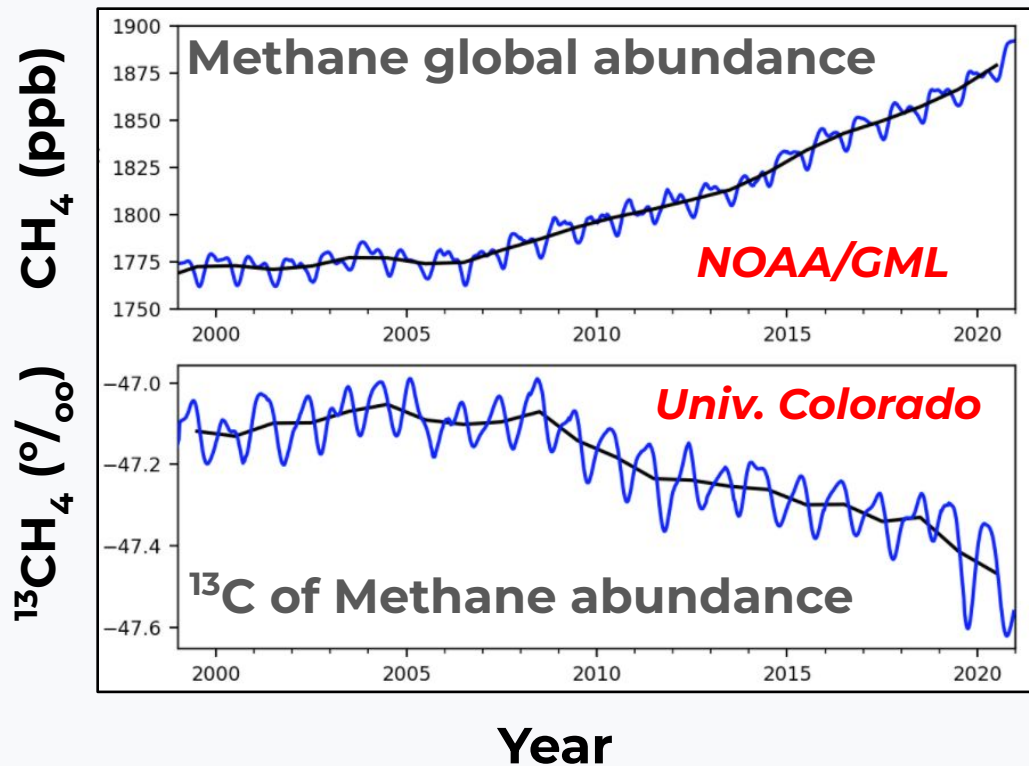


Atmospheric Methane Removal Research

Erika Reinhardt and David Mann, Ph.D.
Spark Climate Solutions

Motivation: Growing natural methane emissions



Rapid rise in global mean atmospheric CH_4 abundance in recent years.

Isotopic methane measurements ($^{13}\text{C}/^{12}\text{C}$) indicate microbial sources may be causing much of the recent global increase in methane (CH_4)

Natural methane removal pathways



Soil Uptake:
30-40 Tg/yr

Tropospheric
Cl: 10-25 Tg/yr

Stratospheric
Chemistry:
30-50 Tg/yr

Tropospheric OH:
530-550 Tg/yr

Limited supply of
OH (UV-limited)
→ **CH₄ lifetime is not
constant**, increases
as concentration
increases

Historically half-life
has been ~10 years



- Not a substitute for emissions avoidance; avoidance always first priority
- Important additional lever to help mitigate additional damages from methane-emitting natural feedbacks (e.g. wetlands), while continuing to pull all other levers to mitigate climate change
 - CO₂ reductions, CDR, CH₄ reductions, etc. in parallel are crucial
- To be a meaningful lever, must target large scale (> ~50 Tg/yr)

Focus of this presentation is on atmospheric concentrations (currently 2ppm) due to focus on mitigating impact of methane-emitting natural feedbacks and climate tipping elements.

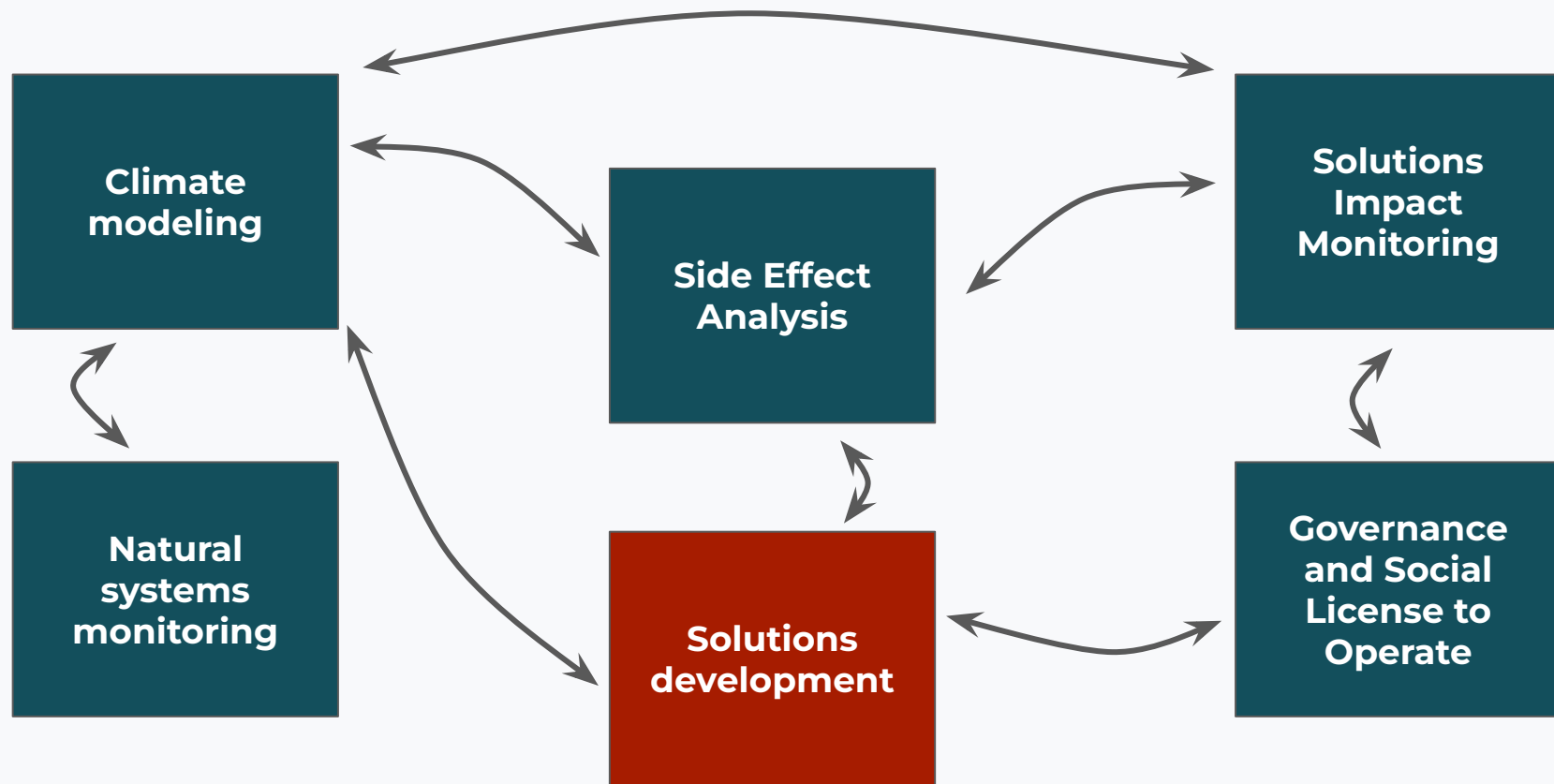
Research Workshop context



- 30+ international scientists
- 3 days in San Francisco
- Multiple disciplines represented
 - Catalyst engineering, methanotrophs, climate modeling, natural systems research / biogeochemistry, atmospheric measurement, atmospheric radicals
- All the following are preliminary results, more details will be published as finalized
- Thank you to our co-organizers: Desiree Plata, Rob Jackson, Gabrielle Dreyfus, Matt Johnson, Alex Wong, Sam Abernethy, Celina Maya Scott-Buechler

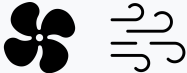


Categories of needs



Categories of possible atmospheric solutions



Category	Description	Examples	Air Movement	Closed vs. Open System
Atmospheric Methane Filters	Creating a CH ₄ sink "in a box"	Flow Reactors: photocatalytic filter, thermocatalytic filter, gas phase radical filter	Active or Passive 	Closed 
Terrestrial Methane Consumption	Increasing the CH ₄ -eating bacteria sink	Seeding or modifying conditions to favor methanotrophs in forests/soils/wetlands/freshwater	Passive 	Open 
Methane-Removing Surface Treatments	Creating a CH ₄ sink over an area	Photocatalyst paint	Passive 	Open 
Atmospheric Oxidation Enhancement (AOE)	Increasing an atmospheric sink of CH ₄ and other gases	Iron Salt Aerosols, aerosolized photocatalysts, enhanced OH sink	Passive 	Open 

Different research areas can fall into multiple categories



	Photocatalysts	Thermocatalysts	Methanotrophs	Radical Generation
Atmospheric Methane Filters				
Terrestrial Methane Consumption				
Methane-Removing Surface Treatments				
Atmospheric Oxidation Enhancement (AOE)				

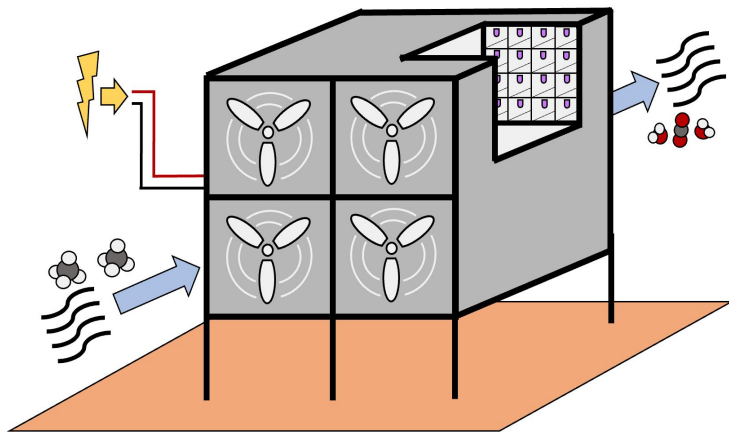
 = Ideas

Atmospheric Methane Filters

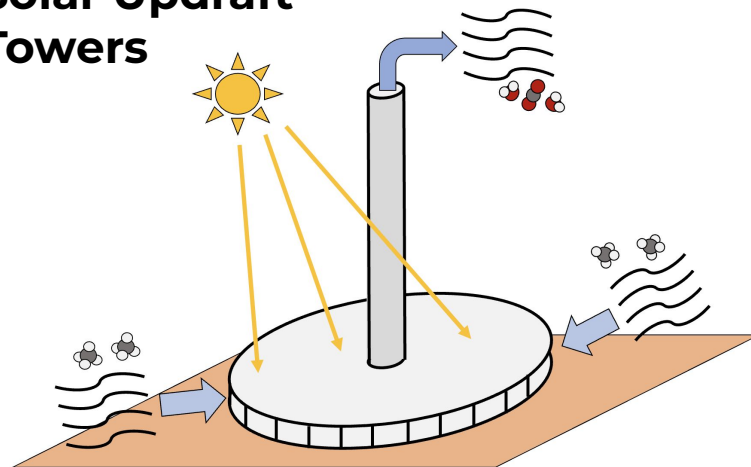


Closed systems with ambient air flowing through, with an internal catalyst, biological system, or radical generation for oxidation

Fan-Driven Reactor



Solar Updraft Towers



Graphics by Richard Randall



Status at 2ppm

Key research needs to contribute to achieving net climate benefit:

Photocatalysts

Demonstrated

- Increase Apparent Quantum Yield (AQY)
- Maintain Conversion efficiency at low residence times
- Characterize Stability

Thermocatalysts

Demonstrated

- Decrease Operating temperature
- Increase Durability

Methanotrophs

Could in principle work

- Find/develop strains with high activity at <10 ppm
- Determine uses for biomass
- Assess and decrease any related N₂O emissions

Radical Generation

Demonstrated

- Increase net Radicals produced per unit energy and material input (e.g., efficiency, recycling)
- Increase Durability

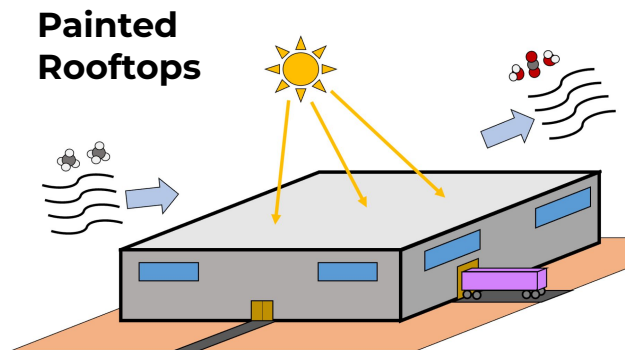
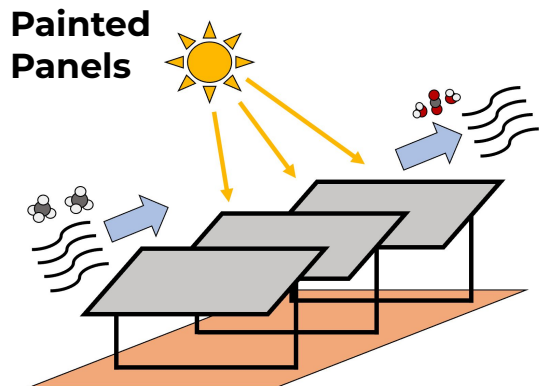
All Categories

More efficiently moving air, by reducing pressure drop, colocating with other processes and/or harnessing passive sources

Methane-Removing Surface Treatments



Photocatalytic coat on surface, flow air over surface passive surface coating. Under research: TiO_2 , Ag-ZnO, Cu-ZnO



Graphics by Richard Randall



Current status

Proof of principle at 2ppm. Apparent Quantum Yield needs major improvement to hit target[1]. Photocatalyst stability needs to be characterized.

Key metrics

- Apparent Quantum Yield (AQY)
- Conversion efficiency
- Stability (lifetime of photocatalyst)
- Byproduct / Air Quality impact

Research need

- **Basic science**
 - What Apparent Quantum Yields (AQYs) are possible?
 - Effect of other gases on reaction selectivity, and efficiency?
 - Effect of temperature?
 - Challenges of immobilizing photocatalysts on support materials?
 - Total amount of potential destruction possible?
- **Tech development:** Best deployment configuration(s)? Sunlight or artificial light? Catalyst durability? Synthesis costs?



Current status

Naturally occurring methanotrophs survive at atmospheric concentrations in multiple environments, but with very low growth rates and low rates of methane oxidation. Higher rates occur at higher methane concentrations, such as in landfill covers, termite mounds, rice paddies, and wetlands, and where methanotrophy can be better managed now.

Research needs for methanotrophy at ambient atmospheric concentrations

- **Can ambient populations be enhanced?** Can existing populations be stimulated or new strains safely introduced that thrive at 2ppm?
- **Interactions with N₂O:** Understand how Cu, Fe, and S additions and other manipulations could affect rates of net methane emissions from methanogenesis and methanotrophy, and how they affect N₂O emissions from denitrification.
- **Ecosystem impacts:** Explore constraints for manipulations in natural forests, wetlands, tundra, etc.



What it is	Released particles/dust to produce additional oxidizing radicals in the atmosphere
Current status	Mechanism works at 2 ppm as shown by natural mineral dust analogues showing promising catalytic efficiency [2], but only under specific conditions, and the dynamics are nonlinear such that higher Cl concentrations may be needed for net CH₄ removal. Still a long way from deployment - will need careful assessment of atmospheric and marine interactions. Early lab and modeling research of one potential mechanism (iron salt aerosols)
Key metrics	• Catalytic efficiency • Net climate and environmental impact
Research need	• Mechanistic Understanding: catalytic efficiency, dependency on atmospheric conditions (especially NO_x), full atmospheric chemistry impact • Performance Optimization: optimal aerosol size, evaluate effectiveness depending on location • Byproducts and Impacts: life cycle impact analysis, study side effects • Scalability: improve measurement abilities, available sources of chlorine • Improve our general understanding of atmospheric chemistry dynamics involving OH and Cl oxidation pathways through modeling and observation

Setting targets to direct solutions research



Conditions for feasibility

Resource efficient

Surface area efficient

Climate beneficial

Cost-effective



Justified assumptions

Best-case 2030 energy scenario

Methane valued highly

Developments in adjacent fields



Necessary breakthroughs

What technological advances are required to make a solution feasible for atmospheric removal?

Supporting needs - current gaps and challenges



Climate Modeling

- Convergence on chemistry representation
- Inclusion of halogen chemistry and improved sinks characterization
- Chemistry-aerosol capability
- Future natural methane emissions
- Dynamic isotopic composition
- Methane lifetime convergence
- High resolution chemistry-aerosol plume modeling

Solutions Impact Monitoring

- Develop proxies for measuring perturbations in oxidation chemistry
- Accurate methane loss rate estimation e.g., OH* and Cl* measurements / proxy / tracers
- Monitoring for potential impacts on ecosystems (atmosphere, ocean, land)
- Updated datasets on isotope compositions of different sources and sinks
- Develop better low-cost, lightweight, ~10 ppb sensitive, in situ and remote methane sensors, including aquatic ecosystems

Natural Systems / Baseline Monitoring

- Global database of measurements, dynamic baseline for sources and sinks
- Establish regional continuous monitoring of natural emissions sources to monitor extent and fluxes using satellites and ground based sensors
- Expand observation networks to support monitoring of methane concentration and fluxes, $^{13}\text{C} + 2\text{H}$ isotopic ratios, OH, Cl, N_2O , NO_x , and other precursors/products of methane reactions



- Research is in early stages across all methods
- Research necessary to prove or develop both feasibility and ability to scale, and understand/improve full impacts of each potential method (e.g. improve life cycle emissions, atmospheric side effects, etc.)
- Pressing need to understand what safe, effective, scalable options we may be able to develop in order to address emissions out of our direct control

Appendices

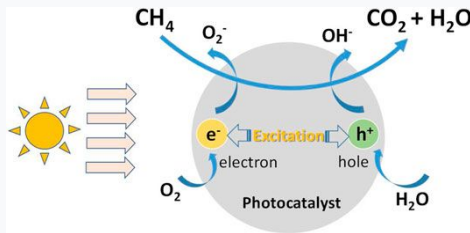
Research Areas and Critical Objectives





Current Status: Lab scale

- **Principles:** Light (natural or artificial) creates electron/hole charge pair, charge pair either breaks first CH bond directly or breaks water to create an OH radical which reacts with CH
- **Varieties:** TiO_2 , Ag-ZnO, Cu-ZnO
- **Potential Deployment Configuration:** Solar updraft tower, trombe wall, passive surface coating, or co-deployment with DAC
- **Approaches to study:** Currently mostly batch reactor, moving toward flow reactors. Typically with artificial UV light and artificially mixed gases (O_2 , Ar, CH_4)
- **Scale constraints:** Energy cost of light and airflow (can be passive to save cost, but then have to consider surface area), apparent quantum yield at 2 ppm



[Huang et al 2021](#)

High Level Assessment

Current TRL: 1-3

AMR: While photocatalysts work at 2 ppm, the cost of energy needed to move air and/or power a light source may limit large scale deployment unless passive sources can be harnessed

Critical Research Objectives

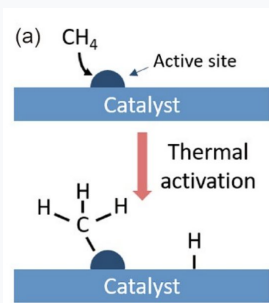
PRELIMINARY

- **Mechanistic Understanding**
 - Better understand the underlying photocatalytic mechanism and identify what levers affect performance and how much of an impact they have
 - Systematic test of many photocatalysts across different environmental variables at 2 ppm
- **Performance Optimization**
 - Improve Apparent Quantum Yield and expand effective light bandwidth
 - Decrease manufacturing energy input (immobilization energy)
 - Increase the surface area interacting with methane and light
 - Increase the methane conversion rate
 - Extend the long-term stability of the catalyst in real world conditions (including “dirty” air, high humidity, a broad range of temperatures, fouling and abrading)
 - Develop catalysts which are low-cost and abundant while remaining effective on other parameters
- **Byproducts and Impacts**
 - Conduct life cycle impact analyses and innovate to minimize impacts
- **Scalability and Techno-economics**
 - Conduct techno-economic analyses and minimize the energy cost of deployment strategies scalably (use of existing air flow, sunlight)
 - Assess ideal deployment configurations and locations

