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# Technical approaches to removing methane from the atmosphere (methane removal)



## Fact check and discussion

### Summary

Methane (CH<sub>4</sub>) is a greenhouse gas with around 30 times the climate impact of carbon dioxide (CO<sub>2</sub>). The short-term climate impact (over a period of 20 years) is even up to 86 times higher than CO<sub>2</sub>. Methane is oxidised to CO<sub>2</sub> in the atmosphere by natural chemical reactions over a period of several years. The maximum greenhouse effect of CH<sub>4</sub> in the air is around 12.4 years (Ehhalt et al. 2018; Abernethy et al. 2021). This reduces the climate impact of a unit quantity of emitted CH<sub>4</sub>, while there are no chemical self-cleaning mechanisms for CO<sub>2</sub> in the atmosphere.<sup>1</sup> However, the natural self-cleaning mechanisms of the atmosphere are not sufficient to compensate for the increase in the atmospheric CH<sub>4</sub> concentration, as methane emissions from anthropogenic sources are increasing and the release of methane from geological reservoirs is accelerating due to global warming. As a result, the CH<sub>4</sub> concentration in the atmosphere has risen from around 0.7 ppm (parts per million air molecules) in pre-industrial times to around 2 ppm and is expected to increase further. As a result, the contribution of CH<sub>4</sub> to climate warming is also increasing. In addition, the sink capacity in the atmosphere decreases with increasing CH<sub>4</sub> concentrations, as the rate of new formation of hydroxyl radicals is exceeded.

Against this backdrop, various technological approaches to accelerate the removal of methane from the atmosphere are being discussed in the literature. These ideas are inspired by technically advanced processes for carbon dioxide removal (CDR) or negative emission technologies for CO<sub>2</sub>. The greatest challenge here is to effectively stimulate the methane present in the air to undergo chemical or physical reactions despite the relatively low concentration of 2 ppm. In contrast to CO<sub>2</sub> with a significantly higher atmospheric concentration of currently approx. 420 ppm, CH<sub>4</sub> in the air is not only much more diluted, but also chemically less reactive at the low concentration level.

The following methods are currently being considered for removing methane from the atmosphere:

1. **Thermal-catalytic oxidation:** In this process, catalysts are used to convert the methane into less climate-impacting carbon dioxide by means of a chemical reaction at high temperatures of several 100°C. However, this approach **is only** relevant for CH<sub>4</sub> concentrations of over 5,000 ppm (0.5 vol%) in the air.
2. **Photocatalytic oxidation:** In this process, (sun)light is used to activate a catalyst that gradually oxidises the methane in the atmosphere. This is a natural process in the atmosphere and is effective even at low methane concentrations of < 2 ppm. Technical approaches to methane removal aim to introduce larger quantities of catalytically active substances into the air. Gaseous hydroxyl or chlorine radicals or solids such as titanium dioxide are suitable catalysts.

<sup>1</sup> CO<sub>2</sub> is partially converted into biomass through photosynthesis or is converted into carbonic acid in bodies of water and subsequently bound by minerals. These mechanisms are not effective for CH<sub>4</sub> as long as it has not been oxidized to CO<sub>2</sub>.

3. **Biological methane removal:** Certain types of bacteria (known as methanotrophs) can metabolise methane and convert it into carbon dioxide or methanol for industrial use. However, this approach is only relevant for CH<sub>4</sub> concentrations of over 500 ppm in the air.
4. **Enrichment with zeolites or other porous solids:** Zeolites are minerals that can absorb methane from the air. When treated with a small amount of copper, zeolites absorb methane very effectively, even at low atmospheric concentrations of around 2ppm.

While the thermal oxidation of methane is a technology that has been practised for decades (flaring of refinery exhaust gases during mineral oil production), this technology only works at significantly high methane concentrations above 500 ppm. Overall, the above-mentioned technological approaches for removing methane from the atmosphere at a concentration of around 2 ppm are still at an early stage of development and will therefore not be ready for application in the foreseeable future.

The aim of this working paper is to systematically analyse the state of development of technical approaches for the removal of methane from the atmosphere. The focus is on technologies that are suitable for removing methane from the atmosphere at the current average atmospheric concentration of approx. 2 ppm.

**Key question:** What approaches are there for removing methane and what potential and costs are associated with them?

The information was compiled by means of literature research in scientific publications. The technology readiness level (TRL) was used to assess the technological development stage of the respective concepts (European Commission 2014).

# 1 Background

The current climate policy debate is centred on the paradigm of avoiding global warming of more than 1.5°C by reducing greenhouse gas emissions. The focus here is on the greenhouse gas (GHG) carbon dioxide (CO<sub>2</sub>), which is currently the largest contributor to anthropogenic climate change in terms of quantity. However, other greenhouse gases are also important due to their high climate impact, in particular methane (with 30 times the climate impact of CO<sub>2</sub> over 100 years), nitrous oxide (approx. 265 times) and various fluorocarbons (up to 24,000 times). These GHGs are also the subject of efforts to reduce emissions (Federal Environment Agency 2022). This primacy of climate policy is based both on the implementation of technical measures to limit GHG emissions and on socio-economic approaches to reduce the production and consumption processes that cause emissions (mitigation).

However, a growing number of voices are emphasising the need to look for more far-reaching solutions. It is argued that the technical and socio-economic measures to reduce GHG emissions will not be sufficient (or cannot be implemented quickly enough) to meet the 1.5° target of the Paris Agreement. Reference is also made to the high costs of the various reduction strategies and to the fact that it will not be possible to completely avoid anthropogenic GHG emissions in the agricultural sector, for example. As a result, there are residual emissions of GHGs that are difficult to avoid, which are to be captured from emission sources using technical means and kept out of the atmosphere through geological storage.

