SCOPE Nutrients and Climate Change: (1) – Aquatic Methane Emissions

This is the first of several **SCOPE Newsletter** special issues addressing the **links between phosphorus, nutrients and climate change**. These special issues are produced in cooperation between the Sustainable Phosphorus Alliance, North America, and the European Sustainable Phosphorus Platform.

As usual for SCOPE Newsletter, this issue is based on short 'layman's' summaries of selected recent scientific papers. We have also tried to draw overall conclusions from these papers.

Currently in preparation are further special issues on:

- **climate change, nutrient losses and eutrophication**
- **interactions between climate change, nutrients and soil carbon**
- **climate change impacts of nutrient recycling and stewardship technologies**

With special thanks to Matt Scholz, Sustainable Phosphorus Alliance, who led the authorship of this issue on nutrients and freshwater methane emission

Members of the European Sustainable Phosphorus Platform

Summary

New studies suggest that methane emissions from freshwaters may be significant for climate change. Nutrient inputs and eutrophication could significantly increase these emissions.

A number of studies have been published in recent years on ***the role that phosphorus loading of waterbodies plays in the production of greenhouse gases via microbial metabolism****.*

Much of this research has focused the ***production and release of methane*** *in freshwater lakes and impoundments.*

Methane has a Greenhouse Warming Potential of 28 – 36 x that of CO_2 (over 100 years, IPCC in Myhre 2013).

Waterbodies function as both greenhouse gas sources and sinks, burying carbon in their sediments and releasing methane, carbon dioxide, and nitrous oxides through biological processes, in particular when organic matter decomposes.

The methane emissions from freshwaters come both from methane production in the water and from sediments and are released to the atmosphere by advection / diffusion or, often, as bubbles (ebullition). In both cases, methane can be generated by breakdown of organic matter, usually by metabolism of microorganisms or possibly by degradation of organic matter by light (photolysis).

By increasing productivity (e.g. microbial, algal and plant growth), nutrient inputs (eutrophication) can increase the amount of organic matter available for methanogenesis.

Recent research (summarised in this Newsletter) shows however that ***methane can also be produced in well-oxygenated (oxic) water****, linked to photosynthesis by algae and cyanobacteria. Eutrophication can increase growth of both of these, but this oxic methane production can also be inversely related to soluble phosphorus.*

Further research is therefore needed to understand how nutrient losses impact overall methane production.

Freshwater methane emissions are a significant greenhouse gas

Saunois et al. (2016), in a Global Methane Budget, calculated that ***freshwaters contribute around ~122 Mt methane (CH_4) per year to climate gas emissions****. This includes open waters in lakes, reservoirs (impoundments), natural ponds, rivers and streams, but not emissions from vegetated areas bordering these. By comparison, the authors estimated wetlands methane emissions at ~185 Mt/yr and total oceanic emissions at only 2 Mt CH_4/yr (from biological sources and "methane hydrates" = sediment release). It should be noted that* ***there is a wide range of estimates for each of these numbers****.*

However, studies in the past 5 years, outlined below, suggest that even these large contributions of lakes and impoundments to methane emissions have been greatly underestimated (e.g. Beaulieu 2019), although there remains a considerable level of uncertainty and a need for further investigations.

It should be noted that, using figures from the International Panel on Climate Change, the "bottom-up" approach to calculating global methane emissions (i.e. summing estimated individual contributions) exceeds by ~60% top-down estimates (based on actual atmospheric measurements) (IPCC WG1AR5, 2013).

Attributing additional methane contributions to freshwater exacerbates this discrepancy, begging the question: Are the new estimates incorrect or are the current estimates for other natural sources overstated or for methane sinks understated?

Implications for nutrient management

Generally, the research outlined above supports the conclusion that we should abate phosphorus-driven eutrophication of freshwater if increasing methane emissions are to be avoided.

Eutrophication will lead to an increase in organic matter potentially available for metabolic conversion *to greenhouse gases either in the water column or, after sinking to the bottom, in anoxic sediments.*

The exacerbating effect of eutrophication on methane emissions has been modeled globally and measured locally in lakes, reservoirs and ponds.

Methylphosphonates

An exception to the generality that P inputs should amplify methane emissions from freshwaters involves ***methylphosphonate metabolism****, which appears to occur only when more readily available phosphates are in limited supply (non-eutrophic waters).*

Methylphosphonates are organic phosphorus molecules. Their consumption may release methane and occurs under aerobic conditions (i.e. in oxic waters). It is not clear how significant is such methane contribution compared to anoxic methanogenesis, nor whether such emissions would significantly increase with reductions in phosphorus loading.

It is to be noted that ***this methylphosphonate metabolism is related principally to naturally occurring phosphonates****.*

The largest anthropogenic input of phosphonates to the environment is in glyphosate herbicide: c. 150 ktP/y (see ESPP factsheet), which would result in insignificant methane emissions even if converted on a 1:1 molecular basis.

Oxic methane: the "Methane Paradox"

We need to better understand the mechanisms driving freshwater methane emissions, including the extent of oxic methanogenesis and the spatiotemporal dynamics of methane ebullition (bubbling) from sediments.

The current dogma states that diffusive fluxes of methane (not in bubbles) contribute little to freshwater methane emissions and that ebullition from sediments dominates production, with some diffusion from littoral sediments.

If it proves, however, that oxic methanogenesis in the water column (which results in diffusive fluxes) is also a major contributor to emissions (see e.g. Günthel et al. 2019, summarised below), then ***this could change nutrient management prescriptions*** *in some catchments.*

Research questions

Many questions are raised:

- *How might oxygenating sediments to reduce their release of legacy phosphorus impact both anoxic and oxic methanogenesis?*
- *Can the concentration of substrates for oxic methanogenesis, such as methylphosphonates, be reduced?*
- *Does fostering macrophyte (plant) dominance over phytoplankton to reduce eutrophication impacts reduce methane emissions?*
- *If photolysis of organics generates significant methane, could efforts to improve water clarity increase emissions?*
- *Or is the effect of reducing suspended organic matter, which may or may not be related to eutrophication, more significant in reducing methane emissions?*
- *Could lake "brownification" (see Graneli 2012) impact methane emissions due to photolysis?*
- *How do nutrient losses potentially influence methane emissions from estuaries and coastal seawaters?*
- *How significant are methane emissions from vegetated zones at the edges of freshwaters? …*

Overall, it can be concluded that ***freshwaters represent a major emission source for methane, making a significant contribution to total global greenhouse gas emissions****, and that* ***nutrient inputs and eutrophication can potentially considerably exacerbate these emissions in many surface waters****.*

However, there are contradictions in emissions estimates and divergences in understanding of mechanisms, and it is clear that more data and more research are needed.

