Han[1,*,†], Xingliang Duan[1,*], Yu Wang[1], Kaikai Zhu[1], Jing Zhang[1], Ren Wang[2], Huali Hu[3], Fang Qi[1], Jincheng Pan[1], Yuanxin Yan[4] & Wenbiao Shen[1]

Summary & Outlook …for biochemists

There might be a physiological role of CH_4 in humans/animals



Boros & Keppler, 2017

Summary & Outlook
Fluxes – regional/global

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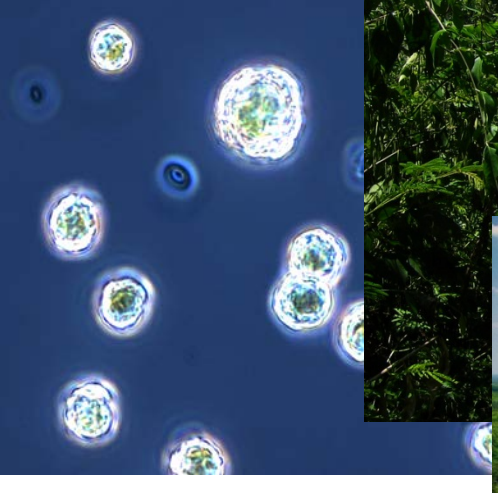
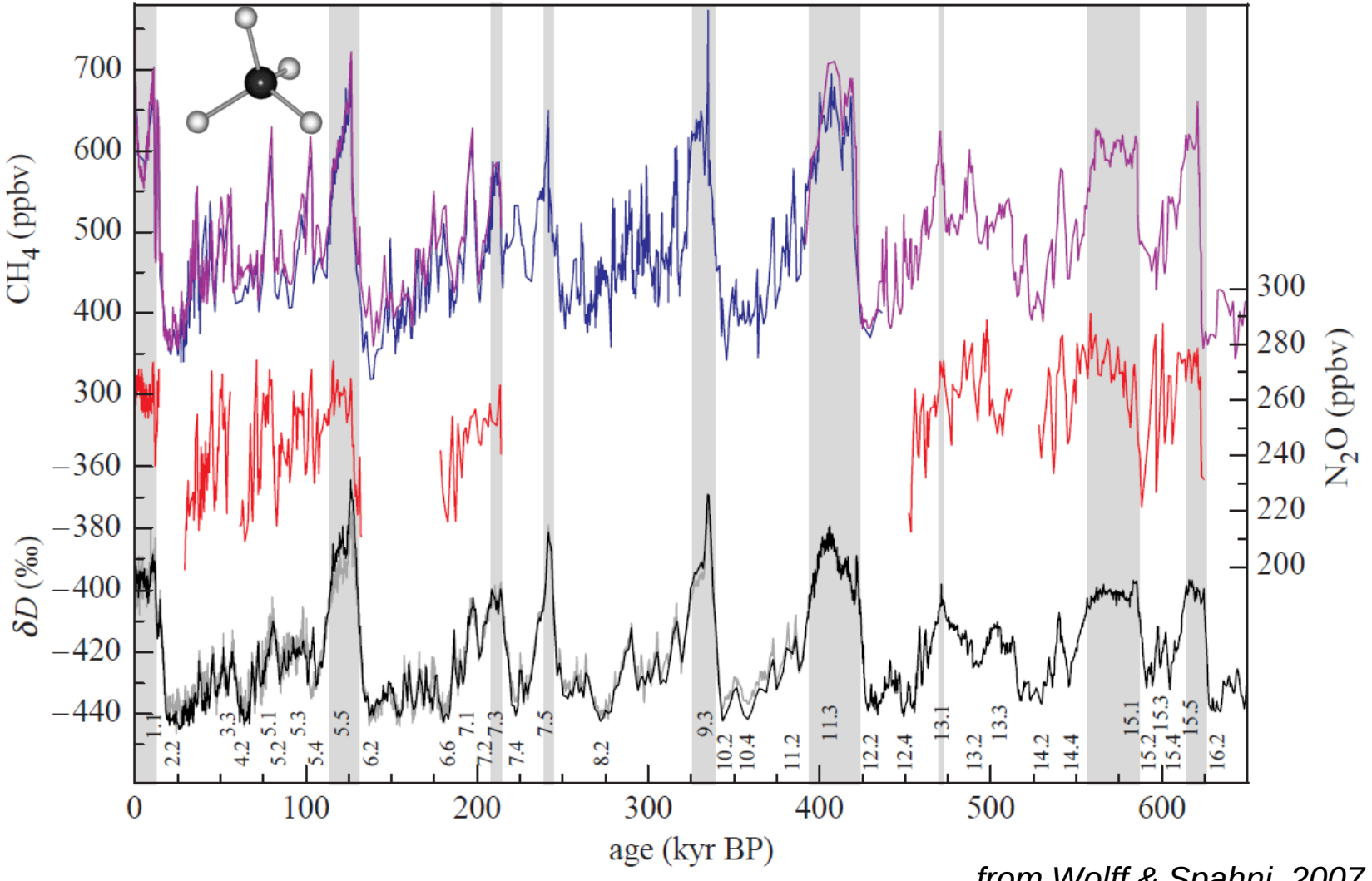
The role of forests/plants/eukaryotes in global cycling of CH_4

???



Methane in the biosphere

Preindustrial CH_4 patterns in ice cores…



from Wolff & Spahni, 2007

"Dem Anwenden muss das Erkennen vorausgehen."

Max Planck

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