For some years now, the option of removing CO<sub>2</sub> already emitted from the atmosphere has been investigated. Various negative emission technologies (NET) for removing CO<sub>2</sub> in low concentrations (currently approx. 420 ppm) from the air are being developed and trialled for this purpose. Examples include Direct Air Carbon Capture and Storage (DACCS), BECCS (a CCS process with upstream biogenic carbon capture in the form of biomass) and accelerated weathering of rocks. These approaches, also known as Carbon Dioxide Removal (CDR), for the technically accelerated removal of carbon dioxide (CO<sub>2</sub>) from the atmosphere are currently being discussed as a possible addition to reducing CO<sub>2</sub> emissions that are difficult to avoid. They are regarded as a variant of post-combustion climate protection but are controversial due to their comparatively high costs and energy requirements as well as technical and socio-economic risks.

Against the background of the NET developed for CO<sub>2</sub> capture from the atmosphere, a discussion has developed as to whether there are also approaches for removing methane from the atmosphere (methane removal). In contrast to established technologies for treating methane-containing exhaust gases (flaring) at significantly higher concentrations, the approaches considered here face the problem of using technical means to remove a GHG that is chemically less separable from the air at significantly lower atmospheric concentrations than CO<sub>2</sub>. In addition, CH<sub>4</sub> is converted into CO<sub>2</sub> in the atmosphere by natural oxidation processes with an average residence time of around 12 years, so that technical approaches to methane removal would have to be significantly faster to be efficient.<sup>2</sup>

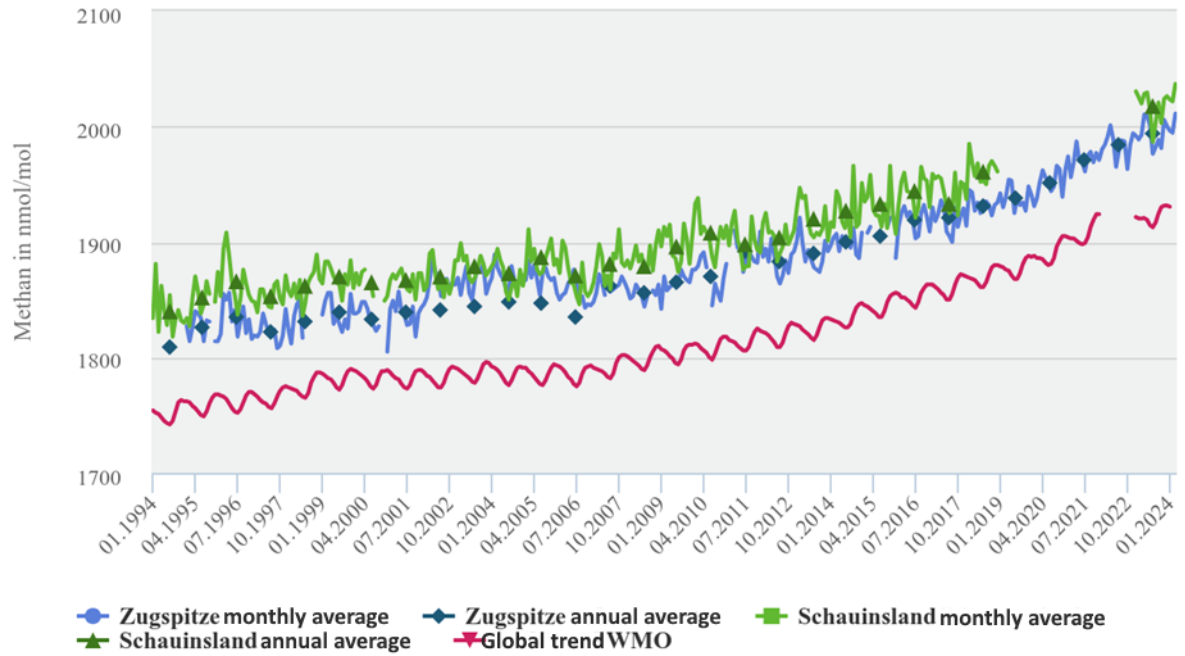
There is also the risk of an additional release of methane from permafrost soils and marine sediments as a result of the increased microbial decomposition of organic carbon due to progressive global warming (Glikson 2018). While such natural methane reservoirs are already unstable today and methane release from them is already underway, reaching climate-relevant tipping points can lead to the irreversible release of extremely large quantities of natural methane in a short period of time. These GHG emissions from natural methane reservoirs contribute to a positive climate feedback loop in which greenhouse gas emissions lead to additional warming, which in turn releases more methane from melting permafrost soils. This carbon loss in the soil is irreversible over several

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<sup>2</sup> However, the greater the amount of methane released, the longer the additional methane remains in the atmosphere. This is due to the fact that the natural quantities of photocatalytically formed hydroxyl radicals in the air, which are the necessary reaction partners for the oxidation of CH<sub>4</sub> to CO<sub>2</sub>, are used up excessively.

centuries (Winkelmann et al. 2023). This harbours the risk of a sharp rise in methane concentrations in the atmosphere, which have a greenhouse effect, and thus the risk of an accelerating increase in global warming (Glikson 2018; Winkelmann et al. 2023 ).