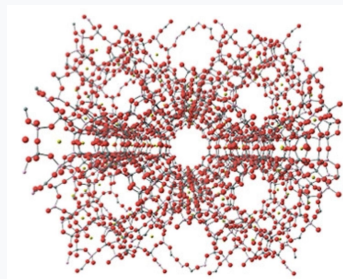
Zeolite Flow Reactors

Current Status: Lab scale

- **Principles:** Heat, usually above 300°C, catalyzes the breaking of the first C-H bond, which is facilitated by many active sites within the high surface area of the zeolite
- **Varieties:** Copper zeolite, iron zeolite
- **Potential Deployment Configuration:** Flow reactor if costs for airflow (passive or co-deployed with DAC) and heat (e.g., waste heat) plummet
- **Approaches to study:** Batch and flow reactors, modeling.
- **Scale constraints:** Energy cost of heat and airflow (can be passive to save cost), conversion efficiency at 2 ppm



[Wang et al 2023](#)



Copper Zeolite [Brenneis et al 2022](#)

High Level Assessment

Current TRL: 1-3

AMR: While zeolites work at 2ppm, the cost of energy needed to move air and/or provide heat may limit large scale deployment unless passive sources can be harnessed

Critical Research Objectives

PRELIMINARY

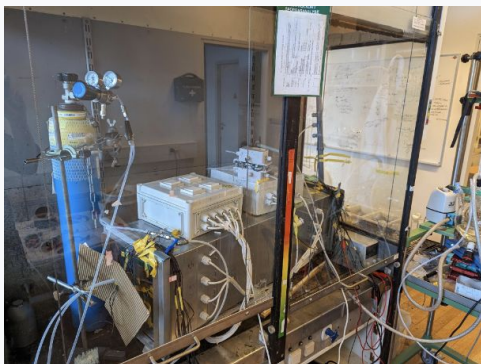
- **Mechanistic Understanding**
 - Understand the underlying thermocatalytic mechanism and identify which levers (zeolite geometry, nature of the active site, temperature) affect performance
 - Systematically test many zeolites under different environmental conditions
- **Performance Optimization**
 - Improve conversion efficiency
 - Decrease heat requirements
 - Extend the long-term stability of the catalyst in real-world conditions
 - Develop catalysts which are low-cost and abundant while remaining effective on other parameters
 - Decrease manufacturing energy input (immobilization energy)
- **Byproducts and Impacts**
 - Conduct life cycle impact analyses and innovate to minimize impacts
- **Scalability and Techno-economics**
 - Conduct techno-economic analyses and minimize the energy cost of deployment strategies scalably (use of existing air flow, waste heat)
 - Assess ideal deployment configurations and locations

Radical Flow Reactors

Current Status: Lab scale, early-stage deployment pilots

- **Principles:** Photocatalytically generate radicals (e.g. photolyze molecular Cl_2) that oxidize methane in the gas phase, capture & recycle byproducts (e.g. HCl) to re-generate radicals
- **Varieties:** OH , Cl
- **Potential Deployment Configuration:** Flow reactor, potentially in line with DAC
- **Approaches to study:** Prototyping, gas phase modeling
- **Scale constraints:** Radical recycling rate (catalytic efficiency), concentration of methane for which the reactor remains energetically feasible, self-limiting reactions

*Cl Flow Reactor
Prototype (Matt
Johnson,
Copenhagen)*



High Level Assessment

Current TRL: 5

AMR: Early indications that this could be scalable for atmospheric removal, more research needed



Critical Research Objectives

PRELIMINARY

- **Mechanistic Understanding**
 - Understand the underlying photolytic mechanism and identify which levers affect performance
- **Performance Optimization**
 - Improve catalytic efficiency
 - Determine low-cost and abundant input materials for radical generation
 - Increase radical concentration (and therefore reaction rate)
 - Understand self-limiting reactions of radicals reacting with each other
- **Byproducts and Impacts**
 - Products of oxidation of non-methane gases and self-reactions
 - Conduct life cycle impact analyses and innovate to minimize impacts
- **Scalability and Techno-economics**
 - Conduct techno-economic analyses and minimize the energy cost of deployment strategies scalably
 - Assess ideal deployment configurations and locations
 - Test in real world conditions (including “dirty” air, high humidity, and a broad range of temperatures)

Terrestrial Methane Consumption

Current Status: Natural systems are currently ~5% of total methane sink, interventions to increase this are theoretical

- **Principles:** Methanotrophs are active in soil all around the world, oxidizing methane at 2 ppm, but in some habitats they are more productive than others
- **Varieties:** Soil and forest nutrient amendments/biome modification, methanotroph population modification
- **Potential Deployment Configuration:** Theoretically could enhance methanotrophs in managed habitats including wetlands, trees, and soil.
- **Approaches to study:** Lab microbiology, modeling, field tests.
- **Scale constraints:** Logistics of deployment in natural ecosystems, environmental impacts, slow growth at low CH₄ concentration, persistence of any modification

High Level Assessment

Current TRL: 1

AMR: Likely limited potential for AMR given slow microbial growth at 2 ppm and risks of ecosystem effects



Critical Research Objectives

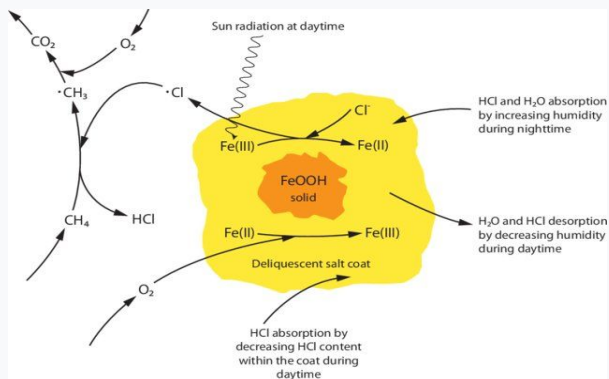
PRELIMINARY

- **General Research Needs**
 - Better understand the underlying oxidative mechanism across different genera of methanotrophs and identify what levers affect performance and how much of an impact they have
 - Better understand the interactions between methanotrophs, other microbes in their community in terrestrial systems, nutrients, and environmental conditions
 - More deeply study methanotrophs that operate at 2 ppm
 - Reduce N₂O co-production with methanotrophic CH₄ oxidation
 - Improve and reduce costs for area scale sensing of CH₄ and N₂O
- **Biocovers**
 - Reduce cost and maintenance to enable expansion to the developing world; reduce risk of N₂O production
- **Soil amendments**
 - Iteratively test different amendment types, in model environments, across different environmental conditions, considering timing, quantity, soil depth, and other factors
- **Natural system enhancement**
 - Study existing environments where methanotroph behavior is enhanced, determine what processes contribute to that enhancement, and replicate those processes in lab/model environments
 - Identify potential unintended environmental effects

Iron Salt Aerosols

Current Status: Lab scale

- **Principles:** Iron particles react with aerosolized sea salt to produce FeCl_3 , which is photolyzed by the sun to produce FeCl_2 and a Cl radical, which oxidizes methane
- **Potential Deployment Configuration:** Spray an aerosol of iron into the atmosphere in the marine boundary layer via towers, balloons, or aircraft
- **Approaches to study:** Sampling mineral dust natural analogue conditions, global and plume modeling, smog chamber studies
- **Scale constraints:** Effects of side reactions, regions with favorable conditions, iron deployment



[Oeste et al 2017](#)

[Huang et al 2021](#)

High Level Assessment

Current TRL: 3

AMR: Mechanism works at 2 ppm but only under specific conditions, and the dynamics are nonlinear. Naturally occurring mineral dust analog currently being studied. Still a long way from deployment - will need careful assessment of atmospheric interactions.

Critical Research Objectives

PRELIMINARY

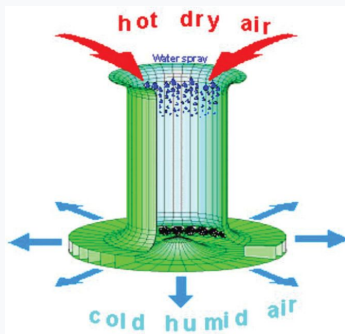
- **Mechanistic Understanding**
 - What is the catalytic efficiency under real-world conditions?
 - How does the presence of ozone and other gases determine whether ISA increases or decreases methane?
 - What else is oxidized?
- **Performance Optimization**
 - Determine optimal aerosol size
 - Evaluate effectiveness depending on location
- **Byproducts and Impacts**
 - Conduct life cycle impact analyses and innovate to minimize impacts
 - What side effects (Fe deposition, acid rain, chlorine gas, other atmospheric chemistry impacts) might be caused?
- **Scalability and Techno-economics**
 - Evaluating scale and cost will require significant improvements in measurement abilities
 - Conduct techno-economic analyses and minimize the energy cost of deployment strategies scalably
 - Assess ideal deployment configurations and locations

Other Atmospheric Oxidation Enhancement (OH, TiO₂)



Current Status: Theoretical

- **Varieties:** OH might be enhanced via increasing NO_x, O₃, H₂O, UV light, or H₂O₂; aerosolized photocatalysts (such as TiO₂) could oxidize methane
- **Potential Deployment Configuration:** Atmospheric aerosol spraying, enhancing humidity with downdraft energy towers
- **Approaches to study:** Global and plume modeling, smog chamber studies, environmental analog studies
- **Scale constraints:** Effects of side reactions, regions with favorable conditions, supply and manufacturing energy of feedstock



OH Enhancing Downdraft Energy Tower [Wang et al 2022](#)

High Level Assessment

Current TRL: 1

AMR: Unclear if these pathways could be effective, safe, and scalable for AMR

Critical Research Objectives

PRELIMINARY

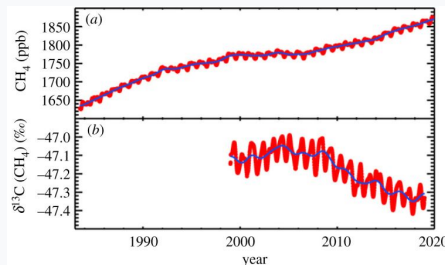
- Improve our general understanding of atmospheric chemistry dynamics involving OH oxidation pathways through modeling and observation
- Study the effects on hydroxyl radical dynamics of current additions of NO_x, O₃, and humidity to the atmosphere through modeling and observation
- Improve our understanding of the limiting factors capping the growth of the hydroxyl radical sink
- Quantify the catalytic efficiency of additions of NO_x, O₃, H₂O₂, TiO₂ aerosol, and humidity in smog chamber studies under a variety of potential model atmospheric conditions
- Identify the effects on weather, ocean ecosystems, terrestrial ecosystems, radiative forcing, and atmospheric chemical composition of inputting any of these materials into the atmosphere
- Improve observational and measurement technology to improve capacity to monitor deployment tests and their downstream effects

Crosscutting Challenge: Understanding and Monitoring Methane



Current Status: Many unknowns about methane sources, sinks, and dynamics that will be critical to supporting methane removal

- The concentration of CH_4 has risen from 0.7 ppm to 2 ppm. It stabilized in the 2000s, started rising and accelerating again in ~2008 with the greatest annual increase in 2021 (potentially driven by wetland emissions and decreased NO_x)
- **Isotopes:** The $\delta^{12}\text{C}_{\text{CH}_4}/\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^1\text{H}_{\text{CH}_4}/\delta^2\text{H}_{\text{CH}_4}$ ratios are affected by source and sink (fossil/biological sources have different signatures, and while OH oxidizes C isotopes equally, Cl oxidizes ^{13}C preferentially). Since ~2008, $\delta^{13}\text{C}_{\text{CH}_4}$ has shifted more negative (see figure) potentially indicating more bio emissions
- **Modeling:** Most ESMs have don't include rising natural emissions and have limited oxidative and cloud dynamics
- **Observations:** Satellites, airborne, ground based, eddy flux covariance towers are all used. Limited C isotope observation and even more limited H isotope observation



[Nisbet et al 2021](#)

Critical Research Objectives

PRELIMINARY

- Fully incorporate methane, OH, and Cl reaction and emission dynamics, and interactions with microbial sinks, into global atmospheric and biogeochemical models and identify where observations would be most impactful
- Expand observation networks to support global, frequent, long-term monitoring from space, air, and ground of methane concentration and fluxes, ^{13}C and ^2H isotopic ratios, OH, Cl, N_2O , NO_x , and other precursors/products of methane reactions
- Develop better low-cost, lightweight, ~10 ppb sensitive, *in situ* and remote methane sensors, including aquatic ecosystems
- Close the gap between bottom up and top down methane budgets
- Improve modeling and observation specifically of tropical wetlands and arctic permafrost regions, and their extent, to better predict and detect variations in the rate of natural emissions
- Better map the spatiotemporal distribution of the rate of methane oxidation

Recommended Papers



Methane Removal Broadly

- [Atmospheric methane removal: a research agenda](#) Jackson et al, 2021
- [Is the destruction or removal of atmospheric methane a worthwhile option?](#) Nisbet-Jones et al., 2021
- Perspectives on removal of atmospheric methane Ming et al, 2022
- [Methane removal and atmospheric restoration](#). Jackson et al. 2019 Nature Sustainability 2:436-438.

Understanding Methane

- [Atmospheric methane and nitrous oxide: challenges along the path to Net Zero](#) Nisbet et al, 2021
- [Atmospheric methane underestimated in future climate projections](#) Kleinen et al 2021
- [Beyond CO2 equivalence: The impacts of methane on climate, ecosystems, and health](#) Mar et al, 2022
- [Mitigating climate disruption in time: A self-consistent approach for avoiding both near-term and long-term global warming](#) Dreyfus et al, 2022
- [Societal shifts due to COVID-19 reveal large-scale complexities and feedbacks between atmospheric chemistry and climate change](#) Laughner et al, 2021
- [Overexplaining or underexplaining methane's role in climate change](#) Prather et al, 2017
- [Attributing composition and climate impacts of future methane changes](#) Staniaszek et al, 2022
- [Methane removal and the proportional reductions in surface temperature and ozone](#). Abernethy et al. 2021
- [The Global Methane Budget 2000-2017](#). Sauniois M et al. 2020
- [Increasing anthropogenic methane emissions arise equally from agricultural and fossil fuel sources](#). Jackson et al. 2020
- [Acting rapidly to deploy readily available methane mitigation measures by sector can immediately slow global warming](#) Ocko et al 2021

Catalysis

- [Catalytic methane removal to mitigate its environmental effect](#) Wang et al, 2023
- [Atmospheric- and Low-Level Methane Abatement via an Earth-Abundant Catalyst](#) Brenneis et al, 2022
- [Feasibility of Solar Updraft Towers as Photocatalytic Reactors for Removal of Atmospheric Methane—The Role of Catalysts and Rate Limiting Steps](#) Huang et al 2021
- [Photocatalytic oxidation of methane over silver decorated zinc oxide nanocatalysts](#) Chen et al, 2016
- [Photocatalytic oxidation of methane over CuO-decorated ZnO nanocatalysts](#) Li et al, 2019
- [Exploring the photocatalytic total oxidation of methane through the lens of a prospective LCA](#) Johansson and Hieta 2022
- [Feasibility of Solar Updraft Towers as Photocatalytic Reactors for Removal of Atmospheric Methane—The Role of Catalysts and Rate Limiting Steps](#) Huang et al 2021
- [New materials for methane capture from dilute and medium-concentration sources](#) Kim et al 2013

Methanotrophy

- [Methanotrophs: Discoveries, Environmental Relevance, and a Perspective on Current and Future Applications](#) Guerrero-Cruz et al, 2021
- [Biofiltration of Methane](#) La et al, 2017
- [Engineered Methanotrophy: A Sustainable Solution for Methane-Based Industrial Biomanufacturing](#). Nguyen, A. D., & Lee, E. Y., 2020
- [Application and development of methanotrophs in environmental engineering](#) Seon-yeong Park & Chang-gyun Kim, 2019
- [Feasibility of atmospheric methane removal using methanotrophic biotrickling filters](#) Yoon et al 2009

Radicals

- [Climate engineering by mimicking natural dust climate control: the iron salt aerosol method](#) Oestle et al, 2017
- [A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane](#) Gromov et al, 2018
- [Atmospheric removal of methane by enhancing the natural hydroxyl radical sink](#) Wang et al. 2022
- [A nature-based negative emissions technology able to remove atmospheric methane and other greenhouse gases](#) Ming et al
- [Environmental implications of hydroxyl radicals](#) Gligorovsky et al 2015
- [Gas-Phase Advanced Oxidation for Effective, Efficient in Situ Control of Pollution](#) Johnson et al
- [Photochemical method for removing methane interference for improved gas analysis](#) Polat et al 2021

Solution Area Intros



Solution Area Intro

Thermocatalysts

Desirée Plata, PhD

Civil & Environmental Engineering, MIT

Introduction to the solution category

Basic principle:

Activate CH_4 -to- CO_2 conversion via catalytic or thermolytic pathways

Why is CH_4 tough to react/sorb?

1. Only van der Waals interactions (small, unpolarizable, no polar bonds, no acid-base chemistry)
2. Negligible electron affinity
3. C-H bond has a high dissociation energy: 104 kcal/mol
4. $^3\text{O}_2 + ^1\text{CH}_4 \rightleftharpoons ^1\text{CH}_3\text{OH}$ is spin forbidden
5. High temperature processes are difficult to control (difficult to arrest at CH_4)

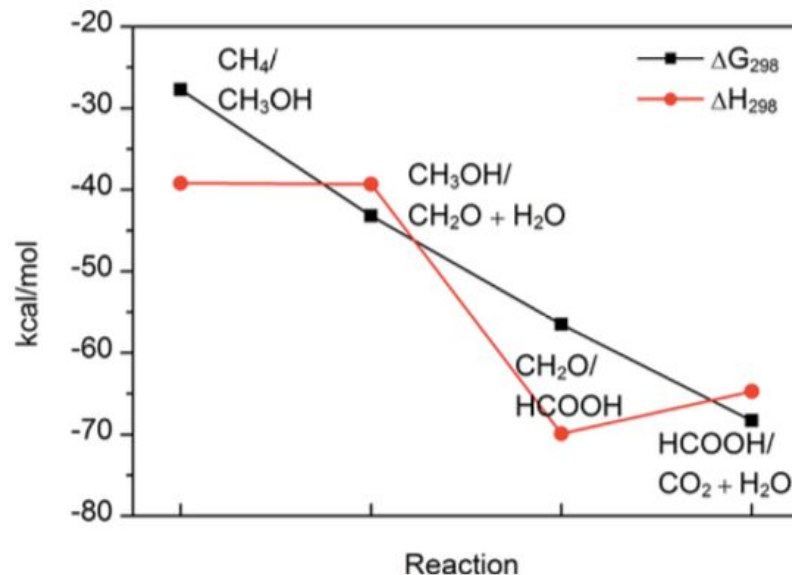
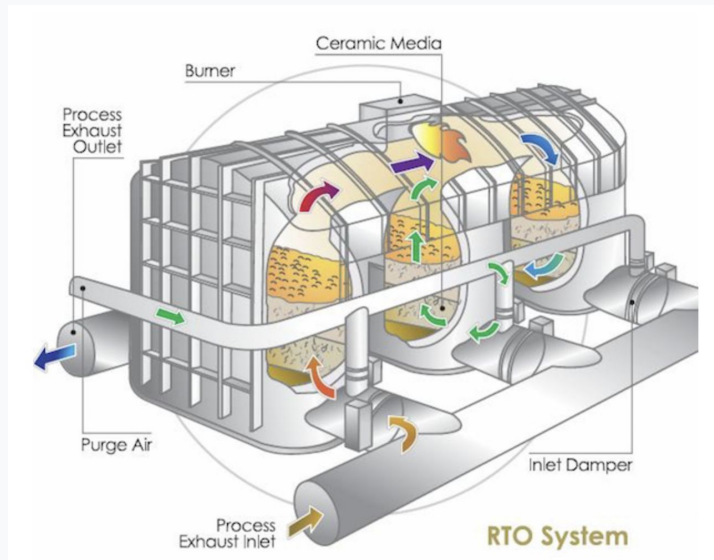


Figure 1. Values of the free energy (ΔG) and the enthalpy (ΔH) for each step of the oxidation reactions of CH_4 to CO_2 by O_2 . The values are given at a temperature of 298 K.