Global Picture

Greenhouse gas emissions from lakes and reservoirs represent around 1/5th of those from fossil fuel combustion, and 75% of this impact is from methane.

DelSontro et al. 2018

DelSontro, T., Beaulieu, J.J., Downing, J.A., 2018. Greenhouse gas emissions from lakes and impoundments: Upscaling in the face of global change: GHG emissions from lakes and impoundments. Limnology and Oceanography Letters 3, 64–75. https://doi.org/10.1002/lol2.10073

DelSontro et al. estimated global emissions of CO_2, CH_4, and N_2O from lakes and impoundments (ponds, reservoirs) to be ~20% of global fossil fuel GHG-equivalent emissions. They did so by first conducting a meta-analysis of 223 studies from >53 countries of GHG fluxes and putative predictor variables, and then analyzing a global dataset of lake size distributions and productivities. The study was a refinement of traditional approaches, which simply multiplied average local/regional emission rates from lakes and impoundments by their global area footprint.

Models that considered waterbody size distributions and productivities were built using global size distributions obtained from each three published studies and productivity data from a prior remote sensing study of chlorophyll measurements from 80 000 lakes around the world. Concentrations of chlorophyll, a proxy for algal biomass, were correlated with total phosphorus (TP) concentrations, as expected. These models made the simplifying assumptions that daily emissions were constant, that areal emissions rates were constant within each lake category (defined by size x productivity), that there was no uncertainty in the emission flux rates reported in the literature, and that basin morphometry (beyond size) was unimportant.

CO_2 efflux was best described by a model that included lake size and TP. The authors note that total CO_2 emissions are higher across smaller systems than larger ones and could be sensitive to watershed changes, including changes to runoff patterns as a result of climate change. CH_4 emissions rose exponentially with chlorophyll concentrations, consistent with past smaller-scale studies. The authors suggest mechanisms, including eutrophication, leading to oxygen-poor but carbon-rich environments. N_2O emissions were best described by a positive interaction of chlorophyll and lake size, and the authors note the link between high biomass and both nitrogen loading (e.g. through fixation) and hypoxia-induced denitrification. In general, **the study found that previous estimates of CO_2 and N_2O emissions were overstated, but CH_4 emissions were understated by half**. Total CO_2-eq emissions estimated by their study—1.25 – 2.3 Mt annually—and previous ones were comparable, but differences lay in apportioning CO_2-eq to each gas. **About 75% of the climate impact was attributable to methane.**

Beaulieu 2019

Beaulieu, J.J., DelSontro, T., Downing, J.A., 2019. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. Nature Communications 10. https://doi.org/10.1038/s41467-019-09100-5

The authors calculated current total methane emissions from lakes and impoundments (only) worldwide at 150 $MtCH_4$/year. That is 25% higher than other recent estimates (Saunois 2016 estimated 95 $MtCH_4$/y for lakes and impoundments), possibly because the lower estimates are based on northern ecosystems.

Building upon the relationships determined in the paper reviewed above, the authors calculated the predicted effect of eutrophication on future methane emissions under a range of plausible phosphorus-loading scenarios. Citing published projections, they considered total phosphorus scenarios ranging from 0.75x to 2.2x current levels and correlated these to chlorophyll concentration scenarios. Modelling suggested increases in diffusive, and particularly in ebullitive, methane emissions from lakes and impoundments.

The authors calculated that a tripling of phosphorus inputs would double the current methane emissions from lakes and impoundments. Even a 1.5x increase in phosphorus inputs could result in an increase to 188 MtC-CH_4/year, which exceeds the current largest methane emissions source, wetlands, 185$MtCH_4$/year (Saunois, 2016). To put this in further perspective, **the authors estimated that the increased CH_4 emissions driven by amplified P loading will have a climate impact of 18-33% of current annual fossil fuel emissions by 2100**. The authors emphasized that this may be an underestimate, because it does not consider the synergistic impact on eutrophication of combining increases in temperature and nutrients, nor emissions from rivers and streams.

Local Analyses

Lake studies show that nutrient enrichment and eutrophication can increase ebullitive methane emissions (bubbles of methane from sediments)

Davidson et al. 2018

Davidson, T.A., Audet, J., Jeppesen, E., Landkildehus, F., Lauridsen, T.L., Søndergaard, M., Syväranta, J., 2018. Synergy between nutrients and warming enhances methane ebullition from experimental lakes. Nature Climate Change 8, 156–160. https://doi.org/10.1038/s41558-017-0063-z

Noting that shallow lakes and shallow areas of lakes tend to be methane-production hotspots, these authors studied the effects of changes in nutrient concentrations and temperature on methane fluxes from a system of fully mixed, shallow lake mesocosms some of which contained submerged plants in central Jutland, Denmark. Ebullitive fluxes—those contained

in bubbles that rise from the sediments—are notoriously difficult to measure because they are episodic and scattered, yet they can make up the majority of methane fluxes. The mesocosm study permitted the monitoring of 0.8% of the surface area of the lakes for ebullition, a relatively large percentage compared to typical lake studies.

Data suggested that both ebullitive and diffusive fluxes of methane increased with temperature, but that only ebullitive flux responded to nutrient enrichment. Nutrients were supplied at low (0.23 mg/L TN and 12.8 µg/L TP) and high (3.53 mg/L TN and 186 µg/L TP) concentrations. At ambient temperature, mean total flux raised from 266 mg CH_4-C/m^2/yr at low nutrient levels (51% ebullitive) to 552 mg/m^2/yr at high nutrient levels (75% ebullitive). By increasing temperature 2-3 degrees C, flux increased from 225 mg CH_4-C/m^2/yr (42% ebullitive) at low nutrient levels to 3988 mg/m^2/yr (90% ebullitive) at high nutrient levels. Increasing temperature 4-5 degrees C, flux increased from 500 (45% ebullitive) to 2369 mg/m^2/yr (75% ebullitive). It was notable that the combined effect of nutrients and temperature on ebullitive flux was synergistic rather than additive, resulting in 7-16 fold increases in ebullition.