**Figure 1 : Time series of methane concentration in the atmosphere**



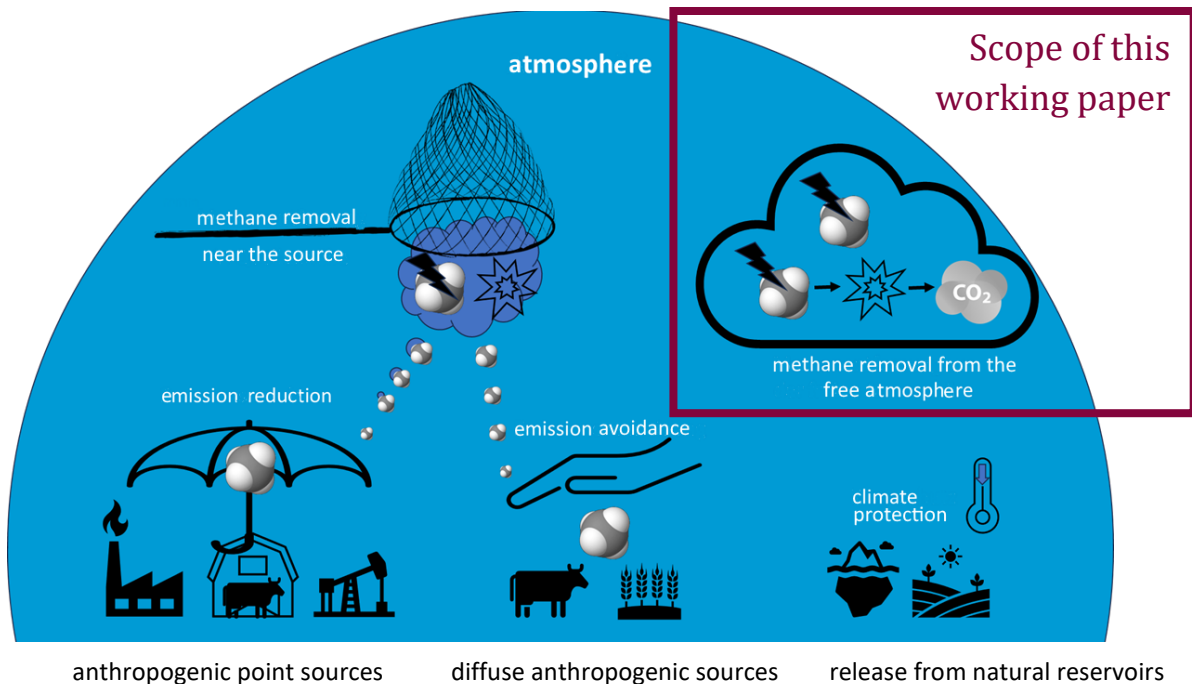
Source: Umweltbundesamt (Schauinsland, Zugspitze), World Data Centre for Greenhouse Gases (UNO/WMO Welttrend)

Source: (Federal Environment Agency 2024)

## 2 Description of approaches to reduce methane concentration in the atmosphere

The scope of this working paper includes various technologies for removing methane from the atmosphere (see Figure 2 - framed in red). There are various overlaps with other technological concepts for methane removal near the source, where the GHG has already escaped into the air but is still present locally in higher concentrations. Such approaches are being discussed in connection with diffuse agricultural sources or leaks from natural gas infrastructures.

**Figure 2 :** Framework of the approaches for removing methane from the atmosphere



Explanation: see following text

Source: Oeko-Institut

Figure 2 schematically illustrates approaches to reducing methane concentration in the atmosphere. They can be roughly categorised according to their position in the cause-effect chain<sup>3</sup>. Since methane also enters the atmosphere through natural processes, the anthropogenic causal relationships of methane emissions and the mitigation measures to be derived from them must be categorised. This also includes amplifying effects on natural processes that are caused directly or indirectly by human activities.

- ▶ Prevention of methane formation: technical measures and management methods to prevent biological processes from converting biomass into methane outside closed systems.
- ▶ Anthropogenic point sources: These include leaks at boreholes, pipelines and industrial plants for processing fossil fuels, coal mines, but also wastewater treatment plants, cattle sheds and slurry silos. The methane concentrations at the location of such closely localisable emission sources are high enough to enable the use of conventional technical processes to reduce CH<sub>4</sub> emissions. Such measures to reduce methane emissions (in Figure 2 symbolised by an umbrella)

<sup>3</sup> The cause-effect chain is the sequence of effects that contribute to global warming. The causes include the formation of CH<sub>4</sub> as a result of human activities or the release of CH<sub>4</sub> from natural reservoirs that were previously stable. The effect of the released methane is the absorption of solar heat re-radiation, which leads to an increase in atmospheric temperature.

are either preventive (avoidance of leaks) or corrective (collection of CH<sub>4</sub> and use or thermal oxidation by flaring). Existing technologies for the thermal oxidation of methane are only suitable for use at anthropogenic point sources with very high methane concentrations of over 5 % by volume (e.g. flaring of oil production and refinery gas; landfill gas treatment). However, these technologies are measures to reduce emissions and do not contribute to the removal of methane from the atmosphere.

- ▶ Diffuse anthropogenic sources: This category includes agricultural activities in the area (e.g. free-range farming, rice cultivation). Changes in land use and inappropriate management can also lead to diffuse methane emissions. These are characterised by low ambient methane concentrations that are technically difficult to control. Emission reduction measures (in Figure 2 symbolised by a hand) are aimed more at preventing methane formation by reducing the processes that cause it (e.g. livestock farming). However, there are also considerations regarding technical mitigation measures for CH<sub>4</sub> from diffuse sources that utilise the increased methane concentration near the source compared to the atmospheric background concentration.
- ▶ Release from natural sources: Naturally occurring methane reservoirs (terrestrial permafrost soils, marine methane hydrates) could become unstable due to anthropogenic influences, in particular global warming, and lead to sudden diffuse emissions on a large scale. So far, there are no concepts for preventing such methane release processes, apart from avoiding the warming of the affected methane reservoirs through preventive climate protection.
- ▶ Depending on the ambient conditions, methane emissions from point sources and diffuse sources sometimes have a significantly higher concentration near the source than the average of the free atmosphere (approx. 1,922 ppm). For example, the ground-level methane concentration in the vicinity of industrial plants can be significantly higher than the atmospheric average, e.g. around 500 ppm (He et al. 2023).
- ▶ Measures for methane reduction near the source (in Figure 2 symbolised by a quiver) are discussed in the literature as an alternative or supplement to measures to reduce (1) or avoid (2) emissions. These concepts are based on the assumption that such technologies can be used relatively independently of the specific conditions of the various methane sources and are therefore easier to scale up for mass application.
- ▶ Geoengineering approaches to remove methane from the atmosphere in the sense of negative emissions (methane removal) have the character of damage limitation. Instead of avoiding the cause of the damage (i.e. the release of methane), climate warming is to be curbed by converting CH<sub>4</sub> into CO<sub>2</sub>, the latter having a lower greenhouse effect. The natural greenhouse gas-effective residence time of methane in the atmosphere is approx. 12 years. During this time, CH<sub>4</sub> is converted into CO<sub>2</sub> via intermediate stages (Wahlen 1993; Abernethy et al. 2021). The methane removal technologies considered here aim to shorten this retention time. As the greenhouse effect of CH<sub>4</sub> in the atmosphere begins as soon as the gas enters the air by absorbing solar heat reflected back into space, the aim of these approaches is to remove CH<sub>4</sub> that has already been emitted as quickly as possible. For example, Abernethy et al. (2021) model the climate effects of an assumed reduction in the greenhouse effect retention time to 6.9 or 8.1 years.