Introduction to the solution category

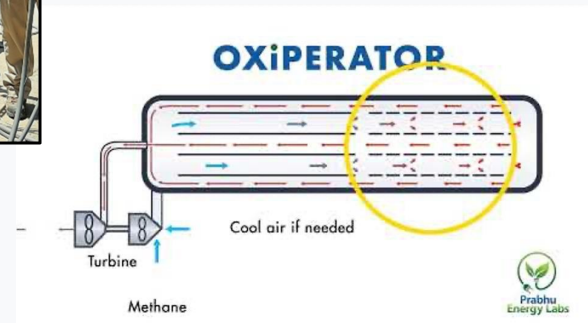
Included technologies and categorization: (1) THERMAL

Regenerative Thermal Oxidizer (RTO)



>0.4% methane; 1200°C
TRL 7

Oxiperator

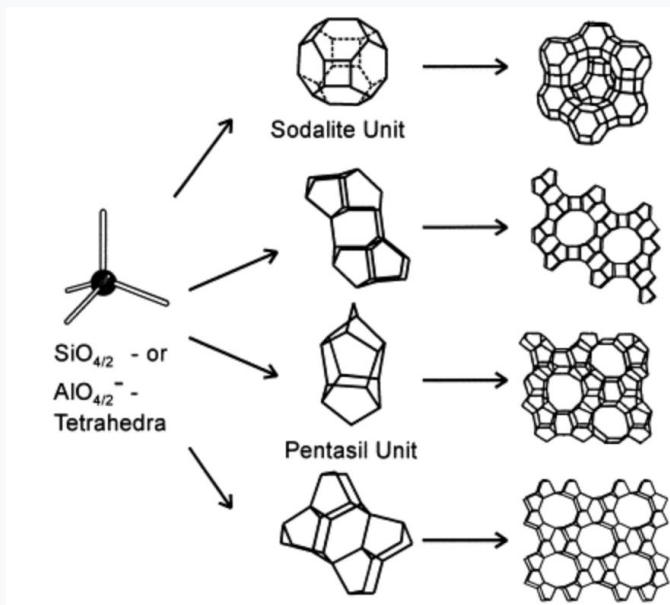


>0.2% methane; 900°C
TRL 3-5

Introduction to the solution category

Included technologies and categorization: (2) CATALYTIC

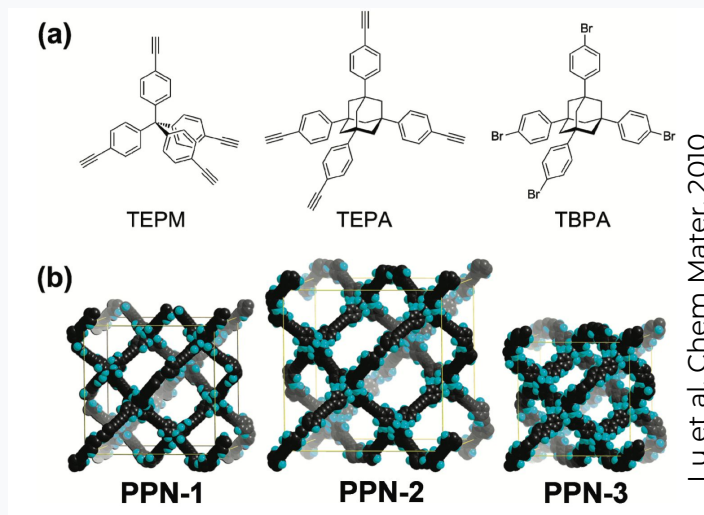
Zeolite-based solutions



Weitkamp Solid State Ionics .2000

$\geq 0.0002\%$; $\sim 250-400^\circ\text{C}$
TRL 3

Porous polymer networks (PPN); Organometallic approaches

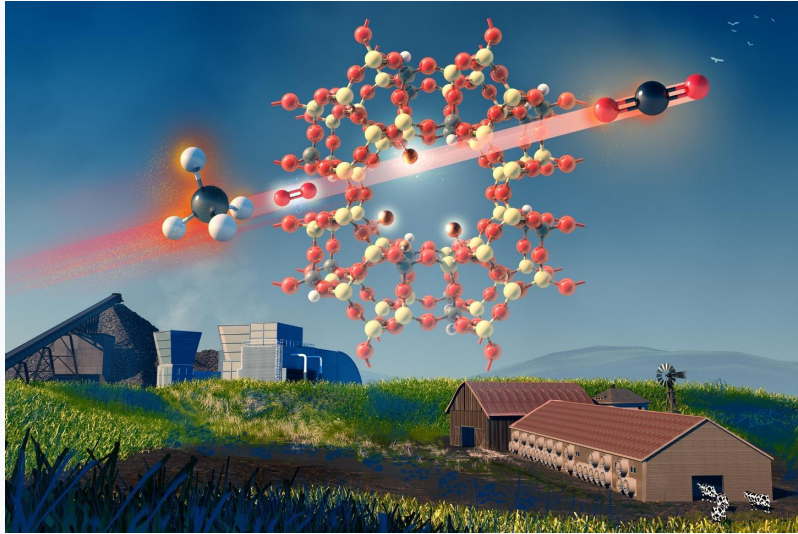


Lu et al. Chem Mater. 2010

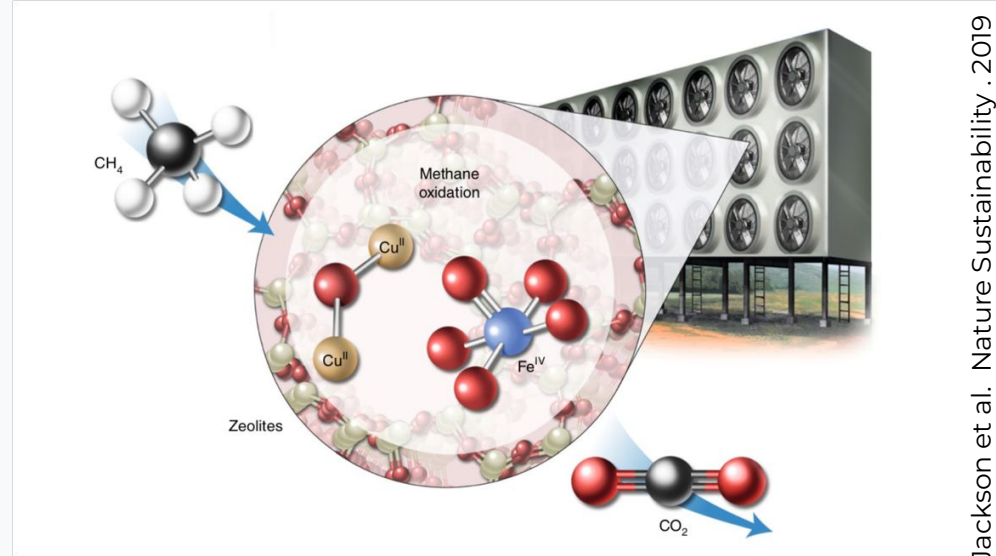
Many bar; cold adsorption (77 K)
TRL 1

Introduction to the solution category

Deployment configurations



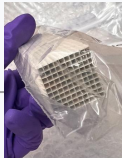
Dairy
Landfill
Coal



Direct air
Permafrost/wetlands

State of the research

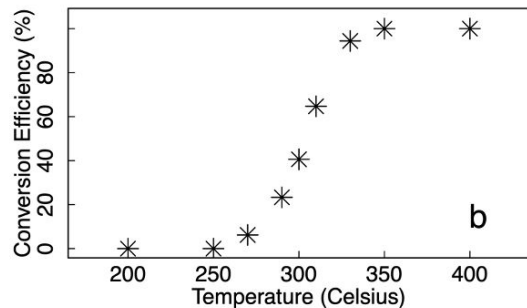
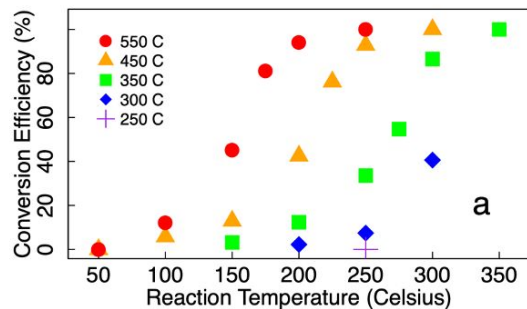
Key metrics for the field

Metric	Why?	Best performance	Notes
Operating temperature	Drives cost (OPEX); E consumption*	~310°C (below auto-ignition) 	f(CH ₄ conc., water vapor, duty cycle)
Pressure drop	Drives cost (CAPEX); E consumption	Monolith (n/a) Packed bed (~20 psi)	OPEX tradeoff
Durability	Drives cost (OPEX); System design	2 weeks (lab zeolites) 6 months (RTO; field)	f("poisons", mechanical strength)

*See Sam's talk!

State of the research

Notable discoveries and research efforts



Brenneis et al. ACS Environ. Au. 2021



ARPA-E REMEDY PROGRAM

Application to coal: 3 funded teams

+9 teams for methane slip from lean burn engines and flares

Goals and vision

- Goals for performance on key metrics
 - No P drop; 85°C or lower OR restricted to enriched methane (>0.6%)
- Potential scale for the solution
 - Want 1M CFM (e.g., in 10 x 100k CFM* modules; each needs 100 m³ catalyst; ~40,000 kg)
 - *For reference: 2030 DAC goals require 50,000 of these.
 - *Current infrastructure order \$100M; OPEX order \$15M (RTOs)
- Key constraints to overcome to reach that scale and those metrics
 - *Resource constraints:* We have the stuff (i.e., the catalysts and the steel)
 - *Technology constraints:* We need to demonstrate durability, flow w/o P drop, feasibility for E/CH₄ concentration tradeoff or lower temperature to improve application space
 - *System constraints:* We need financing schemes and/or governance

Key open questions for proving feasibility

- Basic science
 - Fundamentally distinct way to drop operating T ? (e.g. manipulating pore structure)
 - Structuring material (binders) without sacrifice to function
- Tech development
 - Heat recovery an important driver for cost/ E ; comes with P drop; where's the tradeoff?
 - New materials processing tricks for faster fab *and* stronger materials
 - Lower temperature performance to expand application space
- Environmental and health impacts
 - Unintended products? (esp. at lower T s)

Key open questions for scaling

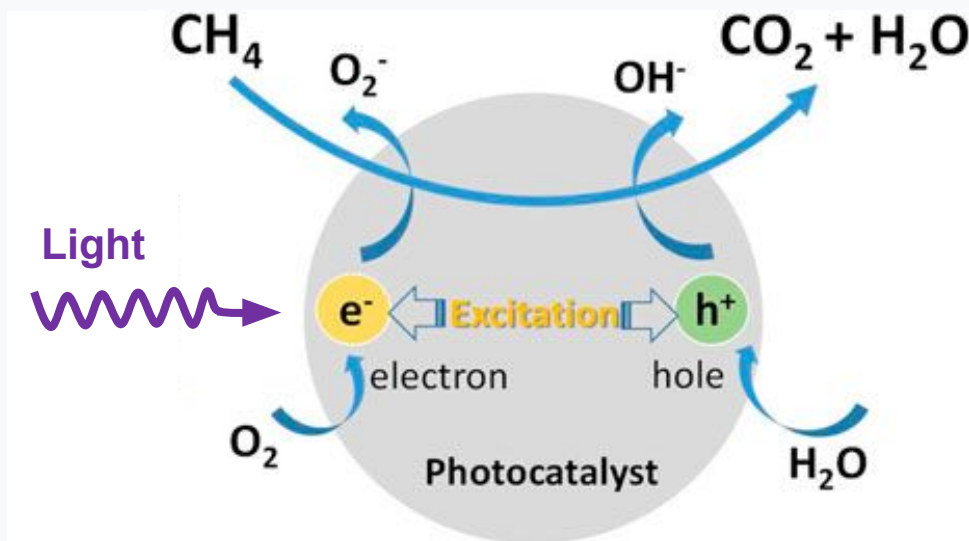
- Expanding addressable segment of methane emissions
 - Lower Ts for lower CH₄ levels
- Designing for deployment
 - Implicitly scalable catalyst processing
- Overcoming resource constraints
 - Business model; building fast
- Achieving a viable cost
 - Business model. (C credit valuation- higher? lower?)
- Social license and governance
 - Regulatory incentive
 - CH₄ market?

Solution Area Intro

Photocatalysis

Max Kessler and Richard Randall
Stanford University

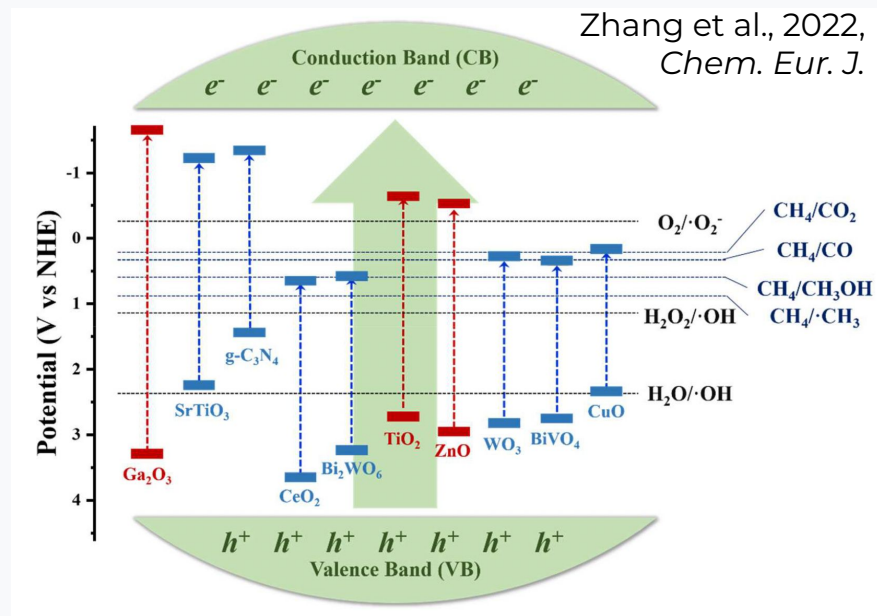
Basic Principles of Photocatalysis



- Photon's energy overcomes activation barrier (instead of particles' thermal energy alone)
- Reactions proceed at room temperature & pressure (!)
- May oxidize methane directly or do so by making radicals
- Continuous input of photons from lamps or sun is required
(quantum yield = # CH_4 's oxidized / # photons)

Basic Principles of Photocatalysis

- Many semiconductor photocatalysts are known, each with unique band structure
- Certain band gaps and band potentials are required for certain reactions (e.g. $\text{CH}_4 \rightarrow \text{CH}_3\cdot$ or $\text{H}_2\text{O} \rightarrow \cdot\text{OH}$)
- ZnO and TiO_2 are most studied; also inexpensive. Excited by UV light.
- Co-catalysts may enable:
 - Enhanced electron-hole separation & scavenging (e.g. Ag)
 - Excitation with visible light (e.g. CuO)

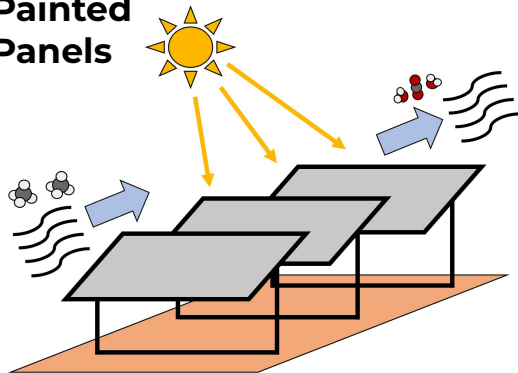


Energy of light (eV) $\propto 1/\text{wavelength}$

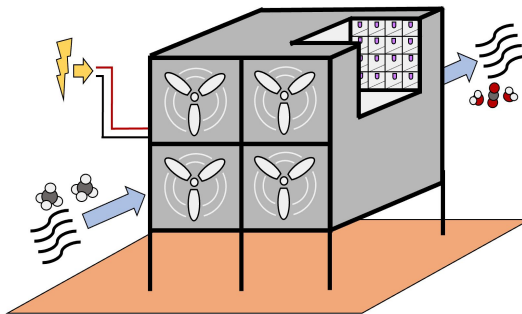
Semiconductor	Band gap (eV)	Excited by (nm)
TiO_2	3.2 eV	≤ 387 nm
ZnO	3.3 eV	≤ 375 nm
CuO	1.7 eV	≤ 730 nm

Catalyst Deployment Configurations

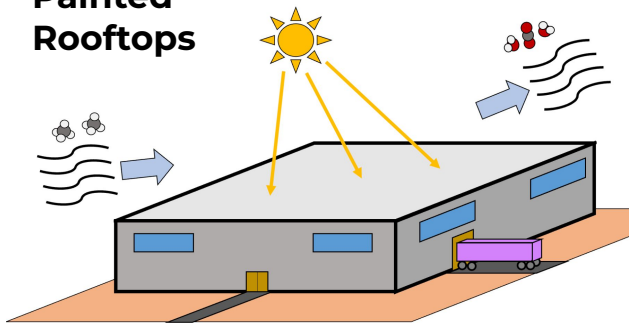
Painted Panels



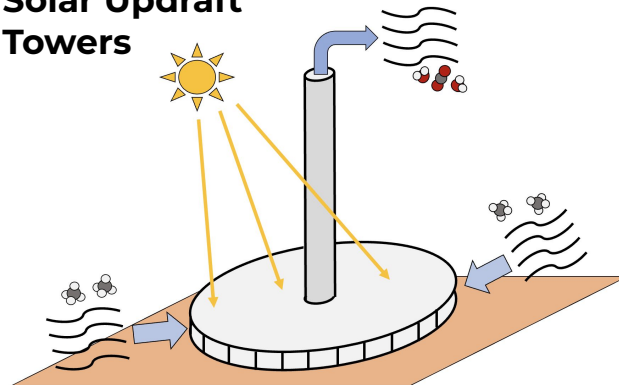
Fan-Driven Reactors



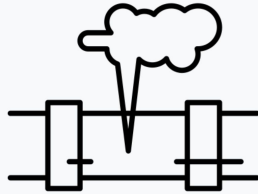
Painted Rooftops



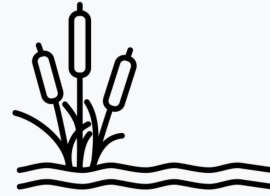
Solar Updraft Towers



Technology Categorization



Point emissions



Area emissions



Atmospheric methane

Ground-based

- Fan-driven reactors
- Passive rooftops
- Passive panels
- Solar updraft towers
- Add to CO₂-DAC

Atmosphere based

- Aerosol particles

All technologies are at low TRL (1-3)

State of the Research and Targets

Key metrics	State of the Art	Target
Apparent Quantum Yield = # CH ₄ 's oxidized / # photons	1% at 5,000 ppm 0.04% at 2 ppm	>1% (painted roof) >5% (electrical lighting) unsure for SUT's
Conversion efficiency = % CH ₄ 's oxidized	~100%	95-100% at sufficiently short residence times
Stability ~ lifetime of photocatalyst	Unknown	2-20 years in real-world conditions (dust, NO _x , VOCs, etc.)
Byproduct impact ~ reaction products formed	High CO ₂ selectivity (in dry, "clean" air) avoids harmful products	Avoidance of harmful products (in humid, "dirty" air)

Open Questions for **Proving Feasibility**

Basic science

- What AQY's are possible?
- Effect of other gases on reaction selectivity & efficiency?
- Effect of temperature?
- Challenges of immobilizing photocatalysts on support materials?

Tech development

- Best deployment configuration(s)?
- Sunlight or artificial light?
- Catalyst durability? Synthesis costs?

Environmental & health impacts

- Co-benefit pollutant reduction?
- Byproducts?

Open Questions for **Scaling**



Are large-scale systems with low ($\leq \sim \$100/\text{tCO}_2\text{e}$) removal costs possible?



Are any key inputs (e.g. energy, resources) barriers to scale-up?