The authors noted that much of the variance in their model remained unexplained, but that submerged macrophyte abundance correlated strongly with decreased ebullitive fluxes. This is perhaps because of methane oxidation (known to occur on plant surfaces), transport of oxygen to the sediments by plants, or other mechanisms. Nutrient enrichment in shallow waters, they noted, often leads to the seasonally dependent replacement of submerged plants by phytoplankton but not necessarily to overall increases in productivity. They argue that, in these shallow-lake systems, **a shift away from submerged plants to phytoplankton dominance may drive increased ebullition** and that managing methane emissions might be optimized by combining nutrient reduction strategies with efforts to foster macrophyte dominance.

West et al. 2016

West, W.E., Creamer, K.P., Jones, S.E., 2016. Productivity and depth regulate lake contributions to atmospheric methane: Lake productivity fuels methane emissions. Limnol. Oceanogr. 61, S51–S61. https://doi.org/10.1002/lno.10247

While much work has studied methane emissions from lakes to the atmosphere at the lake scale, studies on the production of methane are almost always undertaken at the lab or mesocosm scale. In this study, both methanogenesis and methane emissions were quantified across a set of 16 stratified, Wisconsin, US, lakes with a range of phosphorus, dissolved organic carbon, and chlorophyll concentrations. Chemical concentrations, ebullitive, and diffusive fluxes were measured (see paper for detail on the ebullitive measurements especially), and potential methanogenesis rates were inferred from sediment incubation experiments.

The authors determined that mixed layer **chlorophyll concentrations best predicted whole-lake rates of methanogenesis** and observed no significant difference in rates of methanogenesis between the littoral (near-shore) and pelagic (off-shore) zones. Nor did they observe any relationship between methanogenesis and diffusive emissions. However, they did find that total CH_4 emissions were strongly forced by ebullition that occurred almost solely at depths less than 6 m and at sites with a methanogenesis potential of greater than ~6 mmol CH_4/m^2/d.

The observed **positive correlation between methanogenesis rates in the sediments and lake productivity** (microbial, algal, and plant growth) comports with prior studies at the lab scale, and the authors noted that increased phytoplankton densities provide labile substrate for methanogenesis. Depth of methanogenesis plays a key role as hydrostatic pressure prevents bubble formation at greater depths and methane is oxidized in the oxic water column as it leaves the sediment. The authors noted that, while methane is not diffusively released from lakes during the stratified season, fall overturn can release methane stored in the anoxic hypolimnion during stratification, adding a seasonal component to emissions.

Lake Erie study links eutrophication to methane emissions

Fernandez et al. 2019

Fernandez, J.M., Townsend-Small, A., Zastepa, A., Watson, S.B., Brandes, J.A., 2019. Large increases in emissions of methane and nitrous oxide from eutrophication in Lake Erie (preprint). Ecology. https://doi.org/10.1101/648154

Lake Erie has a fairly shallow average depth (~19 m) and has both a long history of eutrophication and a recent history of re-eutrophication that has led to frequent algal blooms of sometimes massive scale. In this study (not peer reviewed), the authors set out to determine the extent to which the lake serves as a source or sink of CH_4, N_2O, and CO_2 at different times of the year.

Methane and N_2O emissions were calculated by comparison of water sample concentrations to air concentrations, adjusted for wind speed and temperature. Measured data were then extrapolated over 12 months and across the whole lake area. CO_2 emissions were measured only for one sampling cruise in the summer, when the lake showed negative emissions (carbon sink). **The sampling data showed that Lake Erie is a source (emitter) of methane throughout the year**, with highest emissions in spring and summer. **The lake was also a net N_2O source** but functioned as a sink in winter and sometimes temporarily during large phytoplankton blooms.

Sampling over five 4-day sampling cruises, covering Lake Erie's three basins, from May 2015 to September 2016, suggested that **methane (CH_4) and nitrous oxide (N_2O) emissions have increased ten times or more with re-eutrophication**.

Measured methane concentrations indicated that emissions were mainly eutrophication-related and not from natural gas extraction wells in the lake. The estimated net total methane

emissions for the lake were higher than the per-site emissions from most landfill sites in the region.

The total estimated greenhouse gas impact (CO_2 equivalent) of annual N_2O and **annual methane emissions from Lake Erie were comparable to burning 250 million tonnes of coal**.

Methane emissions from other surface waters: ponds, estuaries

Peacock et al. 2019

Peacock, M., Audet, J., Jordan, S., Smeds, J., Wallin, M.B., 2019. Greenhouse gas emissions from urban ponds are driven by nutrient status and hydrology. Ecosphere 10, e02643. https://doi.org/10.1002/ecs2.2643

Forty artificial urban ponds were sampled in the middle of the day on two consecutive days in late spring. They included ornamental park ponds, quarries, and stormwater ponds. Dissolved gases (methane, CO_2) and chemical parameters were analyzed. Greenhouse gas emissions were estimated using published gas velocity exchange coefficients (Hogerson & Raymond 2016) and water temperatures, multiplied by 275 ice-free days per year. (Note that this bases the whole year estimate on measured data for midday on one late spring date only.)

Dissolved methane concentrations (median 26 µg CH_4-C/l) were comparable to previous Swedish pond data (Natchimuthu 2014) and an order of magnitude higher than the global median for streams and rivers (3 µgCH_4/l, Stanley 2016). **Methane was correlated with both total phosphorus and DOC (dissolved organic carbon) concentrations, suggesting higher methane release with eutrophication**. Annual methane emissions were estimated to be 30 mg methane/m^2/day. This is noted to be similar to other study data for Swedish agricultural ponds (80 mg – Stadmark 2005), wet stormwater basins USA (88 mg, McPhilips 2015), urban streams USA (80 mg, Smith 2017) but lower than for tropical and subtropical ponds: 287 mg (India, Selvam 2014), 115-453 (Australia, Ollivier 2018). Dissolved CO_2 was correlated with silicon and calcium and was linked to groundwater inputs not eutrophication. 28 ponds were net emitters of CO_2 (during this midday testing) and 14 were net sinks (may not be valid if night was also included). Net annual diffuse CO_2 emissions extrapolated from the sampling data was c. 750 mg CO_2/m^2/day.