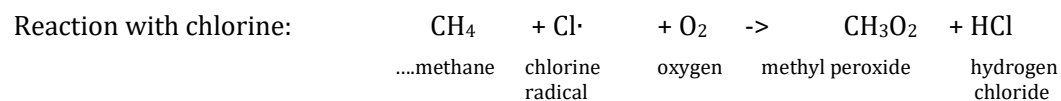
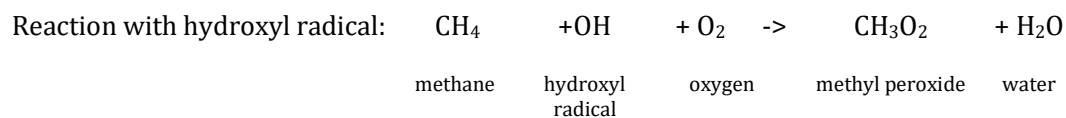
## 2.1 Concepts for removing methane from the atmosphere at the research and development stage (TRL < 5)

A number of approaches to direct methane removal from the atmosphere are discussed in the literature, which could be used to reduce negative emissions or methane (cf. Nisbet-Jones et al. (2022)). Such approaches have the character of geo-engineering in view of the necessary large-scale interventions in the atmosphere. They are still a long way from being ready for practical use.

Under natural conditions, methane is largely removed from the atmosphere by chemical reactions with the photolytically produced hydroxyl radical (OH) and to a lesser extent by reaction with photolytically produced atomic chlorine. The following basic additional mechanisms are discussed in the literature:

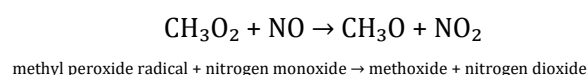
- ▶ Photocatalytic oxidation with hydroxyl radical in the gas phase: Various technical interventions in the atmosphere are intended to stimulate the photocatalytic formation of the hydroxyl radical in order to increase the CH<sub>4</sub> sink capacity of the atmosphere.
- ▶ Chlorine-mediated atmospheric methane removal: Introduction of chlorine or chlorine compounds into the atmosphere, which accelerate the oxidation of methane to CO<sub>2</sub> and water via numerous intermediate reactions (Zhang et al. 2022).

These two chemical reaction pathways, which occur naturally in the atmosphere, are activated by sunlight, producing radicals (hydroxyl radical and chlorine radical), both of which act as catalysts for the formation of the methyl peroxide radical (CH<sub>3</sub>O<sub>2</sub>). Li et al. (2023) give the following diagram of the photocatalytic reaction:



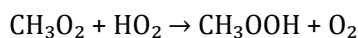
The further reaction process of the methyl peroxide radical that takes place naturally in the atmosphere is as follows: The intermediate product methoxide (CH<sub>3</sub>O) is known in atmospheric chemistry as an important factor influencing stratospheric ozone depletion. The decomposition of the methyl peroxide radical (CH<sub>3</sub>O<sub>2</sub>) in the atmosphere takes place through various chemical reactions, which are mainly influenced by the presence of other radicals. Under the influence of sunlight, the methyl peroxide radical participates in various photochemical processes that ultimately contribute to its degradation (Onel et al. 2017).

- A) The reaction with nitrogen monoxide (NO) is one of the main pathways for the breakdown of CH<sub>3</sub>O<sub>2</sub>, producing methoxide (CH<sub>3</sub>O) and nitrogen dioxide (NO<sub>2</sub>):



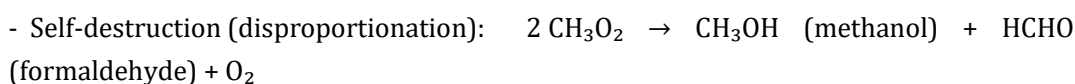


B) Alternatively, a reaction with hydroperoxyl radical ( $\text{HO}_2$ ) takes place, which leads to the formation of methanol peroxide ( $\text{CH}_3\text{OOH}$ ) and oxygen ( $\text{O}_2$ ). This reaction is less prevalent in the troposphere, but plays a role in certain environments:



methyl peroxide radical + hydroperoxyl radical  $\rightarrow$  methanol peroxide + oxygen

C) Reaction of the methoxy radical with other organic peroxy radicals leads to various organic compounds. This reaction is less significant compared to the other pathways, but can occur under certain conditions:



The processes discussed as approaches for the technically induced removal of  $\text{CH}_4$  from the atmosphere are based on the idea of stimulating the formation of hydroxyl radicals in the atmosphere in order to accelerate the degradation of  $\text{CH}_4$  at atmospheric concentrations. The reinforcement of this fundamental mechanism of photocatalytic self-cleaning of the atmosphere by means of technical interventions has been scientifically investigated but is still fraught with uncertainties. Nevertheless, the geoengineering approach of a technically induced increase in photocatalytic  $\text{CH}_4$  oxidation in the atmosphere is largely regarded as promising in the literature. However, the photocatalytic approach requires the introduction of large quantities of photocatalytically active substances into the atmosphere in the form of aerosols. In the simplest case, this is water vapour, which serves as a source for the direct photocatalytic formation of hydroxyl radicals.

In addition, the photocatalytic splitting of water vapour by catalytically active substances such as nitrogen oxides ( $\text{NO}_x$ ) and volatile hydrocarbons (VOC) can be accelerated via the formation of ozone and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). To do this, both water and the catalyst substances ( $\text{NO}_x$ ,  $\text{H}_2\text{O}_2$ ) must be introduced into the atmosphere and dispersed in large quantities. However, the technologies and support infrastructures required for this are still a long way from being ready for application and are largely speculative in nature. To date,  $\text{NO}_x$ , VOCs and ground-level ozone are regarded as air pollutants. As such, they have been the subject of technical and political measures for air pollution control for decades. Applying such approaches to methane removal would be in direct contradiction to the current legal regulations of the Federal Immission Control Act (BImSchG) and the TA Luft (Federal Government 2021).