Social license and governance

- What market incentives are needed?
 - Social cost of methane, methane tax, ...
- How to verify & monetize distributed passive systems?
- What are the risks of aerosol? Political will for geoengineering?

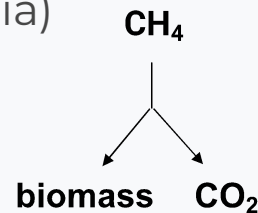
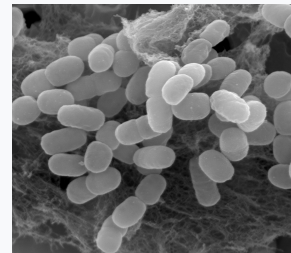
Solution Area Intro

Methanotrophs

Mary Lidstrom
University of Washington

Introduction to the solution category

- Methanotrophs grow on methane as sole carbon and energy source
 - Convert methane to biomass and CO_2
- Different types: which is used depends on methane concentration
 - Those that do not use O_2 to activate methane (archaea)
 - Best for methane above 10,000 ppm
 - Those that use a methane monooxygenase MMO (bacteria)
 - Soluble MMO (sMMO): low affinity for methane
 - Particulate MMO (pMMO): high affinity for methane
 - Best for less than 2000 ppm

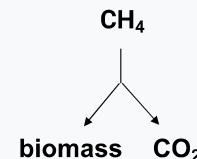
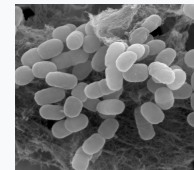


Introduction to the solution category

- Deployment configurations
 - Biology needs to be hydrated (moist): no dry deployment
- Source issues:
 - Dissolved methane is immediately accessible

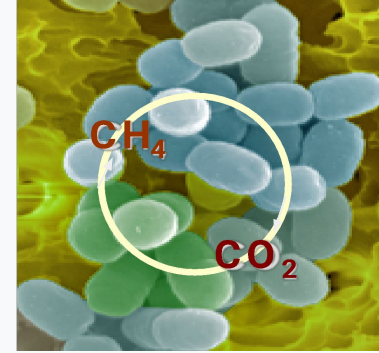
(2000 ppm in air = 2-3 μM)

- Methane in the gas phase must be dissolved in water
 - Mass transfer of methane from gas to liquid is a key issue for treatment
- Atmospheric methane filter (biofilter)
 - Closed system, mass transfer and containment controlled
- Environmental deployment
 - Issue with N_2O
 - Enhancing methanotrophic activity known to increase N_2O emissions (10X worse than methane)
 - Essential to measure both CH_4 and N_2O when testing strategies
 - Containment issues with GMOs



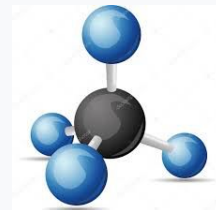
State of the Research

- Key metrics for the field
 - Methane consumed/time/gram dried weight cells
 - Methane consumed/time/ m^3 treatment volume
 - Residual methane after treatment
- Best performance to date on those metrics
 - Depends on starting concentration
 - At 1000 ppm:
 - 7 mg CH_4 /g cell dry weight/hr; residual methane <1ppm (Knief & Dunfield 2005)
 - 7.5 g CH_4 / m^3 /hr (need 20 million m^3 size units/Tg/yr) (Nikiema & Heitz 2009)
 - Using best strains, calculated rate of ~150 g CH_4 / m^3 /hr (need a million units/Tg/yr)
- Notable discoveries and research efforts
 - *Methylocapsa gorgona*: grows at atmospheric methane (slowly) (Tveit et al., PNAS 2019)
 - Rice paddy soil communities increase N_2O generation when methanotrophs stimulated (Chang et al., Appl Env Micro 2021)

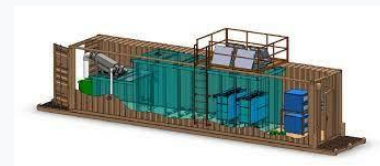


Goals and vision

- Annual goal = 10 Tg = 10 million metric tons
- Challenges for using methanotrophs
 - Current methane consumption rate limits both scale and economic feasibility
 - Existing strains can remove methane to sufficiently low levels
- Goals for performance on key metrics for biofilter systems
 - Increase methane consumed/time/gram dried weight cells (enhance biology)
 - Increase methane consumed/time/m³ (enhance biology and process engineering)
- Units of 10 m³ size with 20X increase = **50,000 units/10Tg**



Suggestion: total enhancements increase consumption **20X**



- Scale:
 - Point sources from landfills, anaerobic digester effluent, sewers, leaking oil and gas wells in the 500-2000 ppm range ~15 Tg/year in US alone

Goals and vision

- **Goal**

- Increase methane consumed/hr/m³ by 20X → 200 tons/yr/10 m³ treatment unit
- Consume 10 Tg/yr in 50,000 treatment units deployed at emission sites

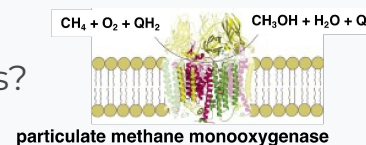
- **Key constraints to overcome to reach that scale and those metrics**

- Land area is small (shipping container-sized units)
- 10 million tons methane/yr → ~8 million tons biomass
 - For fish or livestock feed
 - Requires ~1.4 million tons nutrients (28 tons/unit/yr)
- Current biofilter technology won't support this scale for these point sources
- Requires new bioreactor approaches

Key open questions for proving feasibility

- Basic science

- What limits methane consumption at low methane in methanotrophs?
 - Mass transfer to the pMMO enzyme?
 - Catalytic properties of the pMMO enzyme?
 - Metabolic network constraints, including energy metabolism?
- Are there yet undiscovered strains/methane oxidation systems that would be better for low methane?
- What key microbial community dynamics affect net GHG production in natural populations, especially methane and N_2O ? Need sensitive, affordable N_2O sensors.

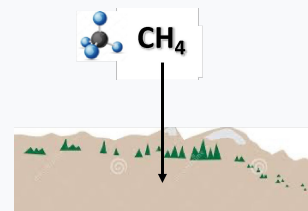


- Technology development

- What is the optimum configuration for maximal mass transfer and biomass production?
- How to design low cost, low water-use, low energy systems with low maintenance and long lifetimes?

- Environmental and health impacts

- Ecosystem disruption questions for environmental deployment



Key Open questions for scaling

- Expanding addressable segment of methane emissions
 - Near ambient concentrations: requires strains with higher activity at <100 ppm
 - Contaminants: volatile compounds (S-compounds; other hydrocarbons; CO)
- Designing for deployment
 - Low cost, low maintenance, low energy; harvesting biomass will require a maintenance/harvesting contract
 - Minimizing added nutrients (use locally available sources e.g. livestock urine)
- Achieving a viable cost
 - Low cost treatment system (no sterilization!)
 - Biomass as a valuable product; market for single-cell protein
 - Carbon credits (34 vs. 85 CO₂ equivalents)
- Social license and governance
 - Environmental deployment must be demonstrated to not increase other GHG
 - GMO strains follow existing guidelines

Solution Area Intro

Radicals

Matthew S. Johnson, Professor
Department of Chemistry
University of Copenhagen

The 3D solution -- what is a radical?

Atmospheric Chemistry 101



Lewis dot diagram:
Gilbert Newton Lewis,
U. C. Berkeley, 1916.

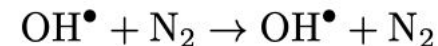
Most molecules have *paired electrons* – closed shell – stable – nonreactive

A *radical* is a species with an *odd number of electrons* – a broken bond – making it very reactive

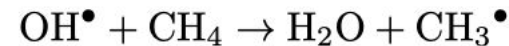
Radicals fly through the atmosphere at > **1000 mph** colliding with a molecule every **70 ns**.

The main atmospheric radical is OH. It can abstract a hydrogen atom H from a hydrocarbon to make water H₂O but *does not react* with most atmospheric molecules like N₂, O₂, H₂O, CO₂.

In the 3D solution, the radical finds the reaction partner!

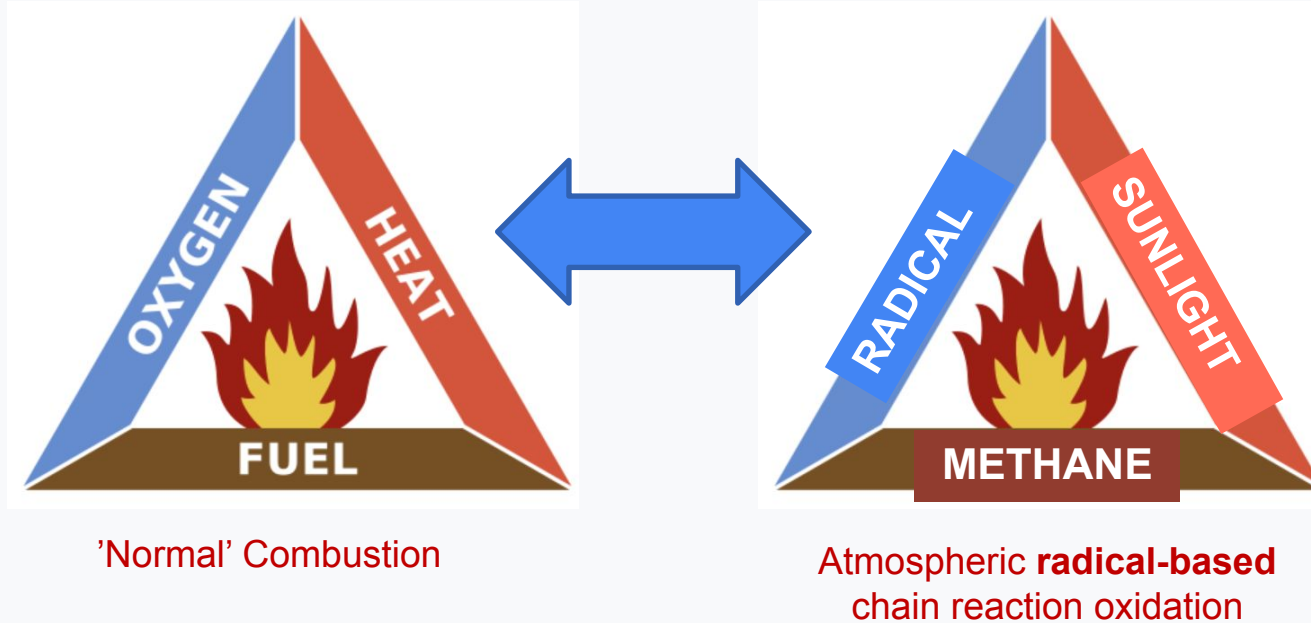


No surface needed for the radical interaction - low pressure drop – high efficiency at low concentration



The rare odd electron persists through thick and thin

Radicals drive chain reactions



Chain reactions are well known self-propagating reaction systems that run until they run out of fuel.

OH is the main tropospheric radical

Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted

Author(s): H. Levy II

Source: *Science*, New Series, Vol. 173, No. 3992 (Jul. 9, 1971), pp. 141-143

Published by: American Association for the Advancement of Science

Stable URL: <https://www.jstor.org/stable/1732208>

Accessed: 30-09-2019 07:14 UTC

H. LEVY II

Smithsonian Astrophysical Observatory,
Cambridge, Massachusetts 02138

Science
AAAS

Features:

- All chain reactions include the basic steps of *initiation*, *propagation* and *termination*
- The oxidation of methane releases energy, thermodynamically it is spontaneous.
- The lifetime ' τ ' of methane is determined by the radical concentration.

$$\tau_X = \frac{[X]}{r_L}$$

$$\tau_{\text{CH}_4} = \frac{[\text{CH}_4]}{k[\text{CH}_4][\text{OH}]} = \frac{1}{k[\text{OH}]}$$

$$[\text{OH}] = \frac{r_P}{\sum_X k_X [X]}$$

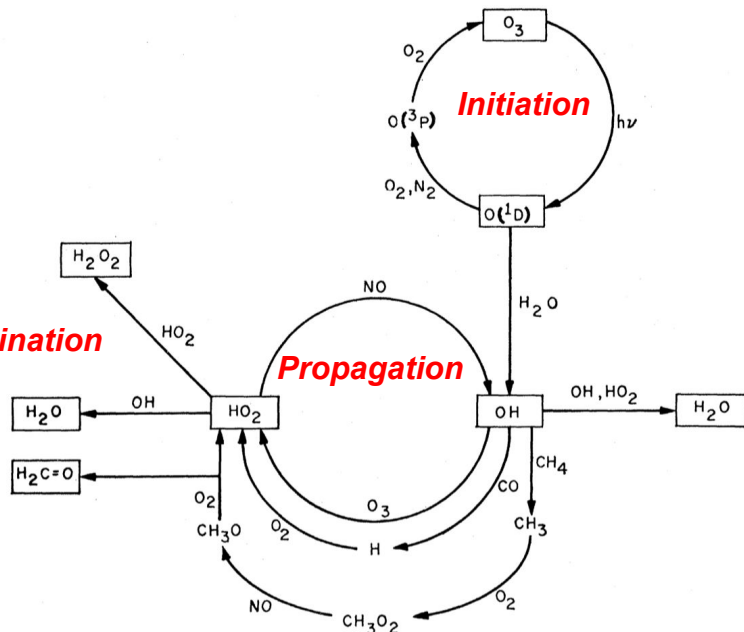
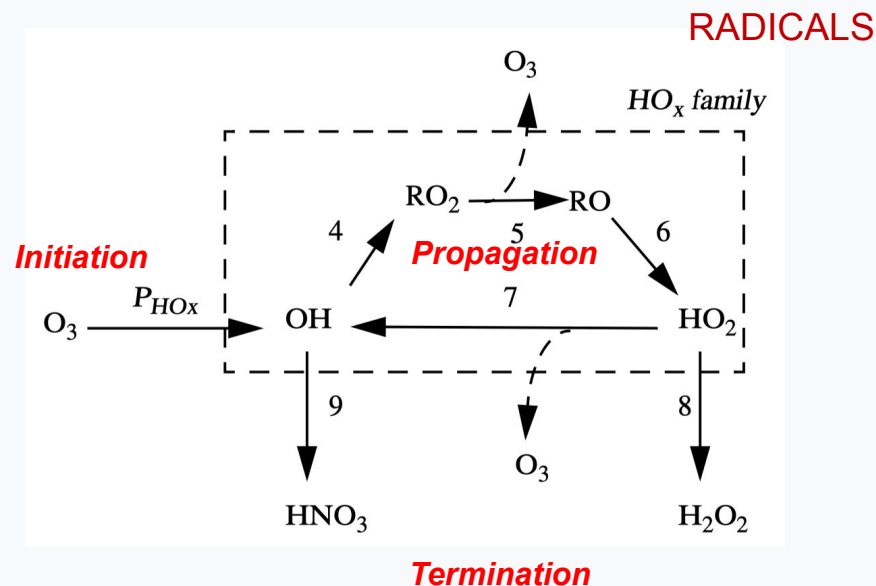


Fig. 1. Simplified photochemical reaction model for the normal atmosphere.

Reaction	Catalytic Efficiency
Break Even	1
Tropospheric Hox-Nox	3 to 30
Iron Salt Aerosol	-1 to 1000
Chlorine catalysed ozone depletion	100,000
Bromine catalysed ozone depletion	1,000,000

The **Catalytic Efficiency** tells how good a chain reaction is. It is the number of reaction cycles per radical entering the cycle.



OH radical based pollution control



GPAO pollution control at windmill blade factory

**\$20/tCO₂e for
VOC removal**

GPAO, Gas Phase Advanced Oxidation,
Johnson and Arlemark, 2009.

M. S. Johnson and J. Arlemark, A method and device for cleaning air, European Patent Agency 08388017.9; International Patent Cooperation Treaty PCT/EP2009/055849, 2009; U.S. Patent 8,318,084 B2, 2011.
M. S. Johnson, E. J. K. Nilsson, E. A. Svensson, S. Langer, Gas Phase Advanced Oxidation for Effective, Efficient In Situ Control of Pollution, Environmental Science & Technology 48(15), 8768–8776, 2014.



GPAO system at water treatment plant, Aarhus Denmark



GPAO system at Daimler-Benz production line



GPAO system at the Royal Danish Embassy in Beijing

Cl is better than OH for CH₄ removal.

OH	Cl
$k(298\text{ K}) = 6.3\text{E-}15\text{ cc/s}$	$k(298\text{ K}) = 1.0\text{E-}13\text{ cc/s}$ (16 x faster)
$\text{O}_3 + h\nu + \text{H}_2\text{O} \rightarrow \text{OH}$ Source is inefficient	$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$ Source is efficient
Self limiting reactions saturate OH concentration at low level	Few and slow self limiting reactions means high Cl concentration
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$ $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$ $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$ $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$
Products are simple	HCl product requires recycling

CI radical technologies and categorization

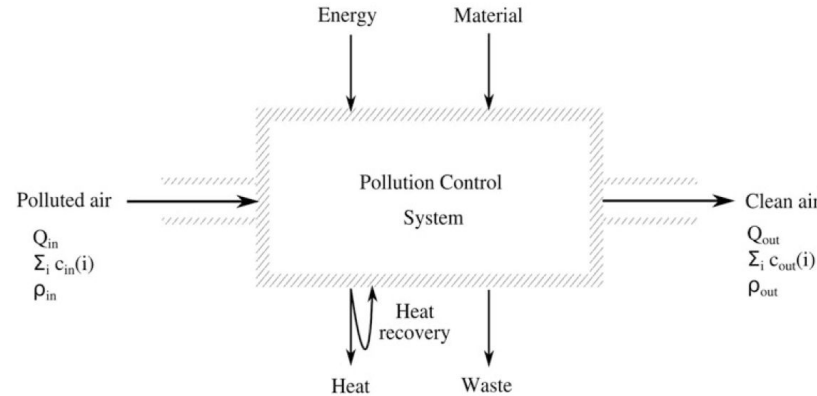
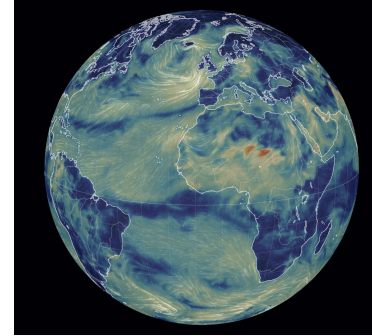


MEPS Methane Eradication Photochemical System

Point source
End of chimney installation
Water treatment plant
Livestock production
Ventilation air methane

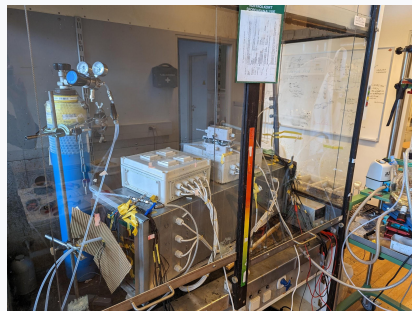
ISA Iron Salt Aerosol

Ambient air
Natural process or plume release
Atmosphere
Ship plume
Dust cloud

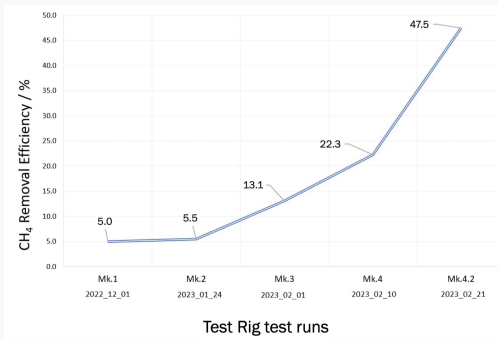


Kwiatkowski, S., Polat, M., Yu, W., & Johnson, M. S. (2021). Industrial emissions control technologies: Introduction. *Air Pollution Sources, Statistics and Health Effects*, 477-511.

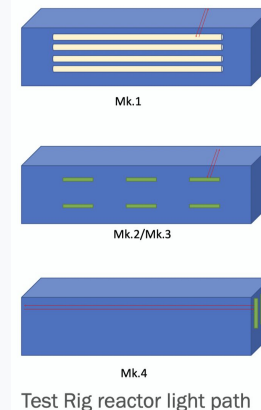
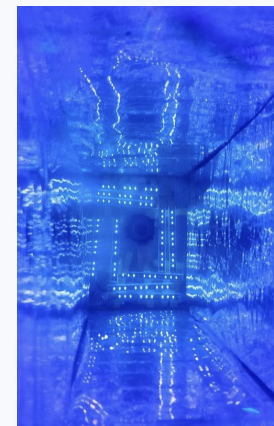
MEPS: Cl radical based pollution control



Uni Copenhagen
laboratory prototype



MEPS, Methane Eradication Photochemical System, Johnson, Schmidt and Pugliese, 2022.