Extrapolating to all Swedish urban ponds, the authors suggest that **small water bodies such as these could alone contribute 0.1% of Swedish agriculture's total greenhouse emissions**, and this does not include ebullitive methane emissions which were not measured in this study.

Myllykangas et al. 2020

Myllykangas, J.-P., Hietanen, S., Jilbert, T., 2020. Legacy Effects of Eutrophication on Modern Methane Dynamics in a Boreal Estuary. Estuaries and Coasts 43, 189–206. https://doi.org/10.1007/s12237-019-00677-0

The authors investigated the seasonal and spatial variability in methane dynamics in the eutrophic Finnish Pojo Bay estuary and in the Baltic Sea over three years. Through periodic sampling for water column and sediment parameters, spatial methane dynamics were studied at 11 sites from the river mouth (start of the estuary) out to sea, and seasonal methane dynamics were studied at 2 sites, one within the deeper main channel and one near an archipelago. In addition to measuring methane concentrations in the water column and sediment, sediment sulfate and hydrogen sulfide profiles were generated. Flux of methane from the sediment to the water column was calculated using Fick's first law, and a published model was used to calculate methane transport from the water column to the atmosphere.

From a spatial perspective, the highest methane concentrations were found near the river mouth entering the estuary (highest = 665 nM), and surface concentrations were consistently lower offshore. In the sediment, areas near the sill (between sea and bay) were largely devoid of methane, which was expected as sediment doesn't accumulate in those areas, whereas it does in bathymetric depressions that showed elevated methane concentrations and fluxes across the sediment-water interface. No correlations were found between sediment and atmospheric fluxes (but ebullitive flux wasn't measured). Seasonally, sediment flux was higher yearlong near the archipelago than in the channel, and while fluxes peaked near the archipelago in summer and dropped to their lowest in spring and autumn, the opposite was true near the channel.

Overall, the estuary acted as a methane source to the order of 5 589 mol CH_4/day, with average surface water saturation of 4 148% as compared to typical Baltic Sea surface water saturation of less than 500%. Concentrations of methane were lower in winter than summer. **The highest methane fluxes were within the estuary but, because of the larger area, the greatest quantitative emissions to the atmosphere came from the maritime archipelago regions along the coast**. Deeper, more stratified locations produced greater diffusive flux from the sediments to the water column, but diffusive flux was observed everywhere except near the organic-poor sill.

The depth of the **sulfate-methane transition zone** varied considerably. In this layer of the sediment, conditions switch from net production to net consumption of methane. Methanogenesis generally occurs below this zone. The greater the depth of the oxidizing layer above, the less chance there is for methane to reach the water surface and be emitted to the atmosphere.

Da Fonseca Viana et al. 2019, 2020

Da Fonseca Viana, A., dos Santos, M., Corrêa Bernardes, M., Amorim, M., 2019. Greenhouse gas emission from a eutrophic coastal lagoon in Rio de Janeiro, Brazil. LAJAR 47, 638–653. https://doi.org/10.3856/vol47-issue4-fulltext-6

Da Fonseca Viana, A., dos Santos, M., Corrêa Bernardes, M., Amorim, M., 2020. Organic matter composition related to methane ebullitive flux of an urban coastal lagoon, southeastern Brazil. Quim Nova in print. http://dx.doi.org/10.21577/0100-4042.20170373

In the first paper, Da Fonseca Viana et al. studied the eutrophic Rodrigo de Freitas coastal lagoon, near Rio de Janeiro, Brazil, 2.2 km^2 area, average depth 2.8m, with one limited canal connection to the sea. The lagoon is fed by the Cabeça, Macacos and Rainha rivers, which pass through urban areas and receive large volumes of sewage. Four sampling cruises, measuring diffusive and ebullitive flux and collecting sediment and water from different depths at 14 -17 sites, were carried out April, June, October and December 2016. Diffusive and ebullitive gas was also collected.

CO_2 diffusive flux ranged from -343 to -1883 mg/m^2/day (mean = -1467 mg/m^2/day), that is, the lagoon is a sink for atmospheric CO_2. Methane diffusive flux ranged from +55 to +159 mg/m^2/day (mean = +114 mg/m^2/day), that is, the lagoon emits methane to the atmosphere. CO_2 ebullitive flux presented a mean of +5 mg/m^2/day, whereas methane mean ebullitive flux was +58.3 mg/m^2/day. The highest flux values occurred near the mouth of the Cabeça and Macaco rivers, a zone with discharge of particulate matter in suspension, indicating that urbanization impacts the lagoon.

The data showed a positive correlation between water temperature and ebullitive gas fluxes, a positive correlation between percentage of sand in the sediment and ebullitive flux, but a negative correlation between depth and ebullitive gas fluxes. Diffusive flux presented an inverse correlation with wind speed at time of sampling, possibly because wind speeds were always low.

The authors conclude that the lagoon was an emissions source for methane but a carbon dioxide sink, this being typical for eutrophic freshwaters. They estimate CO_2 uptake at c. 540 gCO_2/m^2/year, that is c. 1 200 tonnes CO_2 for the 2.2 km^2 area of the whole lagoon. They calculate annual ebullitive methane emissions of 21 42 g/m^2/year and diffuse emissions of 42 g/m^2/year. That is, c. 140 tonnes of methane per year for the 2.2 km^2 area coastal lagoon, greenhouse gas equivalent to c. 4 800 tonnes/year of CO_2 (using an equivalence of 34, IPCC, Myhre 2013).

In the second paper, the authors compare n-alkane and sterol concentrations in the top 2 cm of sediments to data for methane ebullitive fluxes, concluding that these compounds are correlated with methane emissions, and so that the **methane emissions are largely the consequence of inputs of sewage and petroleum derivative chemicals to the lagoon**.

Oxic Methanogenesis

Oxic methanogenesis is the production of methane under aerobic conditions. Previously, it was thought that microorganisms (archaea) only produced methane in the anaerobic sediments, because oxygen suppresses their methanogenesis.