- ▶ Photocatalytic oxidation on solid surfaces can occur when large quantities of air come into contact with sunlit, pigment-containing surfaces. Titanium dioxide, for example, is a suitable catalytically active pigment.
- ▶ Adsorption of methane on zeolites or other porous solids: Zeolites are minerals that can absorb methane from the air. Zeolites treated with copper absorb methane very effectively, even at low atmospheric concentrations. For the purpose of  $\text{CH}_4$  extraction, considerable volumes of air must be contacted with the porous solid material, which requires enormous technical facilities and high resource expenditure.
- ▶ Biological methane removal: Methanotrophic bacterial species can metabolise  $\text{CH}_4$  and convert it into carbon dioxide or methanol for industrial use (He et al. 2023). However, this approach does not work at atmospheric  $\text{CH}_4$  concentrations; optimal methane concentrations of approx. 500 ppm are found in the immediate vicinity of methane sources (Wang and He 2023);



- Separation by membranes: In this technology, a membrane is used to separate CH<sub>4</sub> from other gases. According to the current state of the art, this only works effectively at high methane concentrations.

**Table 1: Selection of approaches for removing methane from the atmosphere at the research and development stage**

Technology*	Type	Technology maturity
Photocatalytic oxidation with hydroxyl radical	Geoengineering	5
Adsorption of methane on zeolites	Geoengineering	4
Solar irradiation management	Geoengineering	3
Release of ferrous aerosols into the air	Geoengineering	2
Chlorine-mediated photocatalysis	Geoengineering	2
Methanotrophic bacteria	Near-source collection of CH <sub>4</sub>	2-3
Photocatalytic processes on solid surfaces	Near-source collection of CH <sub>4</sub>	n.a.

\*The table does not claim to be exhaustive and **does not represent a judgement on the content of the methods.**

Source: (Mundra and Lockley 2024)

### 2.1.1 Photocatalytic oxidation in the gas phase

#### 2.1.1.1 Photocatalytic oxidation with hydroxyl radical in the gas phase

Wang et al. (2022) discuss two hypothetical methods for stimulating the photocatalytic formation of hydroxyl radicals in the troposphere:

- 1 Introduction of water vapour into the troposphere with the help of downdraft energy towers. Downdraft energy towers work by spraying water from large vertical vents into the atmosphere. This water evaporates and creates a downward suction that can be used to generate energy by wind turbines. Such towers are particularly effective in hot and dry regions where water evaporates quickly. This increases the concentration of water vapour in the air, which can contribute to the increased formation of hydroxyl radicals in the atmosphere under the influence of sun light (Wang et al. 2022). The proposed mechanism of hydroxyl radical formation from water vapour is more of a side effect of this as yet untested technology concept for generating renewable energy.  
Ming et al. (2022) also look at various methods for removing methane (CH<sub>4</sub>) from the atmosphere. To generate hydroxyl radicals as a natural methane sink, downdraft wind power plants are also proposed here, which are intended to distribute additional water vapour in the troposphere in order to bring additional quantities of hydroxyl radicals into the atmosphere by means of natural UV radiation or artificial UV light sources. However, the publication does not further develop or evaluate this idea. Reference is only made to start-up companies that are testing these technologies for the photocatalytic oxidation of CH<sub>4</sub> at point sources.
- 2 Wang et al. (2022) discuss the utilisation of artificial UV radiation for the formation of hydroxyl radicals. UV-light sources can help to generate hydroxyl radical directly in the atmosphere at various altitudes between 6 and 12 km. The idea is to artificially irradiate the atmosphere with UV-B light from solar-powered UV-light sources using airships or gliders. The artificial UV irradiation would lead to additional photocatalytic formation of ozone and hydroxyl radicals (ibid.). However, these approaches have so far tended more to be thought

experiments that can be found in various articles and patents, without any evidence of practical testing even in the form of a prototype.

### **2.1.1.2 Chlorine-mediated atmospheric methane removal in the gas phase**

Li et al. (2023) investigated the effects of introducing additional molecular chlorine into the atmosphere as a method of methane removal. Chlorine influences the chemical lifetime of CH<sub>4</sub> in the atmosphere. Various scenarios for the release of chlorine were modelled. The study showed that an increase in chlorine emissions has non-linear effects on the atmospheric methane concentration: Below a threshold value of 90 Tg Cl/year, the addition of chlorine can initially increase methane pollution due to interactions with other atmospheric components such as ozone (O<sub>3</sub>) and hydroxyl radicals (OH). The reason for this is that chlorine can break down ozone, which in turn influences the concentration of hydroxyl radicals, which are crucial for methane oxidation. Only above a threshold of 90 Tg Cl/year of additional release of chlorine does the methane concentration in the atmosphere begin to fall significantly. Methane degradation due to chlorine reactions then begins to exceed the induced loss of hydroxyl radicals. For example, a scenario with emissions of 1,880 Tg Cl/year could reduce methane pollution by up to 70 %.

Ming et al. (2022) report on experiments on the use of seawater aerosols containing sodium chloride as a source of chlorine. This would require the enrichment of combustion exhaust gases, e.g. from ship engines with iron salts, which favours the photocatalytic decomposition of NaCl as contained in marine aerosols (sea spray). No information is provided on the technological maturity of this idea.

### **2.1.2 Photocatalytic oxidation on solid surfaces**

Huang et al. (2021) and Zhang et al. (2022) describe the use of photocatalytically active substances for the oxidation of CH<sub>4</sub> in the air, such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) and other compounds. To ensure effective contact with low-concentration CH<sub>4</sub>, these catalysts must be applied to a porous or honeycomb support material such as zeolites or activated carbon, which also ensures light access.