Cattle barns & manure tanks
(EU+UK, US, Canada)
110,000 barns

Based on industry and government figures from the respective markets, taking northern EU & US regions into account, where dairy cows tend to be kept indoors year-round



Pig barns & manure tanks
(EU, US/Canada)
200,000 barns

Based on industry and government figures from the respective markets, focusing on large farms that tend to have multiple barns



Coal mine shafts
(EU, US, Australia, China)
100 mine shafts

Based on 283 operating underground metallurgical coal mines worldwide, many with more than one mine shaft
Source: Global Energy Monitor

UCPH is working with Arla the largest dairy coop in N Europe, to build a full scale shipping container prototype, field test summer 2023.



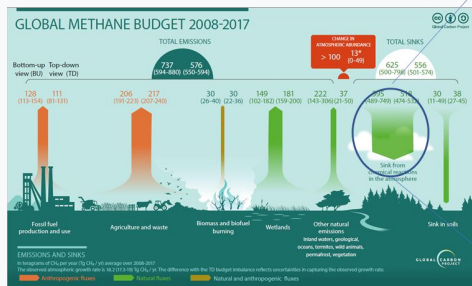
M. Polat, J. B. Liisberg, M. Krogsbøll, T. Blunier and M. S. Johnson, Photochemical method for removing methane interference for improved gas analysis, Atmospheric Measurement Techniques 14(12), 8041-8067, <https://amt.copernicus.org/articles/14/8041/2021/>, 2021.
M. S. Johnson, J. A. Schmidt and S. Pugliese, Photochemical method and device for volatile organic compound pollution control, EP20195550(2020), WO2022053603A1(2022)

Presentation content from Matthew Johnson, shared with permission

State of MEPS research and targets

Key metrics	State of the Art	Target
Volumetric energy input	300 kJ/m ³	3 kJ/m ³
CH ₄ concentration	50 – 250 ppm	Ambient to 30,000 ppm
Space velocity	2000	400
Cost per ton of CO₂e	\$4500	\$15
Byproduct impact = which reaction products are formed	CO, CH ₂ O, CO ₂ , H ₂ O	CO ₂ and H ₂ O

Atmospheric methane is naturally removed by Cl



OH
98%

Cl 2%

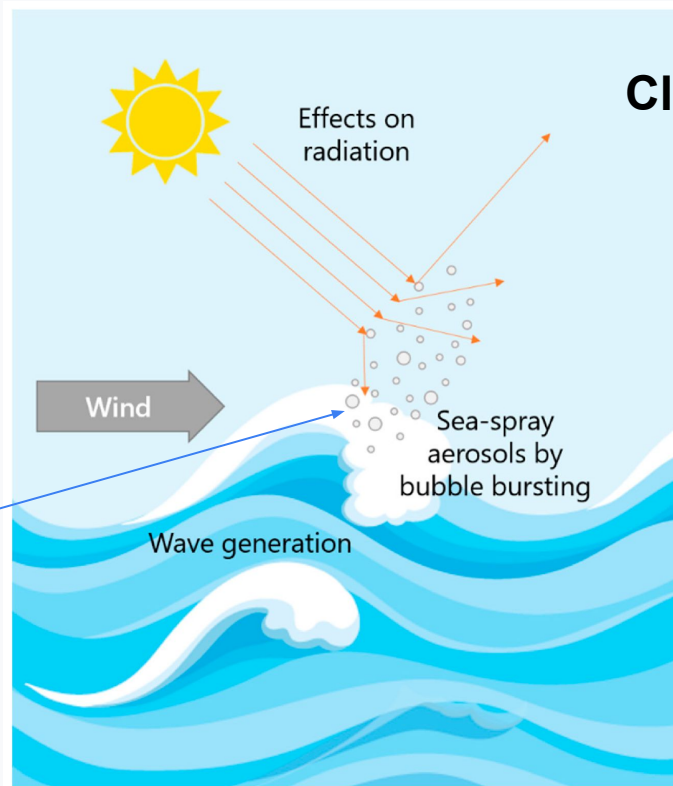
The role of chlorine in global tropospheric chemistry

Xuan Wang¹, Daniel J. Jacob^{1,2}, Sebastian D. Eastham³, Melissa P. Sulprizio¹, Lei Zhu¹, Qianjie Chen⁴, Becky Alexander⁵, Tomás Sherwen^{6,7}, Mathew J. Evans^{6,7}, Ben H. Lee⁵, Jessica D. Haskins⁵, Felipe D. Lopez-Hilfiker⁸, Joel A. Thornton⁵, Gregory L. Huey⁹, and Hong Liao¹⁰

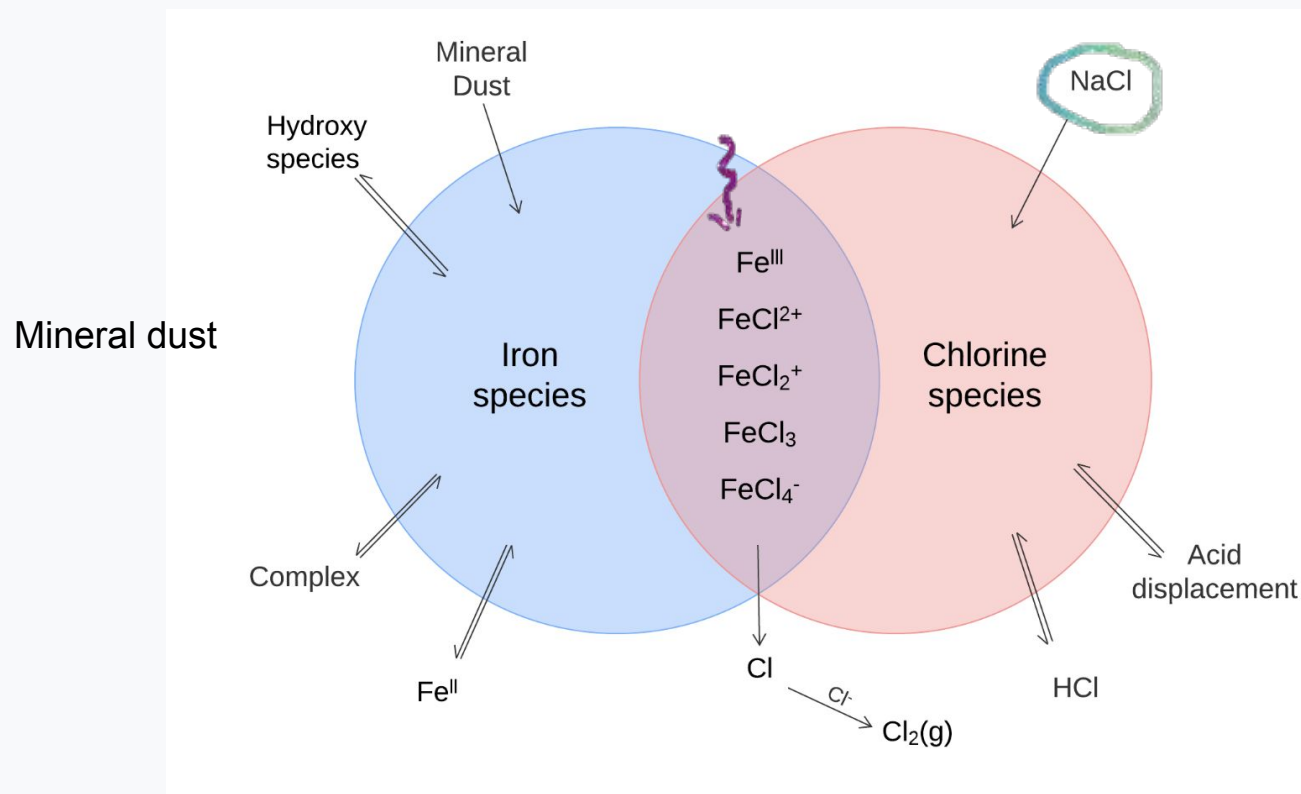
	Cl _y (Gg Cl a ⁻¹)	Cl* (Gg Cl a ⁻¹)
Total source	75 200	25 000
Sea Salt	63 900	11 900

<https://acp.copernicus.org/articles/19/3981/2019/>

Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., Alexander, B., Sherwen, T., Evans, M. J., Lee, B. H., Haskins, J. D., Lopez-Hilfiker, F. D., Thornton, J. A., Huey, G. L., and Liao, H.: The role of chlorine in global tropospheric chemistry, *Atmos. Chem. Phys.*, 19, 3981–4003, <https://doi.org/10.5194/acp-19-3981-2019>, 2019.



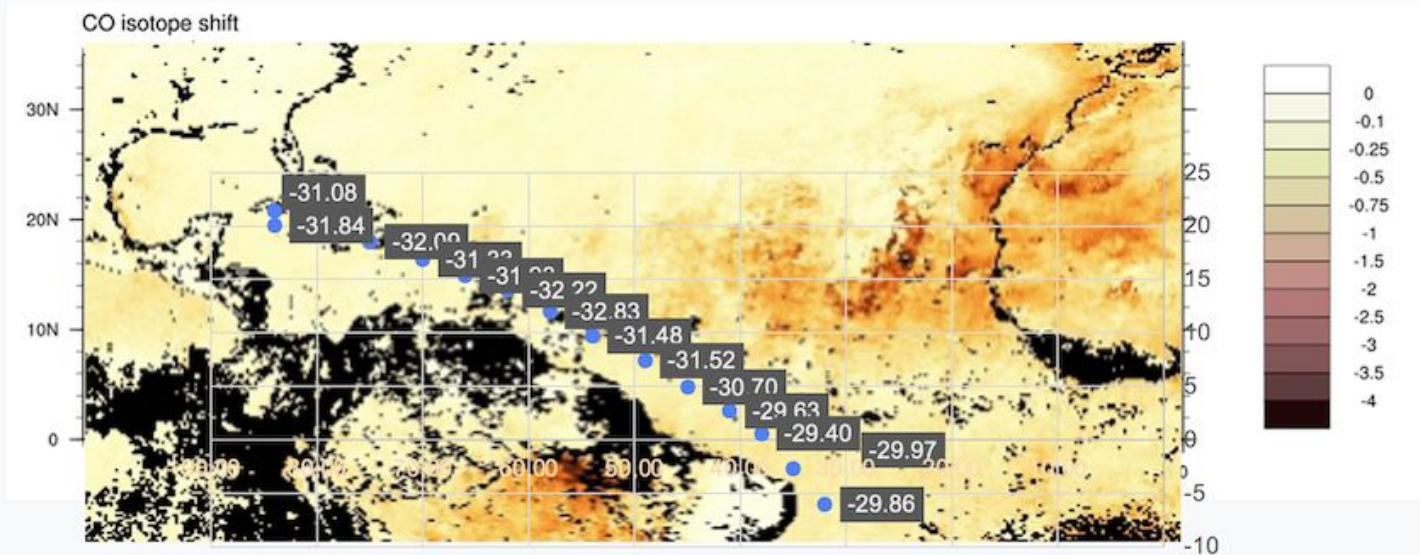
Mineral Dust – Sea spray Aerosol (MDSA) makes Cl



**A New
Mechanism!**

The freshest data confirm: MDSA is a powerful natural process

Terra/MODIS AOD Oct 2022, with transect Oct 2022 data

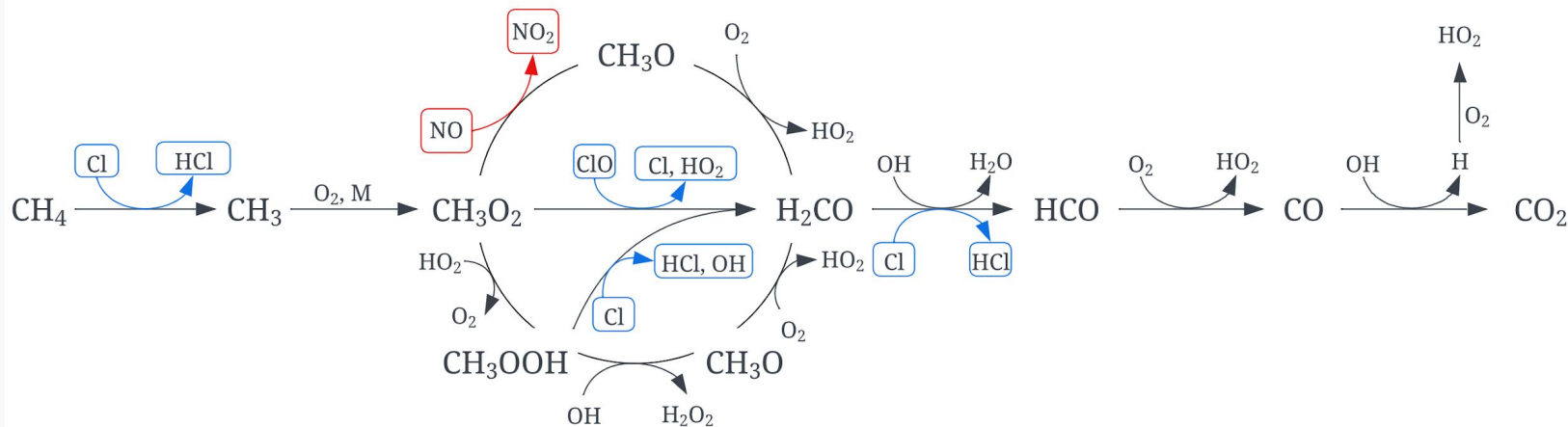


Sampling from the Maersk Stolt Viking transect

First results from the next-largest flask sampling campaign in the world

More Cl can be a blessing or a curse..

High radical chain efficiency side/High Nox: More O_3 , more OH, less CH_4



Low radical chain efficiency side/low Nox: Less O_3 , less OH, More CH_4

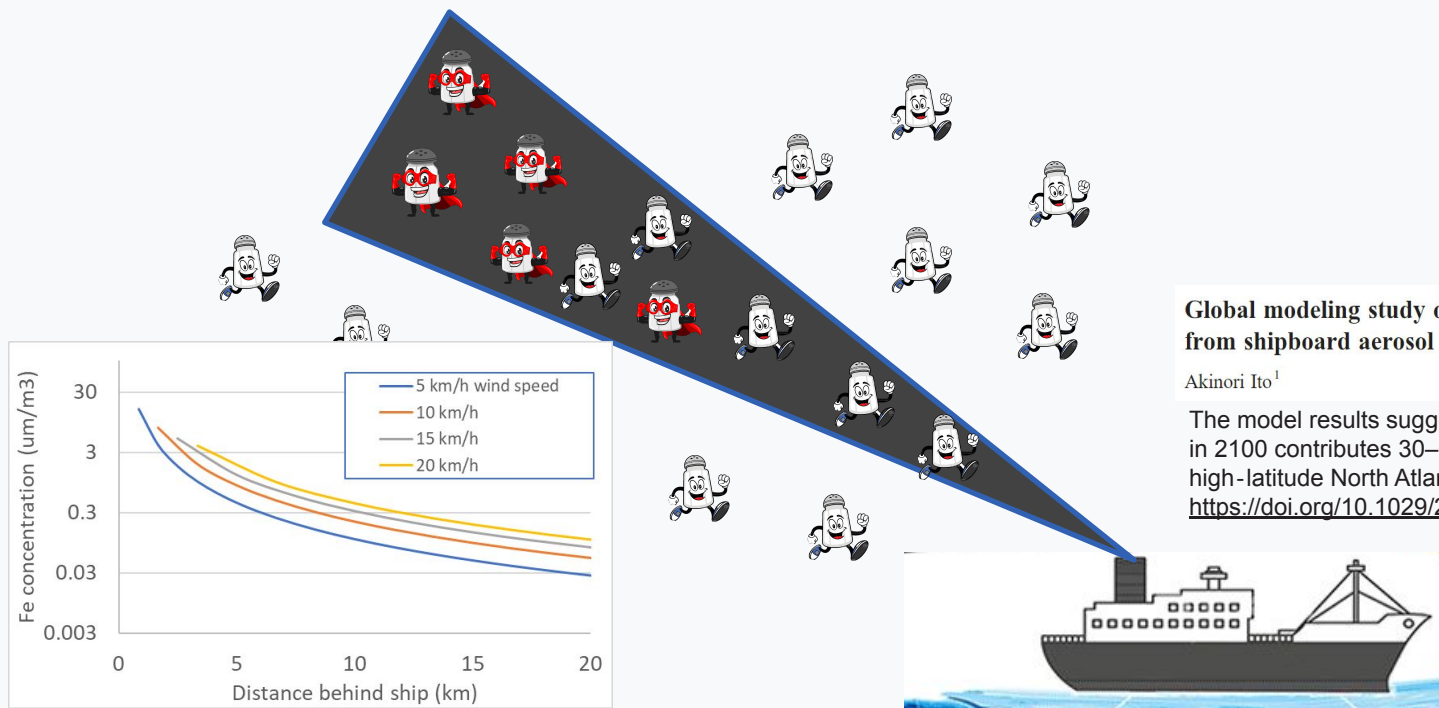
The moral of the story is, use your chlorine wisely!

Next steps: CO isotope observations, lab tests and modelling

- Current focus: **MDSA across the North Atlantic, and feasibility of CI as means for methane removal**
- Field study with CO observations from Tenerife, Cape Verde, Barbados, ATTO tower Brazil, and several shipping trajectories
- Modelling the impact of increased atmospheric CI
- Lab studies to better understand the chemistry, including the role of e.g. humidity, and species like H_2O_2 , organics.
- Climate pathway modelling that includes methane removal technology
- Next year: **anthropogenic MDSA** emissions, especially by ships
- Long term: **application as methane removal technology, if proven safe & effective, and if effective governance is in place.**



Since shipping emissions are a main source of iron above the oceans, we want to study if this creates iron-salt aerosols in their plumes



Global modeling study of potentially bioavailable iron input from shipboard aerosol sources to the ocean

Akinori Ito¹

The model results suggest that deposition of soluble iron from ships in 2100 contributes 30–60% of the soluble iron deposition over the high-latitude North Atlantic and North Pacific.

<https://doi.org/10.1029/2012GB004378>

Key Points

- Radicals trigger a cascade of spontaneous reactions.
- OH is the main atmospheric oxidant
- Cl is cheaper and better than OH
- GPAO is OH radical pollution control
- MEPS is Cl radical methane control
- MDSA is a large natural source of Cl to the atmosphere

Key Questions

- What is the ultimate catalytic efficiency of MDSA (CH_4/Fe)?
- What are the optimal deployment conditions for ISA?
- What is the ultimate efficiency of MEPS \$/tCO₂e
- What is the bottom end of the range of MEPS – ambient CH_4 ?

Acknowledgements / team



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Energetic Constraints for Atmospheric Methane Removal

Sam Abernethy

sabernet@stanford.edu

April 11, 2023

Conditions for feasibility

Resource efficient

Surface area
efficient

Climate beneficial

Cost-effective



Justified assumptions

Best-case 2030
energy scenario

Methane valued
highly

Developments in
adjacent fields



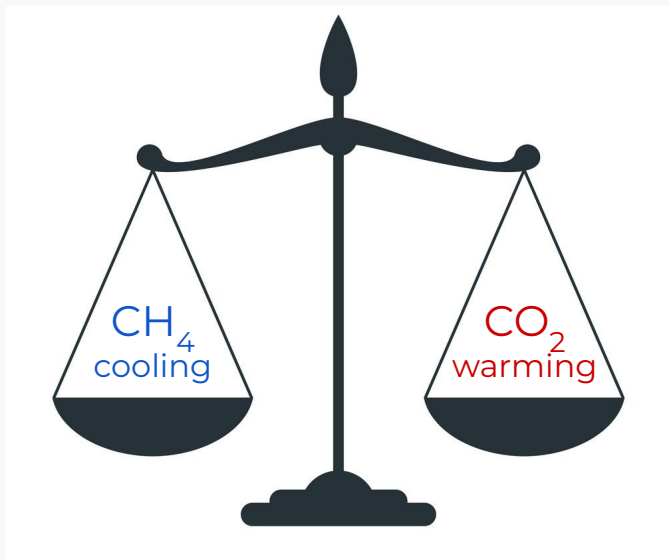
Necessary breakthroughs

What technological advances are
required to make a solution
feasible for atmospheric removal?