*One would thus expect the highest methane concentrations to be observed nearer to the sediments, but this often isn't the case. This the "**Methane Paradox**". Various hypotheses have been put forward to resolve this paradox (see box) and this is an active area of research.*

Mechanisms proposed/demonstrated to explain the Methane Paradox are outlined below.
For a full discussion, see Bizic et al. 2020.

- ***Methane generation in oxic layers near the surface through metabolism of organic compounds***
  - *Suppressed by phosphates: methylphosphonate metabolism (see papers by Khatun, Wang, and Yao below; for an excellent review of phosphonate metabolism, see McGrath, 2013. Note the comment in the introductory summary of this SCOPE Newsletter concerning anthropogenic vs. biogenic origins of phosphonates.*
  - *Not suppressed by phosphates: metabolism of methylated sulforganics (see Lenhart below), metabolism of acetic acid (acetoclastic methanogenesis, see Bogard 2014, experimental demonstration in enclosures Lac Cromwell, near Montréal, not reviewed here)*
- ***Methane generation through photolysis of organics** (Zhang, 2015; Xie, 2019 not reviewed here), which will depend on water clarity (Secchi depth). Methlphosphonates can also be degraded to produce methane in water (Yu, 2018, not reviewed here)*
- *Autotrophic methanogenesis (see Lenhart below), that is **from dissolved CO_2 present in water***
- ***"Classic" methanogenesis***
  - *by oxygen-tolerant, anaerobic methanogens in the oxic layer (Grossart, 2011; not reviewed here)*
  - *by anaerobic microorganisms in anoxic compartments in the oxic layer*
  - *in littoral sediments, then laterally transported to the oxic layer of nearby deeper waters (see Peeters reviewed here)*
  - *in sediments, then transported through aquatic plants after being taken up by their roots, or transported upward by aquatic invertebrates via gas sacs.*

Donis et al. 2017

Donis, D., Flury, S., Stöckli, A., Spangenberg, J.E., Vachon, D., McGinnis, D.F., 2017. Full-scale evaluation of methane production under oxic conditions in a mesotrophic lake. Nature Communications 8. https://doi.org/10.1038/s41467-017-01648-4

The authors attempted to quantify methane sources with the oxic surface layer of Lake Hallwil (non-eutrophic, Switzerland). Monthly water column profiles were developed across multiple parameters (DOC, TP, chlorophyll, etc), and water column and pore water CO_2 and CH_4 concentrations were measured along with ^{13}C isotopic abundance. Sediment organic carbon and ^{13}C were also measured. A mass balance was developed that described methane fluxes across various zones within the lake and from riverine inputs.

The data suggested that 63 – 83 % of lake methane emissions were produced in the lake surface layer (oxic = rich in oxygen, during stratified periods). Carbon isotope ratios confirmed this route for lake methane production. Low observed rates of methane oxidation suggested that methane generated in the lake would mostly escape to the atmosphere.

The lake's net production of methane in surface water in spring-autumn was estimated at c. 110 mmol CH_4/L/day. The authors suggested that **methane production may be related to dissolved organic carbon (DOC), which is related to algal development and breakdown**, perhaps by ultraviolet light breakdown of DOC releasing methane. They note that lake stratification means that methane generated is delivered to the atmosphere, so that climate warming may increase methane release by increasing lake stratification, as well as increasing algal development and imports of carbon from runoff and erosion.

Methane production in well-oxygenated waters may lead to significant atmospheric emissions

Günthel et al. 2019

Günthel, M., Donis, D., Kirillin, G., Ionescu, D., Bizic, M., McGinnis, D.F., Grossart, H.-P., Tang, K.W., 2019. Contribution of oxic methane production to surface methane emission in lakes and its global importance. Nat Commun 10, 5497.
https://doi.org/10.1038/s41467-019-13320-0

In this study, the authors conducted a methane mass balance on two bays and a set of experimental enclosures in meso-oligotrophic Lake Stechlin in NE Germany. Dissolved methane concentrations were measured, while surface methane emissions were either measured with a flux chamber or modeled with a wind-based model that used flux chamber measurements. A model to predict oxic methane emissions from the "surface-mixed layer" as a function of lake morphology was produced.

Consistent with the methane paradox, during the stratified season of June and July, methane concentrations in the basins and in the enclosures at a depth of 5-7m exceeded those at greater depths down to 18m, and none of the water columns experienced anoxia. During stratification, surface methane emissions in the bays increased by an order of magnitude compared to the non-stratified season. Diffusive methane input from the thermocline to the surface-mixed layer was small, and not only was no ebullition observed, but the authors cite previous studies that confirm low methanogenesis in the lake's sediments. Importantly (see Peeters above), the experimental enclosures experienced no lateral methane input from the littoral zone of the bay. This allowed comparisons between methane in the bay and in the enclosures, so enabling estimation of methane transport from the littoral sediments of the bay to the surface-mixed area of the pelagic waters. From this, it was determined that either 64% or 50% (depending on the bay) of the surface methane emissions could be attributed to oxic sources, and that >95% of emissions were explained by summing in situ oxic methane production and methanogenesis laterally transported from littoral sediments.

Differences in the morphology of the two basins suggested that as lake size increases or littoral sediment areas decrease, the oxic methane emissions increasingly dominate over those from the littoral sediments. The authors estimate that this dominance is true of lakes larger than 1 km^2 (oligo to mesotrophic systems). They compared the results of their surface emissions model to those of six alternative emission models that had been published and found that while the results varied somewhat, the oxic methane contribution still accounted for 32-68% of the surface methane emissions they observed. They then applied their empirical model to a global distribution of lakes obtained from satellite data (Cael, 2017) after making rough estimates of likely littoral sediment areas and surface-mixed layer volumes across the distribution. **This model suggested that perhaps 66% of all lake methane emission may be the result of oxic production**.

Peeters et al. 2019

Peeters, F., Encinas Fernandez, J., Hofmann, H., 2019. Sediment fluxes rather than oxic methanogenesis explain diffusive CH4 emissions from lakes and reservoirs. Sci Rep 9, 243.
https://doi.org/10.1038/s41598-018-36530-w

Disputing the findings of Donis et al. above, the authors argue that, for lakes and reservoirs, diffusive fluxes of methane from sediments alone can account for lake surface emissions without positing oxic methanogenesis. The authors also have a discussion paper in preparation questioning the conclusions of Günthel et al. above.