Current developments in the use of titanium dioxide photocatalysts for CH<sub>4</sub> oxidation are focussed on use in basic chemicals production, where CH<sub>4</sub> occurs in high concentrations. In these cases, "over"-oxidation of CH<sub>4</sub> to CO<sub>2</sub> is undesirable. Zhang et al. (2022) argue that the use of photocatalysts, which are considered too strong in the chemical industry, could be just right for CH<sub>4</sub> removal at low concentrations in atmosphere. However, this remains speculative as there is no research to date on photocatalytic oxidation at ~2 ppm of atmospheric methane.

A prerequisite for the use of solid-state photocatalysts for CH<sub>4</sub> removal at atmospheric concentrations would be the contact of large quantities of air with irradiated catalytic surfaces. At a CH<sub>4</sub> concentration of 2 ppm, an air flow rate of 700 million m<sup>3</sup> is required to remove 1 tonne of CH<sub>4</sub>. Various authors have suggested the use of solar updraft towers, which could be designed as photoreactors. In contrast to the downdraft power plants mentioned above, updraft power plants generate a reverse suction (from bottom to top). This is intended to enable the constant transport of large volumes of air along photocatalytically coated surfaces or filter packages at the catchment area of the stacks without requiring additional energy for air circulation (on the contrary: the thermal lift can be used to generate energy). Demonstrators of solar updraft power plants have already been built in Spain and the People's Republic of China and are used to generate renewable electricity (TRL 8). However, the combination with photocatalytic solid-state catalysers for CH<sub>4</sub> degradation has not yet been tested. It is therefore unclear whether this process can contribute to significant CH<sub>4</sub> degradation rates in practice. Model calculations appear to demonstrate the effectiveness of such constructs for CH<sub>4</sub> removal within the model parameters for the example of Manzanares (Spain) (Ming et al. 2021).

## Adsorption of methane on zeolites

Due to its non-polar molecular structure, methane is much more difficult to enrich or chemically bind at low atmospheric concentrations of around 2 ppm than the weakly acidic CO<sub>2</sub> (Jackson et al. 2019). Therefore, chemical gas scrubbing with amines, as used in the DACCS process for CO<sub>2</sub>, is not possible for methane. Other liquid solvents also do not have sufficient affinity for methane (Kim et al. 2013). Instead, nanoporous zeolites have been identified as candidates for increasing methane concentration in industrial applications due to their favourable sorption capacity and selectivity. While a catalytic partial oxidation of CH<sub>4</sub> to methanol (CH<sub>3</sub>OH) is aimed for in industrial processes, a fully continuous oxidation to CO<sub>2</sub> is desired for atmospheric methane separation. For this purpose, zeolites are equipped with catalytically active copper or iron and stabilised in porous polymer networks. However, both Kim et al. (2013) and Jackson et al. (2019) remain unspecific about the concrete technical feasibility and costs of this approach.

Brenneis et al. (2022) describe the development of copper-doped zeolite, which can be used to convert low-concentration CH<sub>4</sub> into CO<sub>2</sub> at relatively low temperatures of around 300°C. Using a two-stage process with activation at 450°C and a reaction at 200°C, a conversion rate of CH<sub>4</sub> to CO<sub>2</sub> of over 60 % was achieved. It was found that the approach is suitable for methane removal at "sub-combustible" CH<sub>4</sub> concentrations, which presumably refers to CH<sub>4</sub> close to a point source.

## 2.2 Uncertainties and risks of approaches for removing methane from the atmosphere

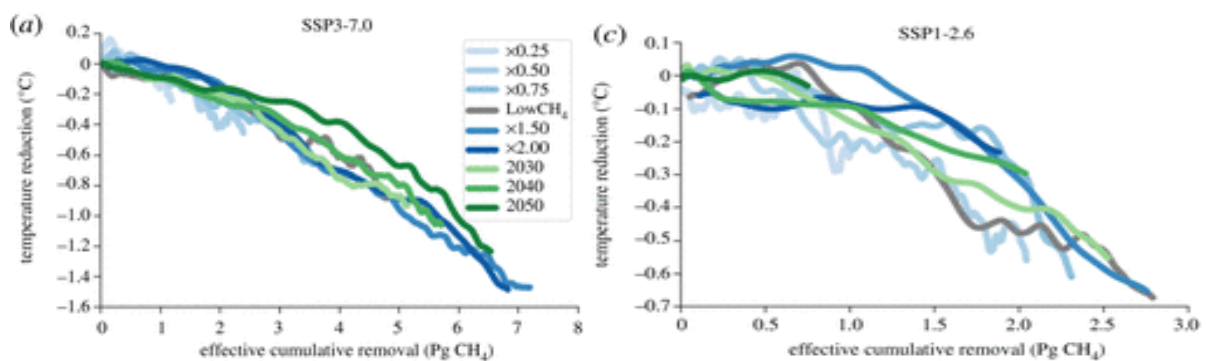
### 2.2.1 Effectiveness of methane removal for climate protection

The approaches to geotechnical methane removal from the atmosphere presented in section 2.1 are primarily aimed at accelerating the natural degradation processes of CH<sub>4</sub> to CO<sub>2</sub>. This reduces the time span in which the higher greenhouse effect of CH<sub>4</sub> contributes to global warming. A mitigating effect on climate warming can be demonstrated by numerical climate simulation if model parameters are chosen that shorten the greenhouse-effective residence time of CH<sub>4</sub> from the standard 12.4 years by means of technically induced methane removal. Jones et al. (2018) have calculated that a reduction in methane concentration of 2 % per year will lead to a temperature reduction of around 0.5 °C by 2100. Abernethy et al. (2021) have modelled that each effectively removed petagram (=giga tonne) of methane causes an average reduction in global surface temperature of  $0.21 \pm 0.04^\circ\text{C}$  and an average reduction in the global concentration of tropospheric (ground-level) ozone of  $1.0 \pm 0.2 \text{ ppm}^4$ . However, the results of these model calculations differ greatly depending on the model scenarios used. Furthermore, the results can only be assessed as reliable for extremely high quantities of removed methane (see Figure 3). For practically realistic approaches to methane removal in an order of magnitude well below the gigatonne range, the model calculations show no significant influence on atmospheric temperature (in some scenarios even a slight increase in the range below 1 Pg CH<sub>4</sub>).