Example conditions: climate-neutral & cost-neutral

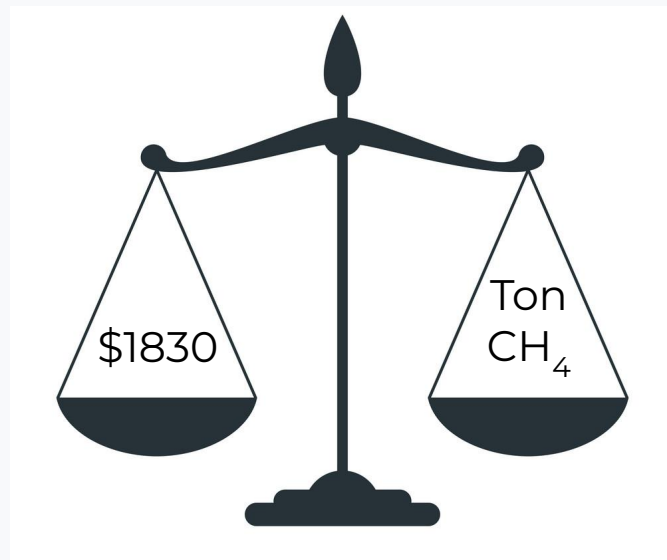
Climate neutrality: cooling benefit equals the warming caused by the energy used.

Fundamental.



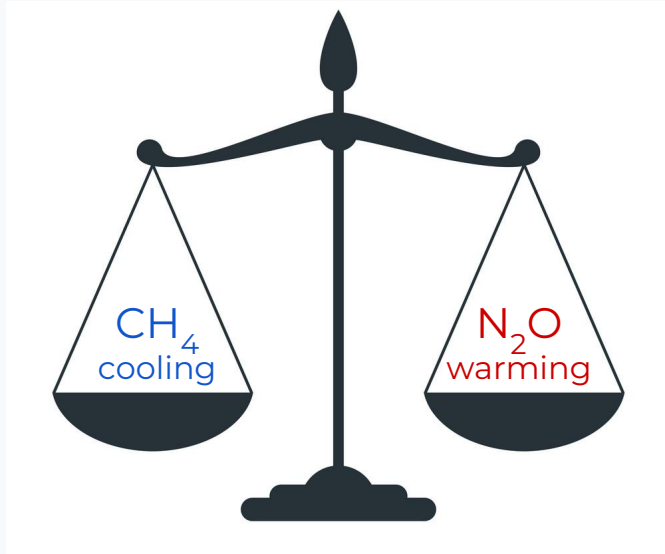
Cost neutrality: economic benefit equals the cost of the energy used.

Practical.

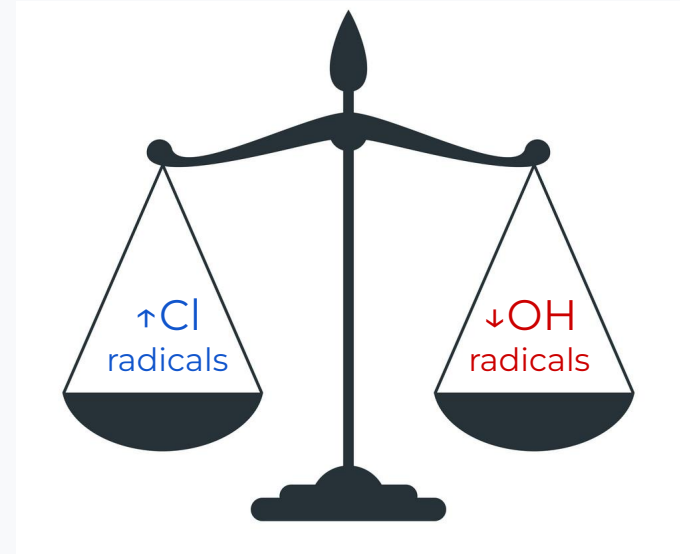


Applying this framework beyond flow reactors

Methanotrophs: is the warming from N_2O production offset by cooling from CH_4 oxidation?



Iron Salt Aerosols: is the decrease in hydroxyl radicals offset by the increase in chlorine radicals?



Methane Modelling Capabilities

Fiona M. O'Connor

Methane Removal Workshop, April 2023

Outline

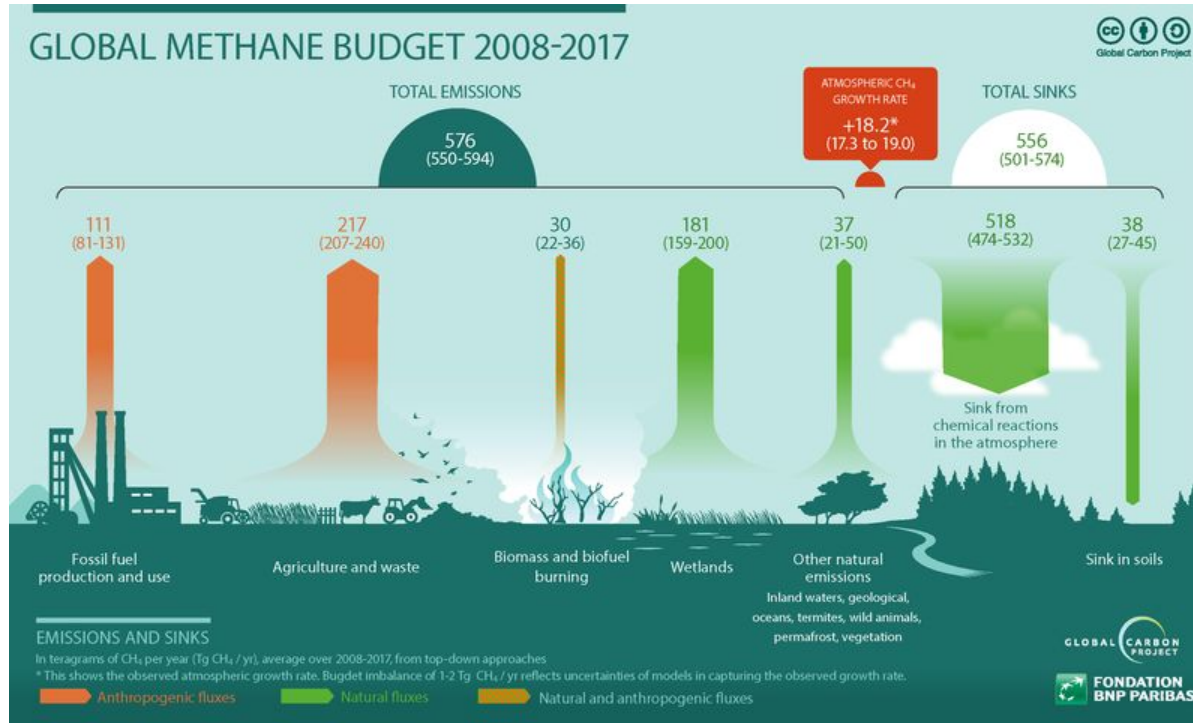
- Current Modelling Capabilities: Global and Regional Scales
- Methane Emissions-Driven Capability
- Methane Modelling: Capability Gaps & Challenges
- Use of Observations
- Conclusions & Future Outlook





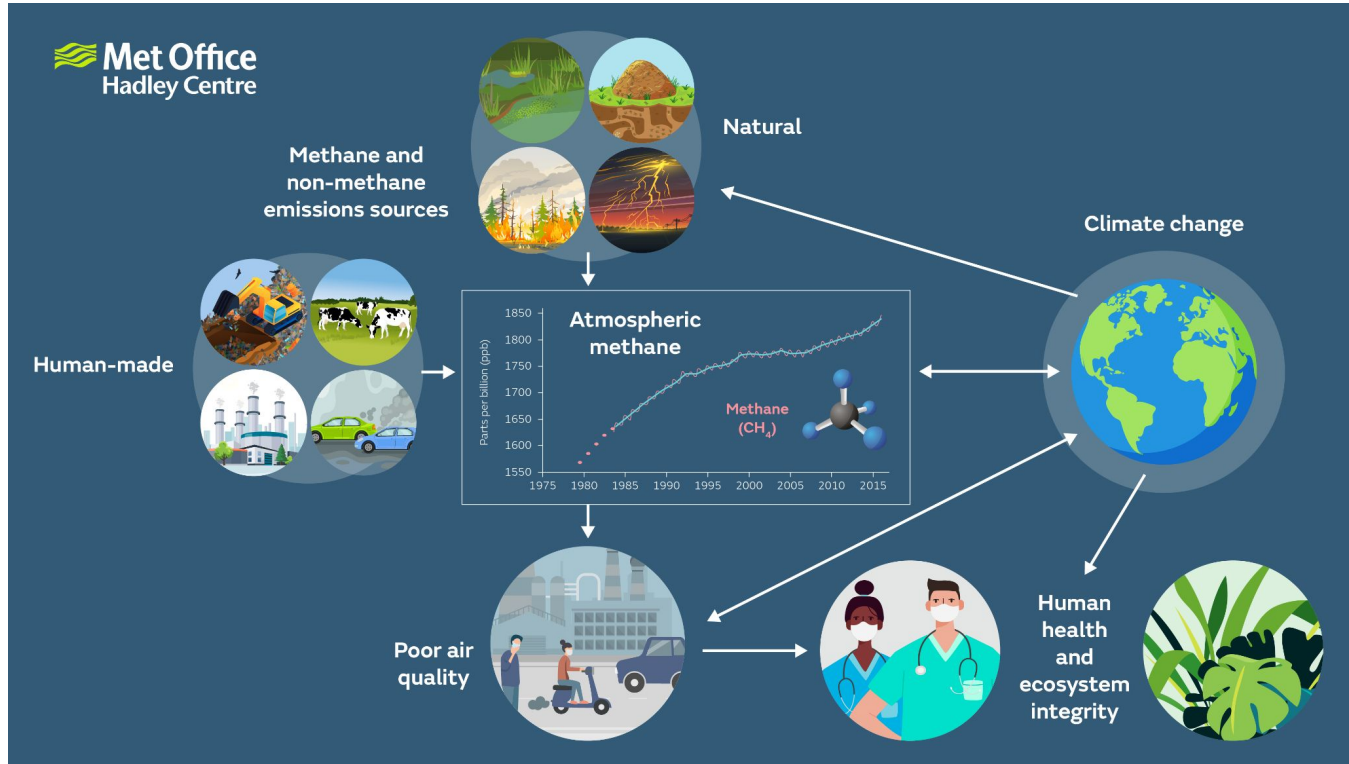
Modelling Capabilities

What's needed to model methane?

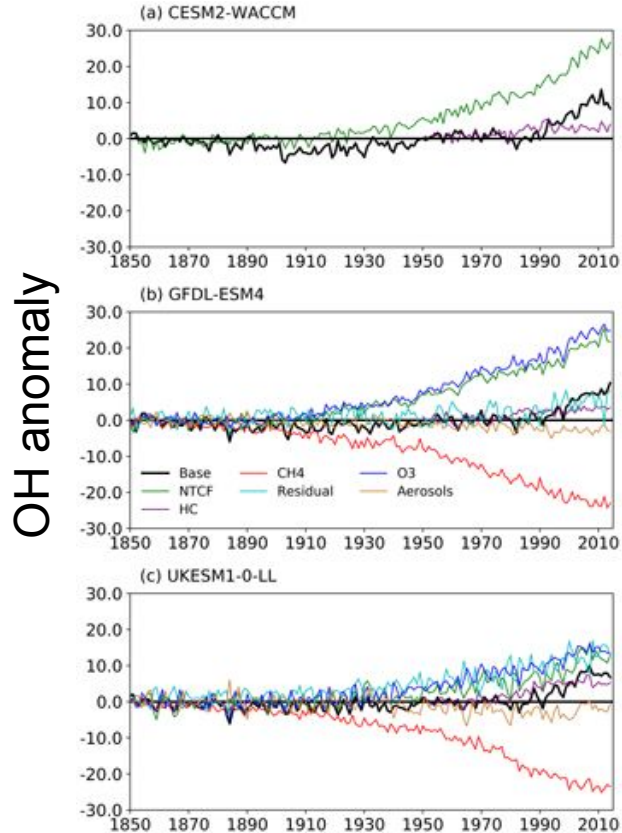


[Saunois et al., ESSD \(2020\)](#)

Role of methane in the Earth System



Drivers of methane lifetime



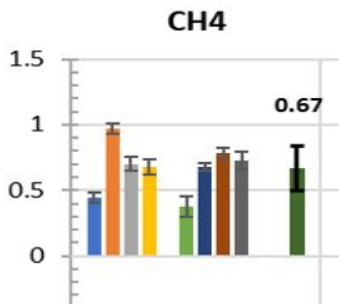
Two main anthropogenic drivers of methane lifetime:

- Methane $\uparrow$ Lifetime $\uparrow$
- Nitrogen oxides $\uparrow$ Lifetime $\downarrow$

[Stevenson et al., ACP \(2020\)](#)

Climate forcing by methane

Climate forcing / Wm^{-2}

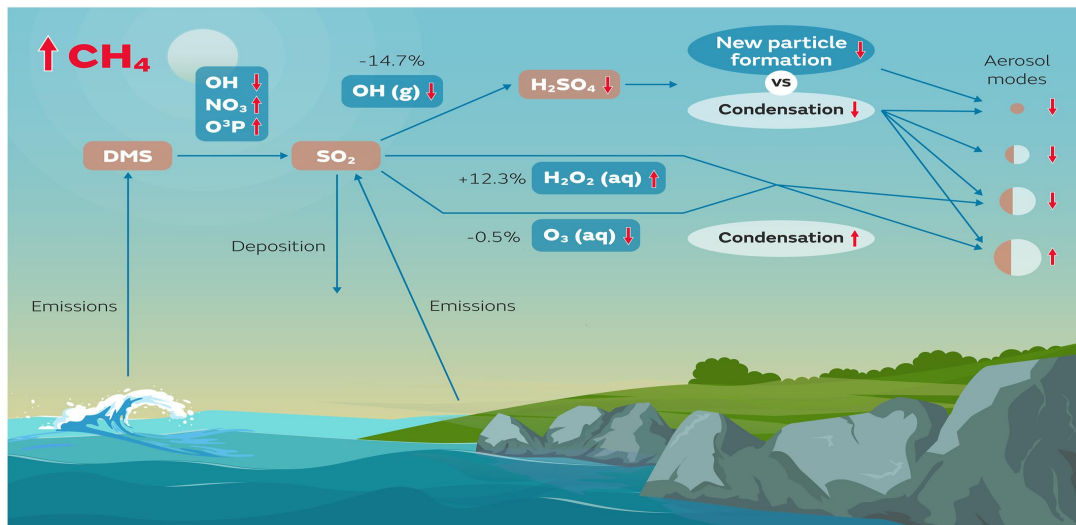


- Strong diversity in climate forcing by methane
- Partly explained by representation of chemistry
- Partly explained by changes in cloud properties

[Thornhill et al., ACP \(2021\)](#)

UKESM1 had the highest forcing, due to changes in cloud albedo related to chemistry-aerosol-cloud interactions

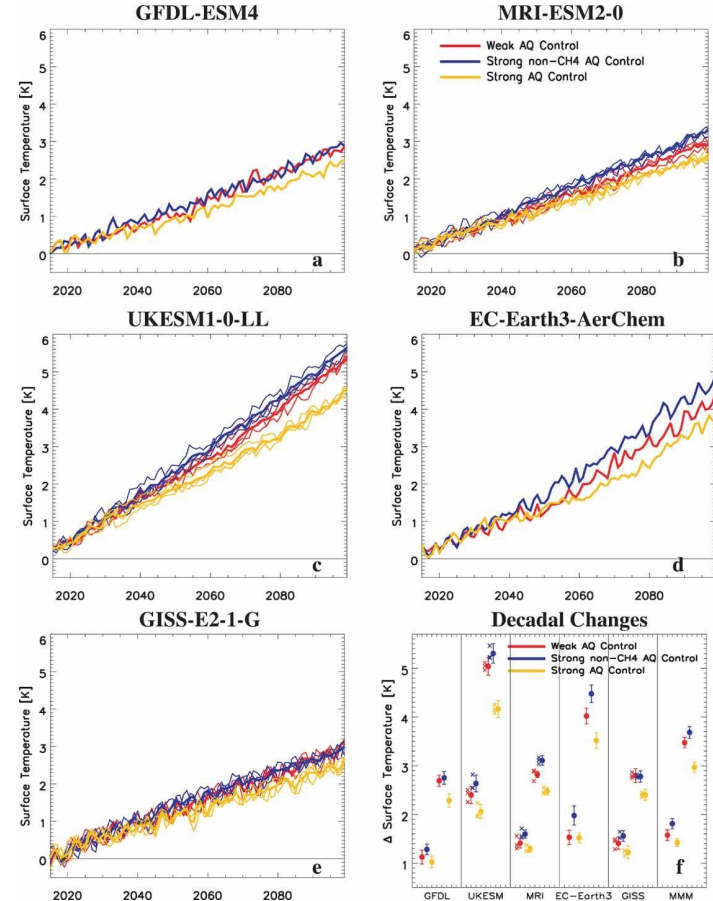
[O'Connor et al., JAMES \(2022\)](#)



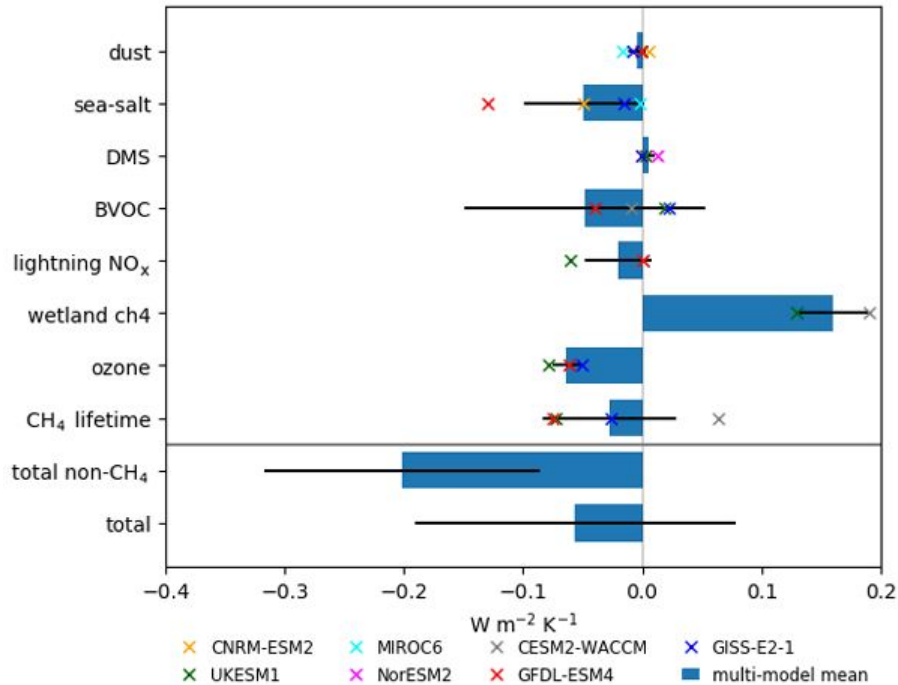
Methane Mitigation

- Base case: ssp3-7.0
- Non-methane air quality improvements result in a climate tradeoff relative to base case
- Including methane mitigation results in a net climate benefit

[Allen et al., ERL \(2021\)](#)