The authors collected 1 346 previously published measurements of methane concentrations in surface waters, spatially distributed across 10 diverse lake basins and reservoirs, including a seasonally resolved dataset for Lake Uberlingen (part of Lake Constance, in Germany), along

with surface temperature and wind data. They used this information to inform a methane mass-balance model within the surface-mixed layer of the waterbodies. They then used the model to re-analyze the data of Donis et al.

The authors calculated an average sediment flux of 2 mmol/m^2/d in their lakes—within the range of published values—and note a strong positive correlation with temperature. Although lower than those observed by Donis in Lake Hallwil, **the calculated sediment fluxes were still sufficient to account for the total diffusive atmospheric emissions of methane** in this lake/reservoir dataset. Furthermore, they found that, contrary to Donis, a re-analysis of the Lake Hallwil (Switzerland) data demonstrated that the sediment flux required to explain that lake's emissions was smaller (not ~26 times greater, as Donis claimed) than what was observed.

Finally, seasonal methane concentrations in Lake Uberlingen over two years - both measured and modeled - suggested that concentrations nearshore were typically larger than they were further out, which would not happen if oxic methanogenesis per unit surface area in the open water zone were greater than sediment methanogenesis per unit surface area nearshore (and atmospheric flux from open water sediment methanogenesis were negligible, as expected).

The authors attribute the discrepancies between their data and that of Donis et al. to a value the latter authors used for the area of the shallow water zone in the surface mixed layer of Lake Hallwil that is ~6 times smaller than the published value, and go on to note that they (Donis) also underrepresented by ~1.7x the concentration gradient from their own measurements of pore-water methane concentrations. They further point out that the isotopic composition of the open water and shallow sediment pore-water methane are essentially the same in the Donis study, suggesting that the latter is the source of the former.

The authors' conclusions are coherent with those of Encinas Fernández et al., 2016 (referenced below) that littoral (nearshore) sediment methane production, which can then be laterally transported to deeper waters, is the dominant cause of methane emissions from lakes. This paper was based on methane sampling in surface water in nine basins in seven lakes in southwest Germany. The paper concludes that mean **surface-water methane concentrations are significantly correlated with the ratio between the surface area of the shallow water zone and that of the entire lake**, but not with the entire lake surface area.

Oxic methane production is linked to Dissolved Organic Carbon

Khatun et al. 2020

Khatun, S., Iwata, T., Kojima, H., Ikarashi, Y., Yamanami, K., Imazawa, D., Kenta, T., Shinohara, R., Saito, H., 2020. Linking Stoichiometric Organic Carbon–Nitrogen Relationships to planktonic Cyanobacteria and Subsurface Methane Maximum in Deep Freshwater Lakes. Water 12, 402.
https://doi.org/10.3390/w12020402

See also the Phosphorus Science Now! Episode, "Carbon, Nitrogen, Phosphorus and Subsurface Methane Production in Freshwater Lakes", available on YouTube
https://youtu.be/iLEohDXOR7M

Building on past studies (Khatun, 2019), the authors sought to better understand the mechanisms behind the development of what they term the "subsurface methane maximum" (SMM) in the metalimnion of nine non-eutrophic (ultra-oligotrophic to mesotrophic) freshwater lakes in Japan during the summer stratification period. They developed vertical water profiles at the deepest point of each lake on a single day by collecting measurements on an array of parameters, including bacterial composition and nitrogen and phosphorus concentrations and speciation. These data were used to inform a model to identify variables that affected methane concentrations in the SMM.

The study confirmed methane production in the oxic surface water of all 9 lakes. Across these 9 non-eutrophic lakes x different depths, **water methane concentration was positively correlated with dissolved organic carbon (DOC), which was the best explanatory variable, and also with dissolved organic phosphorus (DOP),** but was negatively correlated with dissolved inorganic nitrogen (DIN). The peak SMM was positively correlated with DOC, DOP, and the cell density of the cyanobacterium *Synechococcus*, which has been shown in batch-culture experiments to produce methane under oxic, low-phosphate conditions through the metabolism of phosphonates.

The authors note that there were no tributary streams to some of these lakes and that vertical methane profiles and manganese profiles (used to trace water transported from anoxic environments) suggested no substantial contribution of methane from the hypolimnion (bottom waters) or anoxic environments generally, including littoral (shoreline) sediments. They suggest that DOC may control CH_4 production in the oxic layer by sustaining nitrogen-depleting heterotrophs that metabolize the DOC, which facilitates domination by photosynthetic and nitrogen-fixing cyanobacteria that produce methane through phosphonate metabolism in phosphate-depleted lakes.

Hartmann et al. 2020

Hartmann, J., Günthel, M., Klintzsch, T., Kirillin, G., Grossart, H-P., Keppler, F., Isenbeck-Schröter, M., 2020. High Spatiotemporal Dynamics of Methane Production and Emission in Oxic Surface Water

The authors measured methane production in the water column of the mesotrophic Lake Stechlin, northeast Germany. Previous studies have shown methane concentrations over 1.4 µM in the oxygenated upper water column but low sediment methane (Grossart 2011, Tang 2014, McGinnis 2015). Methane concentrations and stable carbon isotopes ratios ($\delta^{13}C\text{-}CH_4$) were measured continuously over 11 days at one site in June to assess methane production rates. During this period, weather was sunny and the water column was well oxygenated.

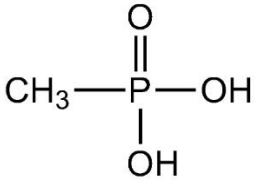
Laboratory incubation tests of methane production were carried out using two different experimental designs, one using ^{13}C-labeled bicarbonate as the sole carbon source, with 8 different phytoplankton species, representing each of the lake's main phytoplankton types: 2 green algae, 3 diatoms, and 1 cryptophyte from Lake Stechlin, and 2 cyanobacteria from a culture collection in Sevilla, Spain.

Water column methane concentrations were variable over the sampling period in the upper water layer but always higher than saturation (>3nM) and showed correlation with pigment abundance of various phytoplankton types. Concentrations (~200 nM) were more stable below the thermocline (> 7 m depth). Methane emissions to the atmosphere depended principally on wind speed, varying from 0.5 to 2.7 mmol-CH_4/m^2/day. **All 8 phytoplankton species tested showed methane production in oxic conditions in the laboratory experiments**.