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<sup>4</sup> Together with other volatile organic compounds (VOCs) and nitrogen oxides, methane is a building block for the formation of ground-level ozone in high UV radiation in sunlight (summer smog). A reduction in harmful ozone near the ground would be an additional positive effect.

**Figure 3 :** Simulation results for the climate impact of methane removal in comparison of two scenarios



Source: Abernethy et al. (2021)

### 2.2.2 Differences between methane removal and carbon dioxide removal (CDR)

From an infrastructural perspective, the technological approaches to atmospheric methane removal differ considerably from carbon dioxide removal (CDR) technologies. CDR technologies for removing CO<sub>2</sub> from the atmosphere, such as DACCS or BECCS, are based on the removal of CO<sub>2</sub> from the air - combined with subsequent transport and storage of the CO<sub>2</sub>, e.g. in geological reservoirs. In contrast, the discussed geoengineering technologies for methane removal do not involve capturing and storing the methane. Instead, in most processes the methane is chemically converted into the less climate-impacting CO<sub>2</sub> via various intermediate steps. This happens directly in the atmosphere, where the resulting CO<sub>2</sub> remains for tens of thousands of years. Capture and storage as CH<sub>4</sub> are not planned, with a few exceptions. It is unclear whether the methane capture approaches can be combined with CDR processes to capture the resulting CO<sub>2</sub>. In view of the considerable differences in concentration of the two greenhouse gases in the atmosphere (2 ppm for CH<sub>4</sub> vs. 420 ppm for CO<sub>2</sub>), combined operation of both approaches with the aim of storage does not appear to be expedient.

However, approaches to generating negative emissions for both GHGs require considerable infrastructural expenditure in order to achieve significant effects to limit global warming.

### 2.2.3 Other risks

No studies were found in the literature search that carried out a more detailed risk analysis or life cycle analysis for the approaches to removing methane from the atmosphere considered in this paper. This is not surprising given the low level of technological maturity of these approaches. Nevertheless, at an early stage of technology development, it would be useful to consider the risks and costs of such development paths in parallel with technological innovation, in order to make informed decisions about further investment in development work before large investments are made with uncertain outcomes. The absence of a comprehensive examination of potential adverse effects and outcomes associated with the scaled-up deployment of geoengineering technologies underscores the limited practical applicability of the proposed approaches. Some of the studies analysed touched on the following risk aspects but did not examine them in depth.

The photocatalytic oxidation of methane can have a number of effects on other atmospheric components. When **using hydroxyl radicals**, it is important to consider the following:

- ▶ Formation of ground-level ozone: During the oxidation of methane in the troposphere, ozone is formed through photochemical processes in the presence of nitrogen oxides. This gas is a powerful greenhouse gas and is also considered a harmful air pollutant when ozone occurs in populated areas. It can lead to inflammation of the respiratory tract, asthma, reduced lung function and impaired physical performance.

- ▶ Reduction in the natural concentration of hydroxyl radical in the atmosphere: As methane emissions increase worldwide, the level of hydroxyl radical decreases because the oxidation reaction with methane takes place more frequently. This can lead to an increase in the half-life of CH<sub>4</sub> in the atmosphere, and it only degrades after a longer period of time. This effect increases the climate impact of CH<sub>4</sub>.
- ▶ Depending on the type of input and the dispersion dynamics in the atmosphere, the input of large quantities of water vapour into the atmosphere above the natural level can increase global warming, as water vapour acts as a greenhouse gas.

The **use of chlorine** as a source material for removing methane from the atmosphere can lead to the following side effects:

- ▶ The reaction leads to the formation of methyl chloride, which is itself a greenhouse gas, albeit less potent than CH<sub>4</sub>. In addition, hydrogen chloride (HCl), which is released into the atmosphere as a by-product, can contribute to acidification (acid rain).
- ▶ Free chlorine atoms are known to trigger stratospheric ozone depletion, which ultimately contributes to the formation of polar ozone holes. High halogen concentrations in the stratosphere favour ozone depletion and are therefore considered undesirable. Possible damage to the ozone layer represents a serious environmental problem. The introduction of chlorine into the atmosphere, for example from chlorofluorocarbons (CFCs), has been successfully prevented by the implementation of the Montreal Protocol to protect the ozone layer. A targeted release of chlorine on the scale mentioned above for the purpose of methane removal harbours the risk of undoing this success and leading the decades-long efforts to reduce emissions of ozone-depleting substances ad absurdum. A thorough risk assessment of this geoengineering idea is therefore required in order to rule out the possibility of chlorine being transported into the stratosphere.
- ▶ Safety concerns regarding the use of chlorine: As it is a highly toxic and reactive gas, accidents during the transport and application of chlorine can have a significant impact on health and the environment. For these reasons, the tropospheric application of chlorine in populated areas is not advisable. In the literature, application in remote areas (oceans) is therefore being considered. However, it is unclear whether wind transport to populated areas can be ruled out.
- ▶ Energy required for chlorine production: Chlorine is produced by electrolysis of sodium chloride, where it is currently a by-product of the production of sodium hydroxide. Using chlorine as part of geoengineering to remove CH<sub>4</sub> would significantly increase the demand for chlorine, meaning that additional chlorine production capacities would have to be created. This would multiply the energy required for chlorine production.