Climate feedbacks relevant to methane



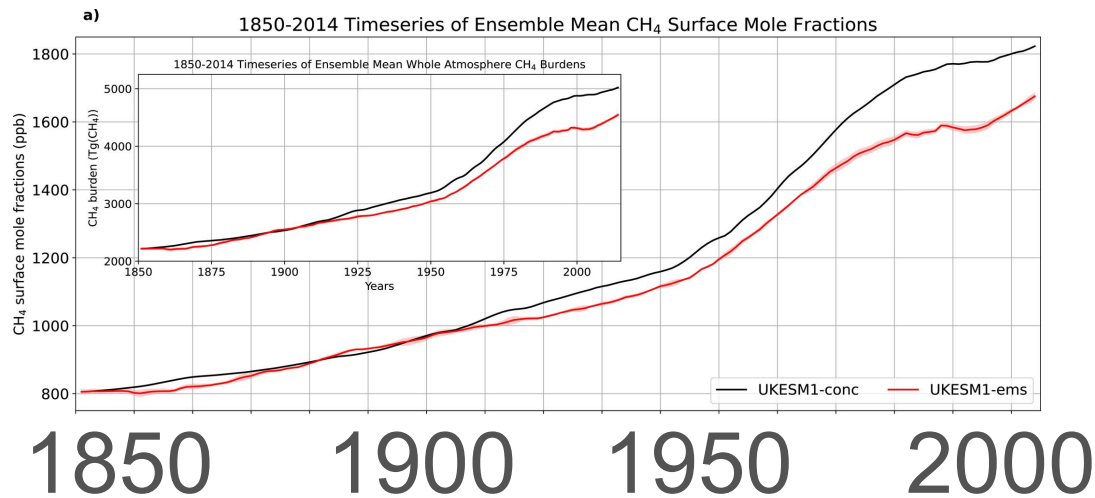
- Wetlands show a strong positive feedback
- Methane lifetime shows a negative feedback
- Understanding these feedbacks is crucial for quantifying the efficacy of methane mitigation/removal

[Thornhill et al., ACP \(2021\)](#)



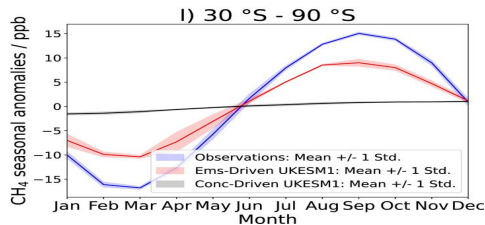
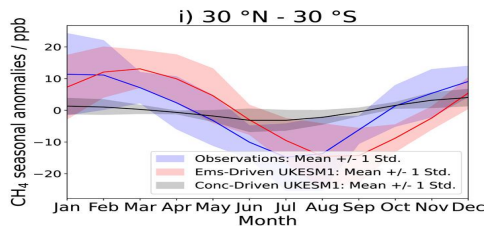
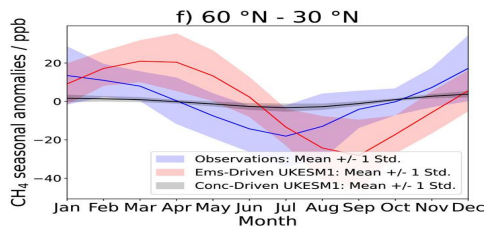
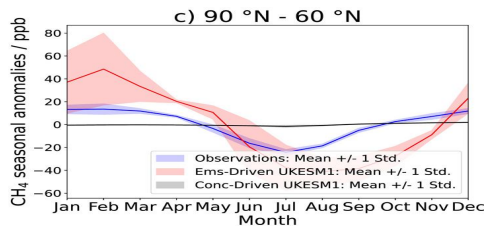
Methane Emissions-Driven Modelling Capabilities

UKESM1: Methane Emissions-Driven Capability

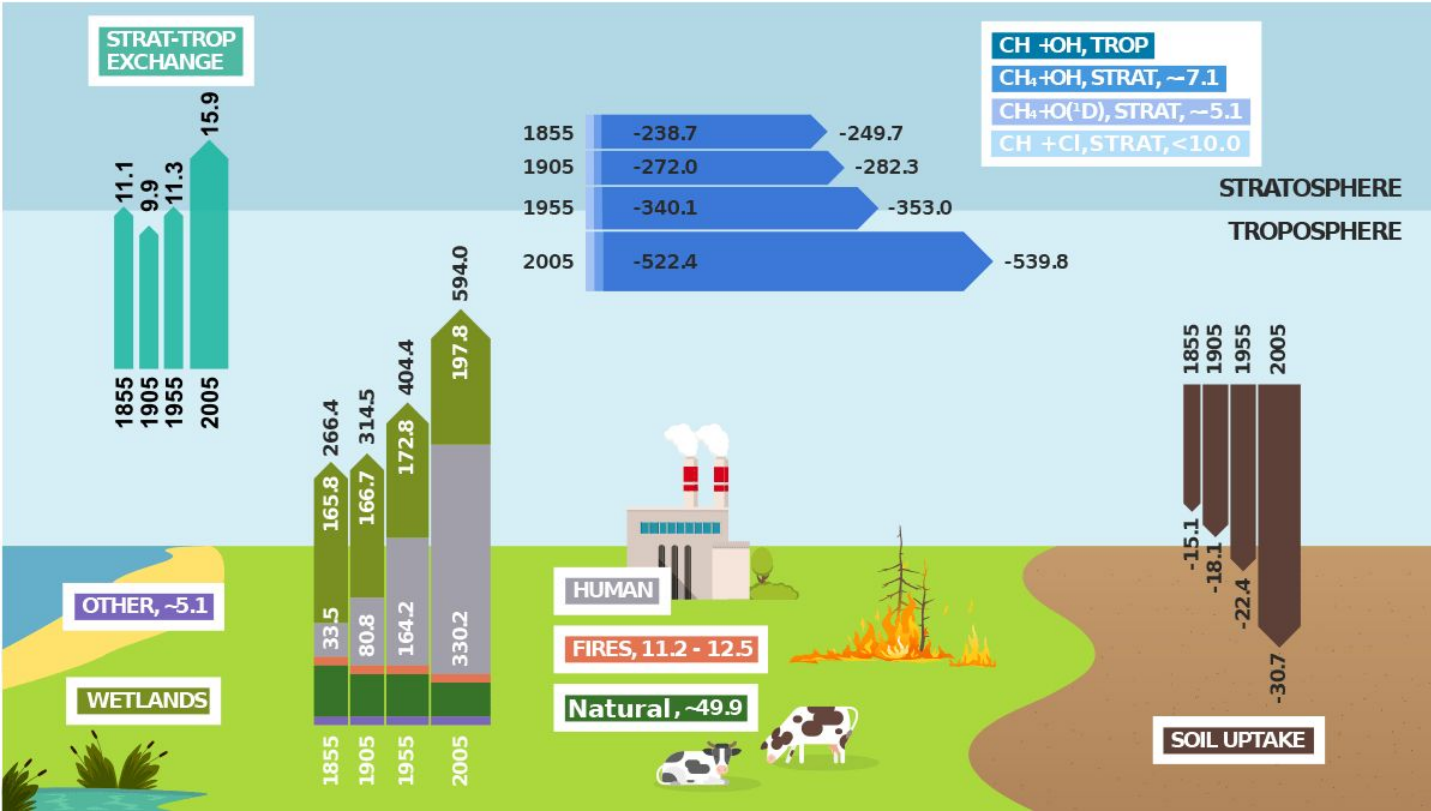


- Good representation of global mean changes over historical period
- Negative bias relative to observations post-1920
- Improved representation of latitudinal distribution and seasonal cycle

[Folberth et al., JAMES \(2022\)](#)

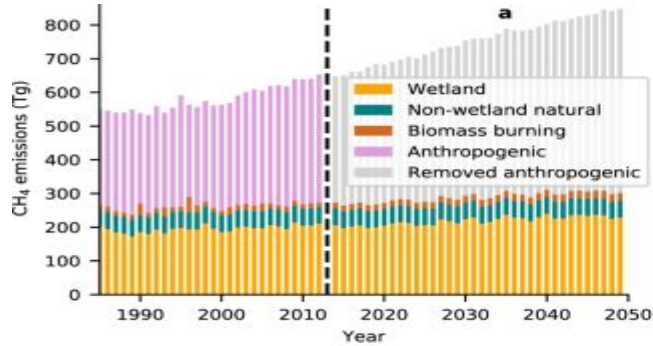


UKESM1: Methane Emissions-Driven Capability

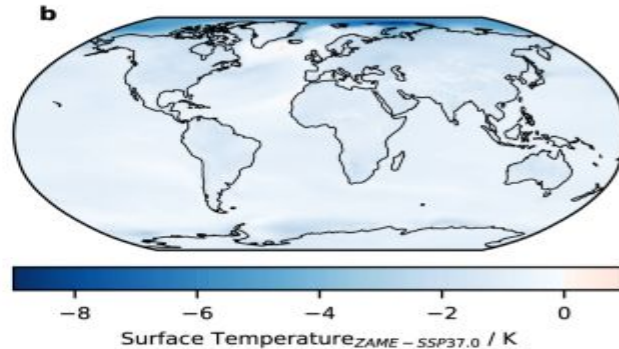
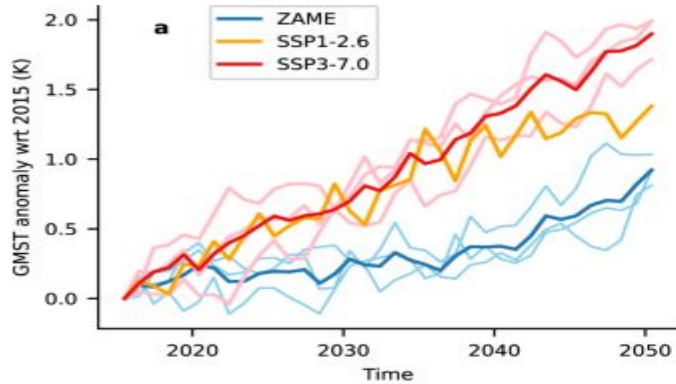


[Folberth et al., JAMES \(2022\)](#)

Methane Mitigation

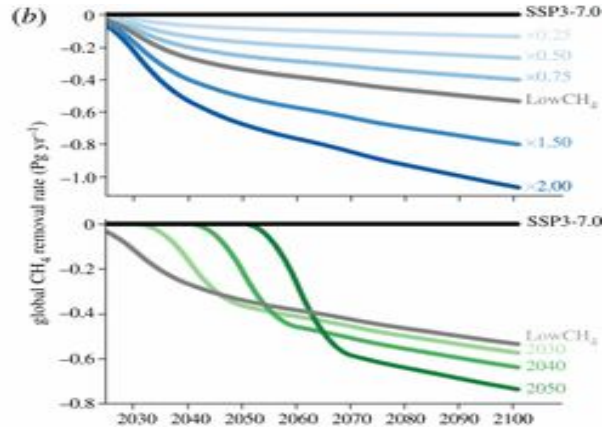


- Exploration of a deep, rapid and sustained cut in anthropogenic methane emissions
- Rate of warming reduced relative to base case (ssp3-7.0; red)
- Strong air quality and human health co-benefits
- Stronger climate benefit in Arctic than global mean

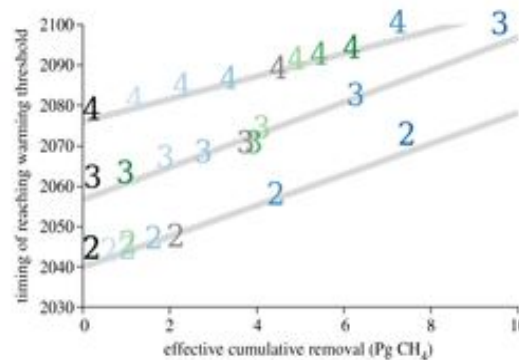
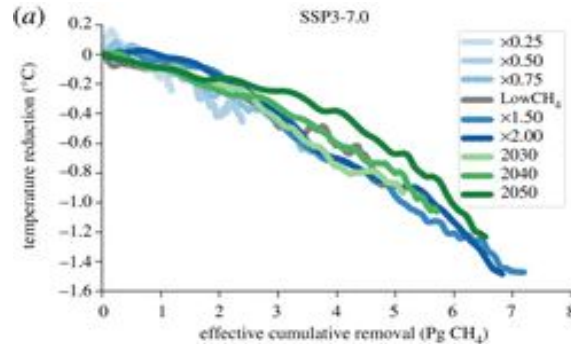


[Staniaszek et al., npj Clim Atmos Sci \(2022\)](#)

Methane Removal

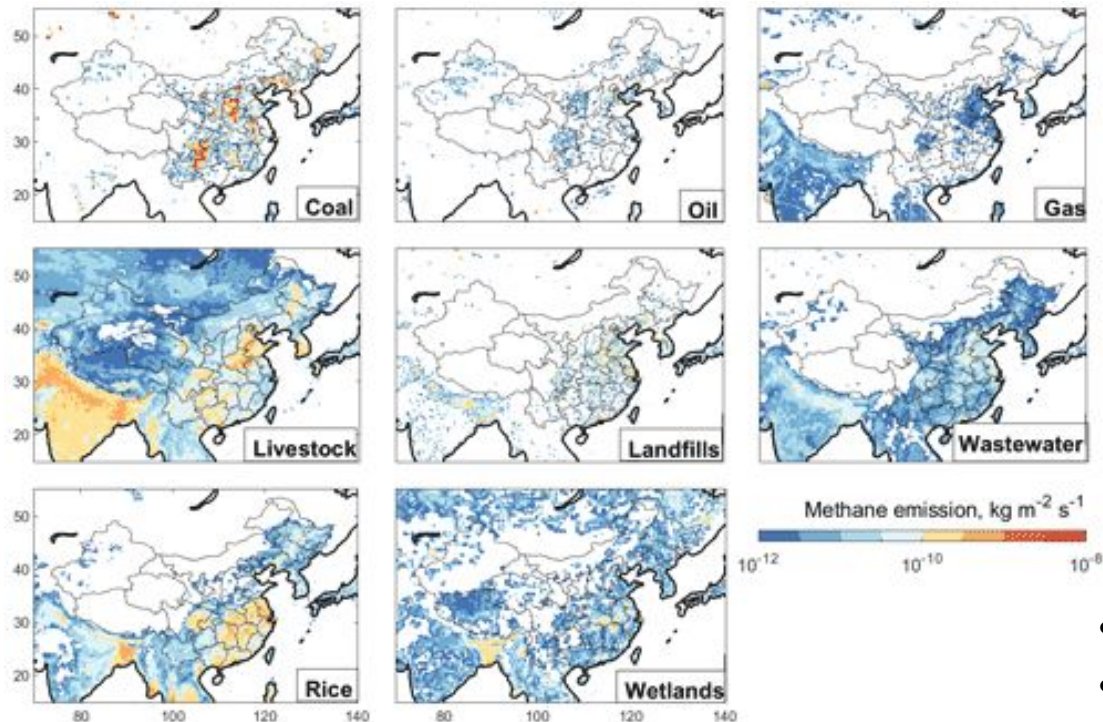


- Range of mitigation/removal pathways, varying in depth (blue) and timing (green)
- Linear relationship between global mean temperature (and ozone) change and effective cumulative removal
- Delay in passing temperature thresholds also linearly related to effective cumulative removal



[Abernethy et al., Phil Trans Royal Soc \(2021\)](#)

GEOS-Chem Inversions: Emission Estimation

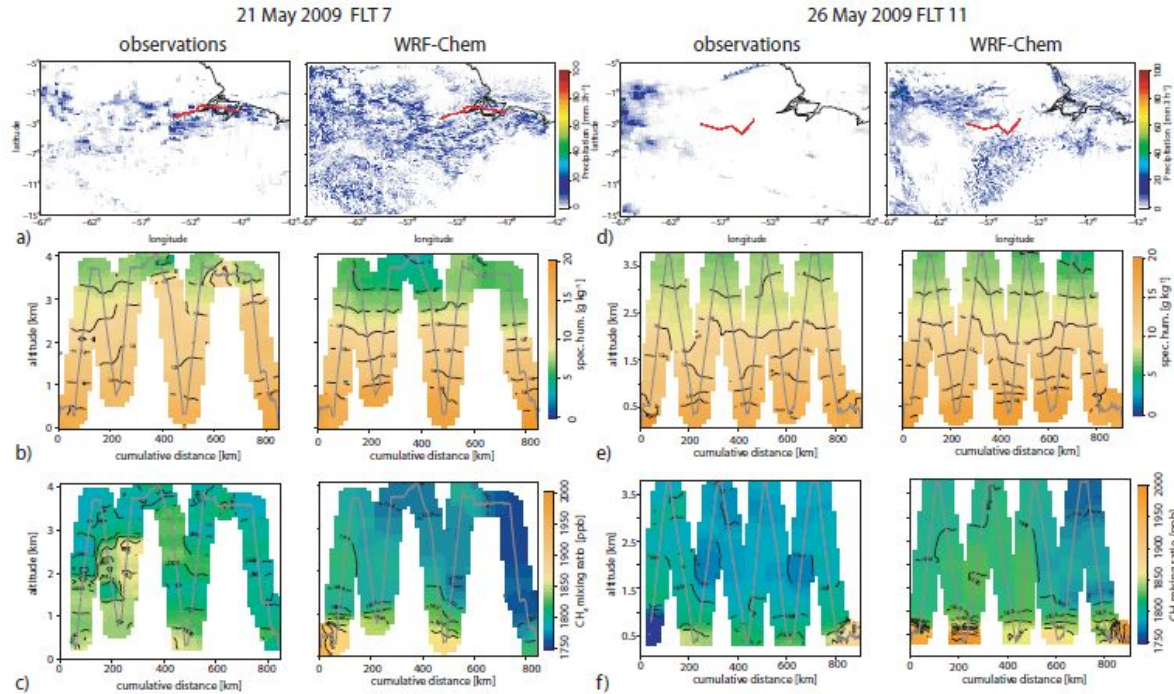


Forward and inverse modelling at global scale with GEOS-Chem

- High resolution ($0.25^\circ \times 0.3^\circ$)
- Based on GEOS-Chem
- TROPOMI observations

[Chen et al., ACP \(2022\)](#)

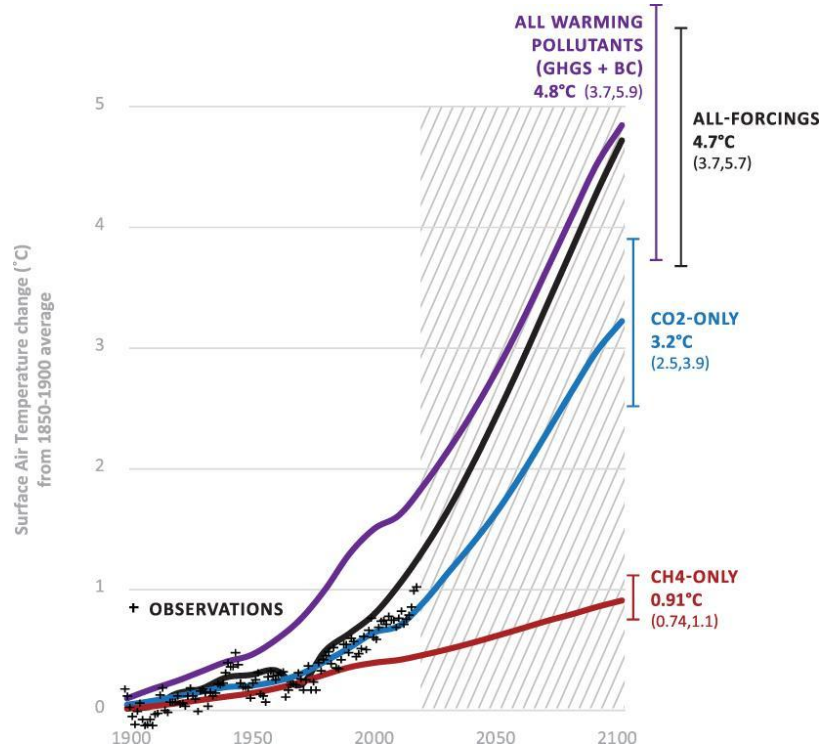
Regional-Scale Modelling Capabilities



[Beck et al., ACP \(2013\)](#)

Forward and inverse modelling at regional scale with WRF-Chem

Simple Models



[Ocko et al., ERL \(2021\)](#)

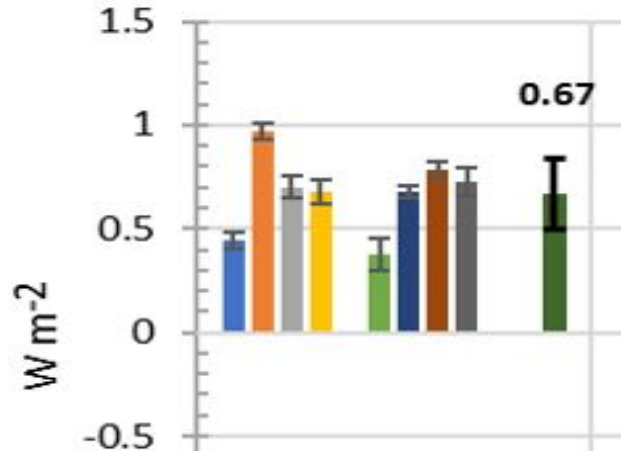
Rapid assessment of methane mitigation (or removal) feasible with simple climate models or emulators (e.g., MAGICC, FaIR)