Interestingly, results showed that oxically produced methane has a substantially higher carbon isotope signature compared to anoxically produced methane, offering an experimental path to discriminate between these two methane sources.

Methylphosphonates and methane production

Methylphosphonates (MPn), widely-present, biogenic, organo-phosphorus compounds, may be significant in methane production



Methylphosphonic acid

Yao et al. 2016

Yao, M., Henny, C., Maresca, J., 2016. Freshwater Bacteria Release Methane as a By-Product of Phosphorus Acquisition. Appl. Environ. Microbiol. 82, 6994–7003. https://doi.org/10.1128/AEM.02399-16

The authors tested the hypothesis that **methylphosphonates (MPn), which may contribute up to 10% of dissolved organic P in some lakes, may be aerobically catabolized (broken down, producing methane and phosphate) to produce at least some of the methane** in the methane-supersaturated, permanently stratified, and P-limited Lake Matano, Indonesia. They tested this through a combination of metagenomic and gene expression analyses and physiological experiments. They searched for the presence in the lake water of genes known to catabolize methylphosphonates, tested 7 strains of bacteria isolated from the lake water for their ability to use MPn as their sole phosphorus source, and measured the expression of MPn catabolizing genes and methane generation from lab cultures of these bacteria.

They found that all the genes necessary for breaking down methylphosphonates (MPn) were available in the lake water but that those required for methanogenesis were missing at depths > 10 m, suggesting either a failure to detect or no aerobic methanogenesis at these depths. However, 4 bacterial isolates could use MPn as a sole phosphorus source, and 3 of these produced methane when grown on MPn phosphorus alone. Methane production was inhibited by phosphate addition, as was the expression of the phnJ gene responsible for C-P lysis in MPn.

The authors note that genes in the phosphonate metabolic pathway are widely distributed in freshwater systems but that phosphonates themselves may be difficult to detect because of rapid metabolism—something that has been demonstrated in marine systems.

Wang et al. 2017

Wang, Q., Dore, J., McDermott, T., 2017. Methylphosphonate metabolism by Pseudomonas sp. populations contributes to the methane oversaturation paradox in an oxic freshwater lake: Methylphosphonate and aquatic CH 4 oversaturation. Environ Microbiol 19, 2366–2378. https://doi.org/10.1111/1462-2920.13747

The authors studied methanogenesis in the narrow (1-2 m) pelagic methane enriched zone (PMEZ) of Lake Yellowstone, US. The PMEZ can occur in oxygen-saturated lake water just below the thermocline in stratified water columns.

In laboratory studies, water samples from the PMEZ were spiked with a number of substrates labeled with 13C, including bicarbonate, formate, acetate, methylamine, and methylphosphonate (MPn) to study generation of radiolabeled methane.

Of these substrates, **only methylphosphonates (MPn) yielded radiolabelled methane**. Colonies of 3 bacterial species isolated from the lake water grew best on MPn as a sole P source and were selected for further study. A species of Pseudomonas grew the fastest of the three on methylphosphonate, generated the most methane, and possessed genes known to participate in phosphonate metabolism. This Pseudomonas species was highly abundant in lake water samples at the depth of the maximal methane concentration in the PMEZ, where the other two bacteria were not abundant or not detected. Tests for other species of methanogens in the PMEZ failed to detect, suggesting this species contributed to the methane maximum, though the authors note that methanogens harbored in larger organisms or in clumps of material would have been filtered out and missed in their tests.

The authors note that the lab experiments suggest a methane pool turnover time of 67 +/- 19 days, which is consistent with the seasonal development of PMEZ during summer stratification. They further note a number of microorganisms as plausible synthesizers of MPn in the lake. **They conclude that oxic methanogenesis from methylphosphonates by these bacteria could contribute to explaining the methane paradox in Lake Yellowstone.**

Algal methane production

Both photosynthetic algae and blue-greens can produce methane

Lenhart et al. 2016

Klintzsch et al. 2019

Lenhart, K., Klintzsch, T., Langer, G., Nehrke, G., Bunge, M., Schnell, S., Keppler, F., 2016. Evidence for methane production by the marine algae Emiliania huxleyi. *Biogeosciences 13, 3163–3174.* https://doi.org/10.5194/bg-13-3163-2016

Klintzch, T., Langer, G., Nehrke, G., Wieland, A., Lenhart, K., Keppler, F., 2019. Methane production by three widespread marine phytoplankton species: release rates, precursor compounds, and relevance for the environment, Biogesciences Discussions https://doi.org/10.5194/bg-2019-245

The methane paradox also applies to the oceans, where the surface-mixed layer is frequently oversaturated with methane despite the fact that the methane is unlikely to have arisen from deep-water sediments or have been transported laterally transport from coastal sediments. In Lenhart et al., 2016,he authors searched for direct evidence of methane production from a ubiquitous photosynthetic marine algae, *Emiliania huxleyi*, and to identify substrates for methanogenesis.

Isotopically (^{13}C) labeled bicarbonate or methionine, a sulfurous amino acid, were supplied to cell cultures of the algae as grown under autotrophic conditions with supplemental phosphate. Both produced methane in oxic cultures that were carefully screened to ensure absence of methanogenic bacteria. However, only ~3% of the methane generated in the methionine cultures could be traced to ^{13}C-labeled methionine, and the authors suggest that either methionine synthesized *de novo* by the organism had become a substrate of methanogenesis or another, unidentified methane precursor was metabolized.

While this study revolved around a marine organism, it offers a demonstration that **methane can be generated in oxic environments by algae** from both CO_2 via bicarbonate (i.e. autotrophically) and methionine. Because the algae were not phosphorus limited, the substrate for methane production would not have been methylphosphonates.

Further experiments presented in Klintzsch et al., 2019, showed also **oxic methane production by the widespread marine haptophyte algae** *Phaeocystis globosa* and *Chrysochromulina sp*. ^{13}C labelling showed oxic methanogenesis **both from bicarbonate and from methylated sulphur compounds** (dimethyl sulfide, dimethyl sulfoxide and methionine sulfoxide).