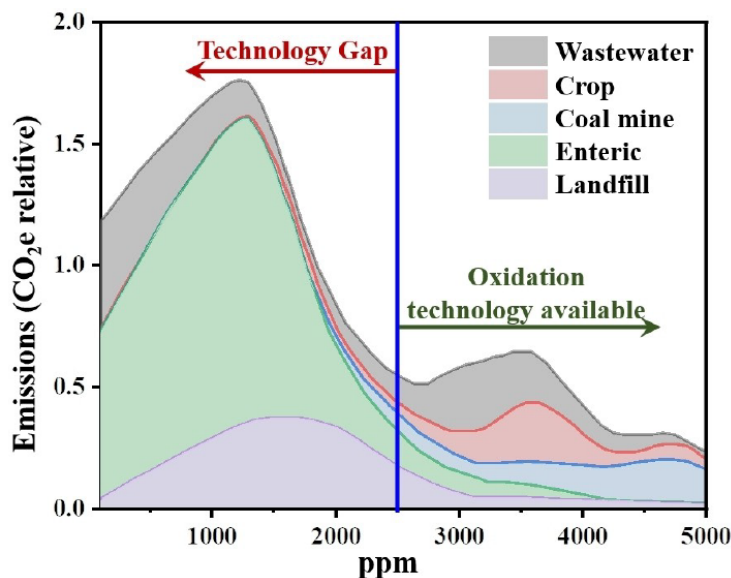
### 3 Conclusions

The technologies considered in this working paper for the direct removal of methane from the atmosphere are at an early stage of technological development and are not ready for application. For the most part, these are rather conceptual ideas with a technology readiness level (TRL) of 1 or 2 (technology concept formulated) with a few experimental studies on a laboratory scale (TRL 3-4). Even if individual technological components of the various approaches are already available for other applications (e.g. updraft power plants), the technological maturity of overall geotechnical concepts for methane removal is still a long way from being trialled (TRL 6-7).

In view of the considerable lead time for the further development and upscaling of the various approaches to atmospheric methane removal, a significant contribution to climate protection appears questionable.

Zhang et al. (2022) describe the technological gap in the availability of applicable methane removal technologies. According to them, the vast majority of CH<sub>4</sub> emissions from anthropogenic sources worldwide contribute to the increase in atmospheric concentration, while available emission reduction technologies are mainly effective at much higher CH<sub>4</sub> concentrations above about 2500 ppm (Figure 4). For atmospheric CH<sub>4</sub> concentrations around 2 ppm, to the knowledge of these authors, there is no mature technology for removing CH<sub>4</sub>.

**Figure 4 :** Gap in the availability of technologies to remove methane from the atmosphere



Source: (Zhang et al. 2022)

The challenge of atmospheric methane removal is that methane is much more diluted than CO<sub>2</sub>, which makes capture technically very complex and uneconomical (Lackner 2020).

In view of the low level of technological maturity of the various approaches to atmospheric CH<sub>4</sub> removal, any assumptions about the design and future operating conditions of such technologies tend to be hypothetical in nature. Therefore, no realistic estimates of the costs per tonne of methane to be removed are possible with these approaches, at least are costs subject to high uncertainties. Jackson et al. (2019) assume that the costs for the removal of CH<sub>4</sub> will be significantly higher than the cost of removing CO<sub>2</sub> from the atmosphere due to the higher atmospheric dilution. In addition, the socio-economic effects and the associated social acceptance of geo-engineering approaches in the atmosphere have not yet been sufficiently clarified.

There are also concerns that the geoengineering approaches under discussion could be associated with significant risks. For example, there is still great uncertainty about the ecological and health-related side effects of releasing large quantities of chlorine or other chemicals to form photocatalytically active radicals. This also applies to the release of large quantities of water vapour into the atmosphere (water vapour is the most important greenhouse gas in the Earth's atmosphere). Depending on the type of input and the dispersion dynamics in the atmosphere, such massive interventions in natural atmospheric processes can lead to unexpected effects.

Against this backdrop, it seems all the more important to apply approaches to prevent methane formation and reduce emissions consistently and on a large scale, as these already have a high degree of technological maturity and can be implemented immediately. It makes more sense, both technically and economically, to stop the release of methane at source than to remove the highly diluted greenhouse gas from the atmosphere afterwards. To this end, it is necessary to minimise the formation of CH<sub>4</sub> as a result of anthropogenic activities (prevention) or to reduce the release of existing CH<sub>4</sub> (emissions reduction).

Nevertheless, approaches for the direct removal of CH<sub>4</sub> from the atmosphere could become increasingly important in the future. In a scenario in which all international efforts to prevent climate change by avoiding greenhouse gas emissions fail and global warming accelerates, it is conceivable that unstable terrestrial (permafrost soils) and marine (methane hydrates) methane reservoirs will collapse. In the event of such a development, attempts could be made to counteract the consequences of increased global warming by using technologies to remove CH<sub>4</sub> directly from the atmosphere (Lackner 2020). This would require suitable geoengineering technologies to be brought to operational maturity in a short period of time and to be scaled up globally. The necessary scope of such a development and the use of geoengineering technologies is difficult to plan so far, as the occurrence of tipping effects in the Earth's climate system and other effects of advancing climate change are subject to great uncertainty. It is therefore questionable whether methane removal technologies will be developed in time and on a sufficient scale to effectively counter the ongoing rise in atmospheric methane concentrations. In view of the uncertain prospects of success for the use of such processes, it appears more effective from today's perspective to avoid the negative effects of global warming, including reaching climatic tipping points, through preventive climate protection measures, i.e. the reduction of greenhouse gas emissions such as CH<sub>4</sub> and CO<sub>2</sub>.



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## List of abbreviations

<b>CCS</b>	Carbon Capture and Storage
<b>CDR</b>	Carbon Dioxide Removal
<b>CO<sub>2</sub></b>	Carbon dioxide
<b>BECC(S)</b>	Process for CO <sub>2</sub> capture from combustion exhaust gases with upstream biogenic carbon capture in the form of biomass, the "S" stands for optional storage of the CO <sub>2</sub>
<b>DACC(S)</b>	Direct Air Carbon Capture (and Storage)
<b>HCl</b>	Hydrogen chloride (hydrochloric acid),
<b>n.a</b>	No data available
<b>mol</b>	Mol (amount of substance)
<b>NaCl</b>	Sodium chloride
<b>NET</b>	Negative emission technologies
<b>nmol</b>	Nano-Mol
<b>ppm</b>	Parts per million (parts per million particles)
<b>THG</b>	Greenhouse gases
<b>UV</b>	Ultraviolet light
<b>TRL</b>	Technology maturity level
<b>CH<sub>4</sub></b>	Methane
<b>LDAR</b>	Leak detection and repair
<b>RTO</b>	Regenerative thermal oxidation
<b>vol%</b>	Volume per cent

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