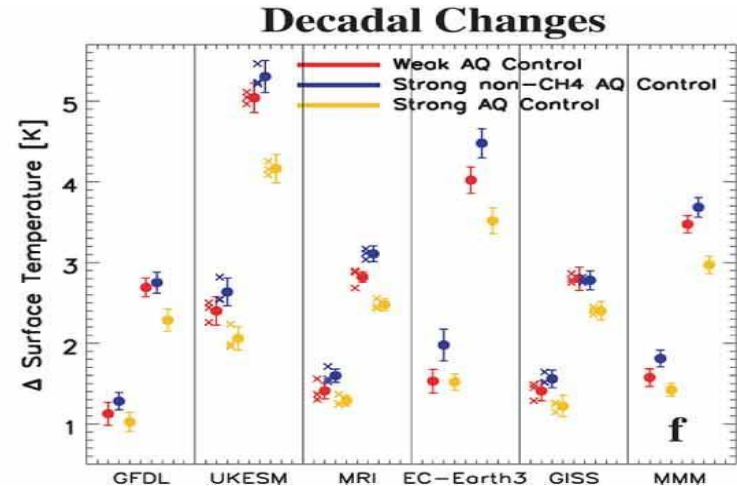
Capability Gaps & Challenges

Capability Gaps (1): Chemistry

Climate Forcing

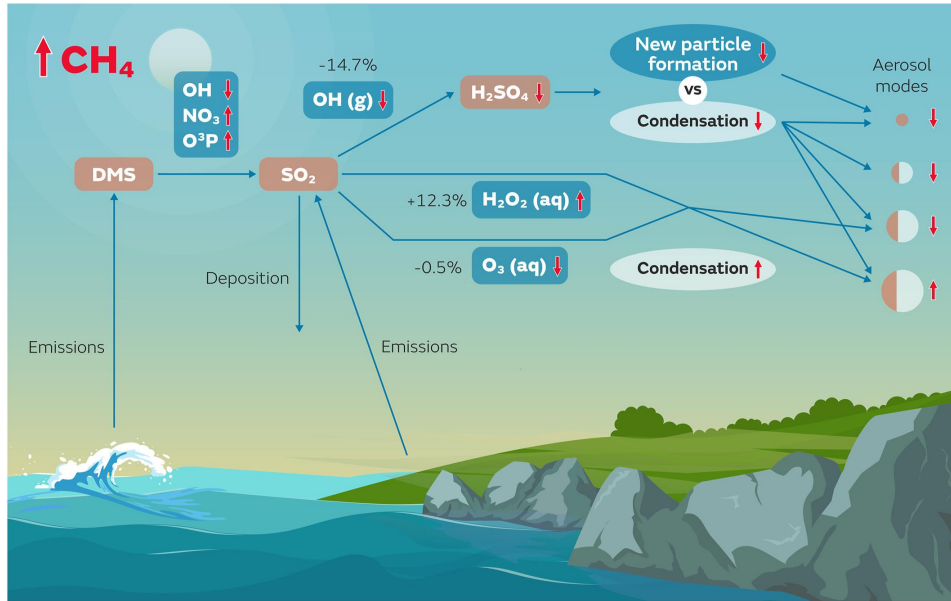


Methane Mitigation



- Variety of chemistry representations (i.e., lower forcing)
- Link from emissions $\rightarrow$ concentration $\rightarrow$ response is absent
- Response is not directly attributable to changes in CH_4 ems

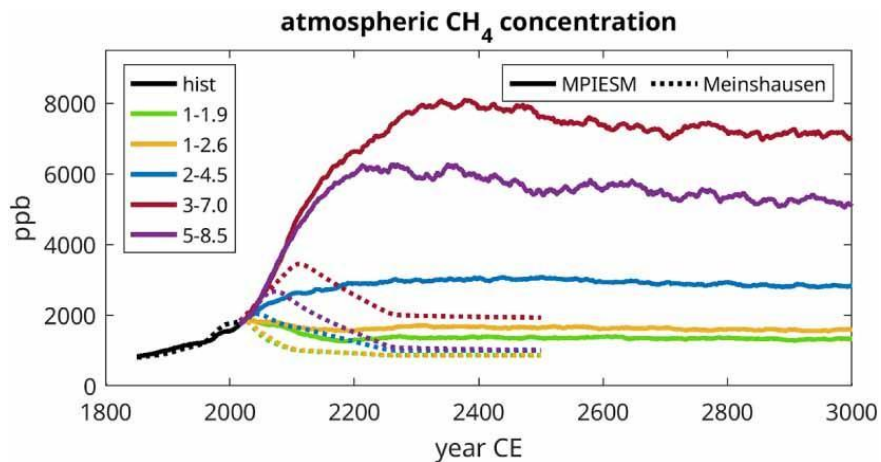
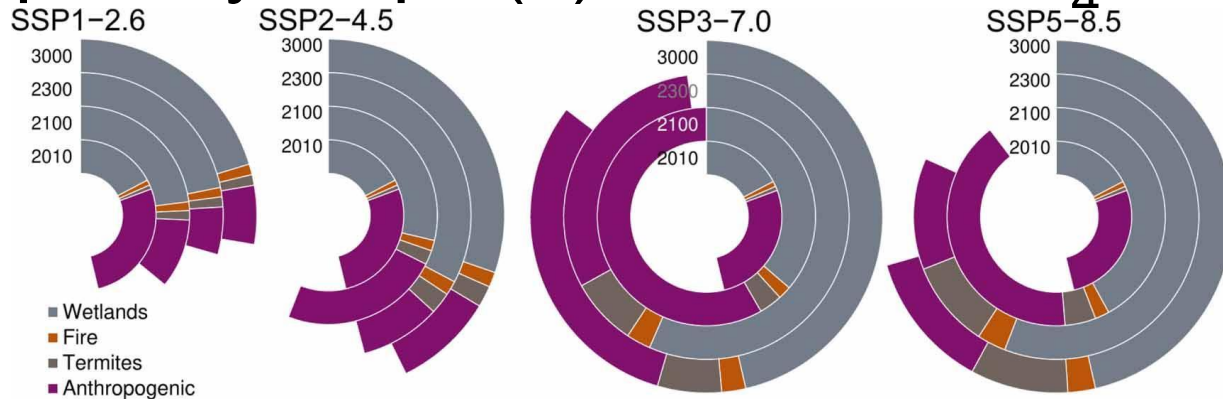
Capability Gaps (2): Chemistry-Aerosol



[O'Connor et al., JAMES \(2022\)](#)

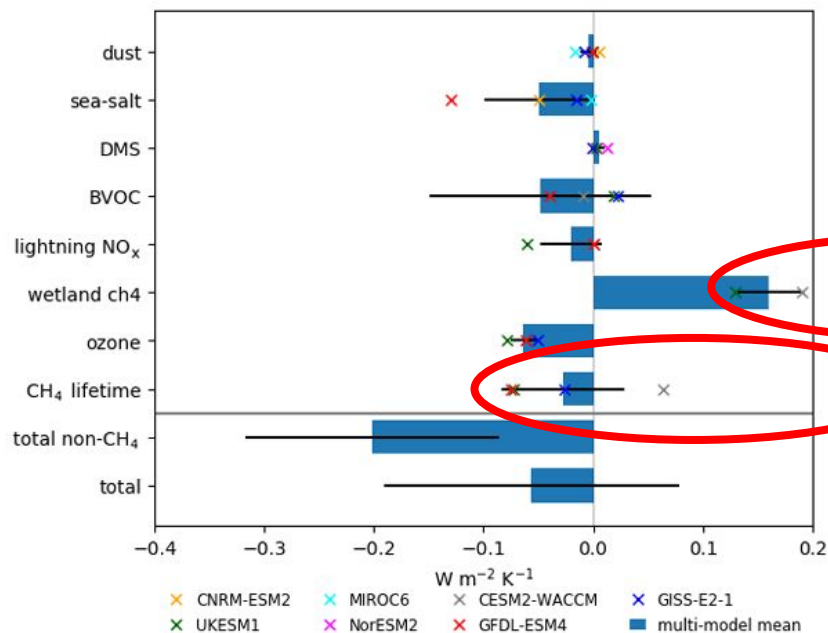
Chemistry-aerosol capability, including use of two-moment aerosol schemes could strongly influence methane forcing

Capability Gaps (3): Wetland CH₄ Emissions



- Future IPCC pathways assume constant wetland emissions
- Wetland emissions increase by 22-149% by 2100
- As climate warms, more methane removal required to counteract increases in wetland emissions

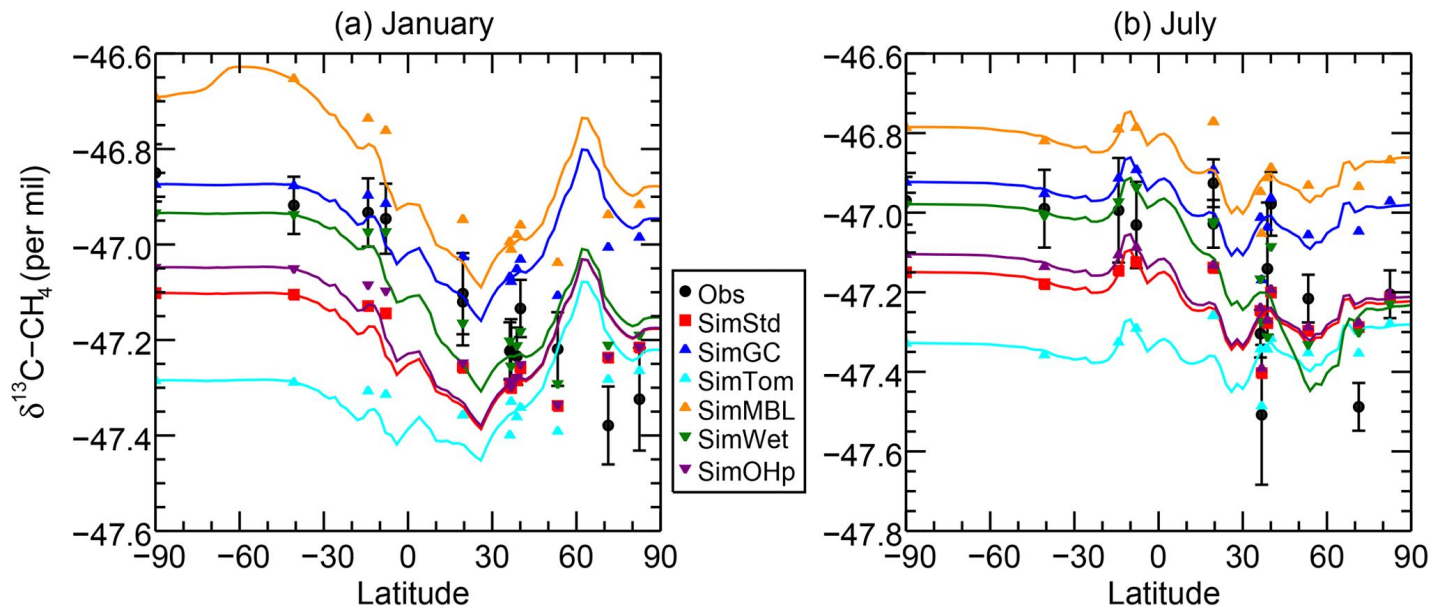
Capability Gaps (4): Natural Emissions & Lifetime



Future projections have missing processes and do not include potential feedbacks on methane lifetime

- Wetland emissions are only included in two models!
- Missing processes, e.g., permafrost, fires, soil NO_x
- Large uncertainty in future lifetime changes (non-CH₄ emissions)

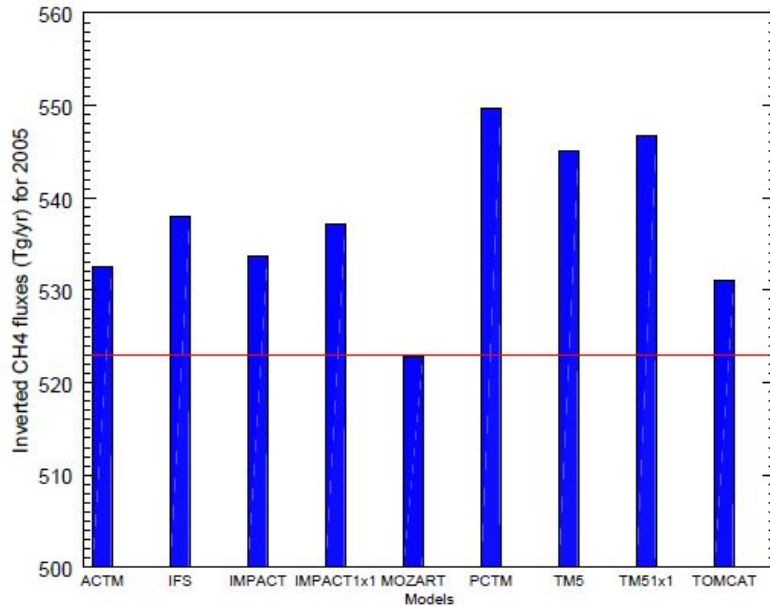
Capability Gaps (5): Isotopic Composition



[Strode et al., ACP \(2020\)](#)

Few models consider tropospheric chlorine sink of methane despite isotopic composition being very sensitive to chlorine

Challenges (1): Transport Errors

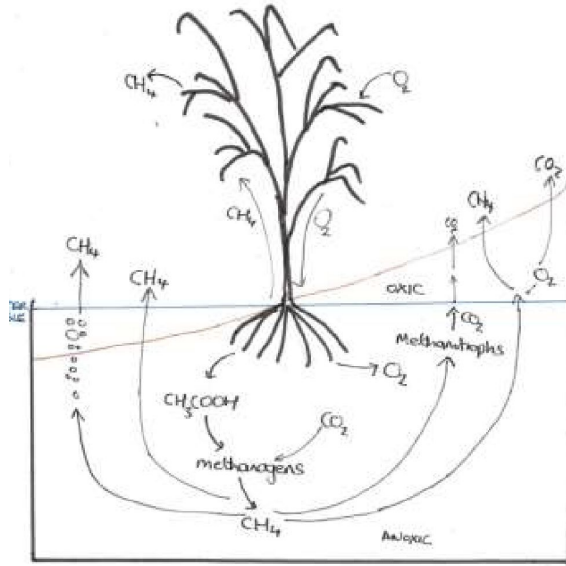


[Locatelli et al., ACP \(2013\)](#)

Transport errors in models contribute significantly to overall uncertainties in emission estimates by inverse modelling, particularly at small spatial scales

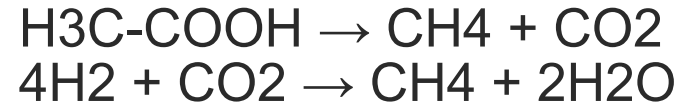
Challenges (2): Emissions

Courtesy of Nic Gedney



Wetland drivers show non-linear behaviour; Wetland type also important; Many individual processes making it challenging to model; Similar challenges with all natural emissions

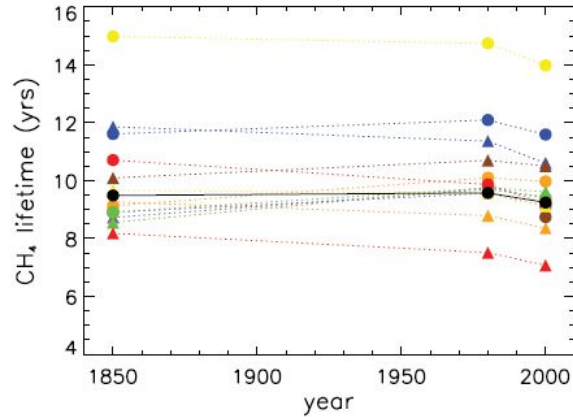
- CH_4 produced by anaerobic respiration in methanogens:



- CH_4 consumption by microbes in oxic (unsaturated) soil more efficient than methanogenesis in saturated soil

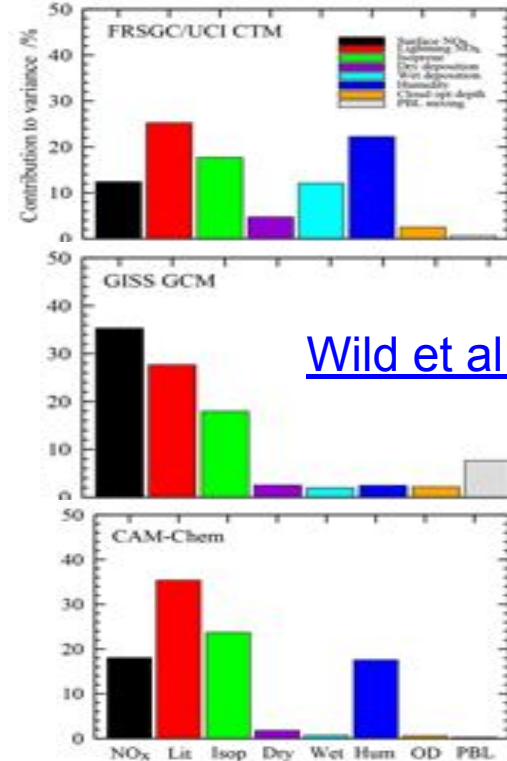
- Transfer by ebullition, diffusion & plant transport (via roots)
- Many individual processes

Challenges (3): Methane lifetime



CESM-CAM-superfast
 CICERO-OsloCTM2
 CMAM
 EMAC
 GEOSCCM
 GFDL-AM3
 GISS-E2-R
 HadGEM2
 LMDzORINCA
 MIROC-CHEM
 MOCAGE
 NCAR-CAM3.5
 STOC-HodAM3
 UM-CAM
 ACCMIP_mean

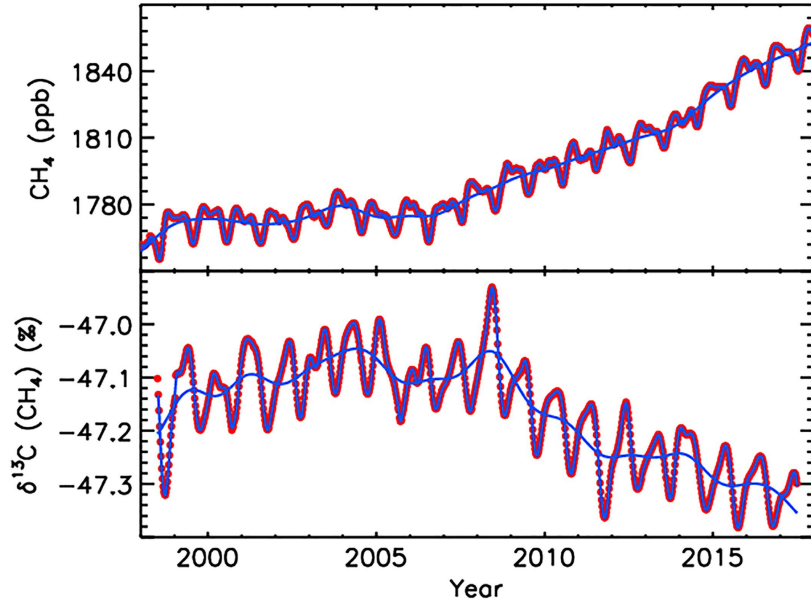
[Voulgarakis et al., ACP \(2013\)](#)



[Wild et al., ACP \(2020\)](#)

Understanding diversity in methane lifetime & its drivers

Challenges (4): Methane growth rate



[Nisbet et al., GBC \(2019\)](#)

Post 2006 increases:

- Agriculture, fossil fuels &/or wetland
- Fossil fuel biomass burning

Record growth rates in 2020 and 2021

Understanding sources and sinks: methane growth rate

Potential Opportunities

Future Outlook

- Development of multi-model methane emissions-driven capability (e.g., ESM2025)
- Development of methane isotopic modelling capability (UKESM1, NIWA)
- New PhD project on tropospheric halogen sink (Starts Oct 2023)
- Development of coupled methane-carbon dioxide capability (UKESM2)
- Potential for Methane Removal Model Intercomparison Project (CMIP7)
- Inclusion of methane emissions-driven capability in climate emulators (e.g., MAGICC, FaIR)
- ML to detect positive/negative methane anomalies