Bižić et al. 2020

Bižić, M. (Bizic), Klintzsch, T., Ionescu, D., Hindiyeh, M.Y., Günthel, M., Muro-Pastor, A.M., Eckert, W., Urich, T., Keppler, F., Grossart, H.-P., 2020. Aquatic and terrestrial cyanobacteria produce methane. Sci. Adv. 6, eaax5343. https://doi.org/10.1126/sciadv.aax5343

Bižić-Ionescu, M. (Bizic), Ionescu, D., Günthel, M., Tang, K.W., Grossart, H-P., 2018. New evidence for methane formation in oxic lake water, In: Stams, A.J.M., Sousa, D.Z., (ed), Handbook of Hydrocarbon and Lipid Microbiology Series. Biogenesis of Hydrocarbons, Springer International Publishing https://doi.org/10.1007/978-3-319-53114-4_10-1

In the 2020 paper, citing evidence of widespread oxic methanogenesis observed across multiple biological domains, the authors showed that **methane can be produced also by a wide range of different cyanobacteria, from freshwater, saltwater and soil, in both light as well as dark and oxic and anoxic conditions**.

13 different cyanobacteria were incubated in nutrient-replete, sterile cultures, using ^{13}C-labelled sodium hydrogen carbonate as carbon source. All tested cyanobacteria produced methane from this carbon source, up to 110 pmol $CH_4/10^6$cells/hour for marine cyanobacteria. The authors ruled out methylphosphonate metabolism, methanogenesis by co-cultured archaea, methanogenesis during nitrogen fixation, and fermentation of storage compounds as sources of the observed methane.

Observed methane production rates were several orders of magnitude lower than those reported for archaea (in anoxic

conditions) but several orders higher than for eukaryotes, such as plants, fungi, and algae. However, the authors note the ubiquity of cyanobacteria in Earth's ecosystems and their increasing prevalence in eutrophic waters.

In the 2018 paper, the authors cultured cyanobacteria and bacteria from Lake Stechlin, northeast Germany, in the laboratory, showing **methane formation from methylphosphonates and also from methylamines, which are a common decomposition product of organic matter in freshwaters**.

In a further paper currently under finalization (Günthel M. et al., Limnology and Oceanography), the authors present further studies on Lake Stechlin and laboratory culture tests of methane production by lake water and by pure diatom cultures, including using ^{13}C labelling, under different conditions. Labelling experiments with lake water containing microorganisms in oxic conditions showed net methane production in light and net methane oxidation in darkness, whereas methane oxidation rates were not light dependent. Oxic methane production was observed throughout the entire water column with highest production rates in surface water (mimicking the in situ chlorophyll and methane concentration profile). Methane production was reduced by addition of dissolved phosphate. Tests with lake water filtered at 20 µm suggested that methane production was mainly related to larger fractions, probably mainly cyanobacteria, diatoms and green algae, whereas smaller fractions contributed more to methane oxidation.

Several points suggest that methane production is linked to photosynthesis: methane correlation to pigment concentration in the lake, in situ methane concentration aligning with the diurnal cycle, net methane production related to light in culture tests and higher production in > 20 µm filtered water, conversion of ^{13}C labelled bicarbonate to methane.

The authors conclude that **methane production in well-oxygenated (oxic) water, linked to photosynthesis, and in particular to cyanobacteria, could be widespread and significant, posing questions for climate predictions and water management.**

Eutrophication may affect oxic methane production via different mechanisms:

- long-term effect: **total increase of phytoplankton** -> more oxic methane production
- long-term effect: **more biomass may provide more precursor molecules** (methylphosphonate metabolism)
- long-term effect: **natural selection** - increasing the ratio of phytoplankton species with higher production rates (i.e., cyanobacteria)
- short-term effect: **depleting the existing phytoplankton community of phosphorus** may lead to temporal burst of methane emission.

See also the review by Tang et al., 2016.

León-Palmero et al. 2020

León-Palmero, E., Contreras-Ruiz, A., Sierra, A., Morales-Baquero, R., Reche, I., 2020. Dissolved CH4 coupled to Photosynthetic Picoeukaryotes in Oxic Waters and Cumulative Chlorophyll-a in Anoxia (preprint). Biogeochemistry 17 (12): 3223-45 https://doi.org/10.5194/bg-17-3223-2020.

Many of the potential sources for methane in the oxic zone have been tested in lakes but not reservoirs. These authors considered various possible explanations for oxic methanogenesis in reservoirs, including vertical and lateral transport of methane, production by Archaea, release in methylphosphonate degradation, and production by cyanobacteria and photosynthetic "picoeukaryotes" (diverse eukaryotic organisms of around 3 µm or less in size). They studied 12 physically and chemically diverse reservoirs in southern Spain during both summer stratification and winter mixing periods.

Though all reservoir depths, oxic and anoxic, were consistently supersaturated with methane, the authors discovered great variability in concentrations across both depths and seasons. In each reservoir, dissolved methane concentration gradients across depths displayed one of three different profiles, but in none was the methane peak in the "surface mixed layer" observed (peak reported in other studies). In the anoxic water column, waterborne methanogens were ruled out on genetic and other grounds as methane sources. Rather, methane concentrations were found to depend on chlorophyll-*a*, a proxy for phytoplankton biomass in the whole water column, and it was assumed that decomposition of this biomass in the sediments fueled methanogenesis and subsequent upward methane diffusion. In oxic waters, lateral transport from shallow sediments and methylphosphonate metabolism were all ruled out as suitable explanations for methane concentrations.

The authors found that the abundance of photosynthetic picoeukaryotes, more than that of cyanobacteria, predicted methane concentrations during both mixed and stratified seasons. The mean depth of the reservoirs, as a surrogate of the vertical methane transport from sediment to oxic waters, also contributed notably to the methane concentration in oxic waters.

The authors suggest that photosynthetic metabolism by picoeukaryotes and cyanobacteria may trigger internal biochemical pathways involved in methane production (c.f. Lenhart et al. 2016 above) or that organosulfur compounds generated during photosynthesis may degrade to release methane. Thus, **picoeukaryotes and cyanobacteria in the oxic water column may directly generate methane or its precursors**, prior to and in addition to their subsequent decomposition in anoxic sediments, which fuels anaerobic methane production. **In both cases, eutrophication would drive greater methane release**.

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