Review

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GREENHOUSE GASES | SCIENCE AND TECHNOLOGY

Atmospheric removal of methane by enhancing the natural hydroxyl radical sink

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Abstract: According to the latest report from the intergovernmental panel on climate change (IPCC), currently, global warming due to methane (CH_4) alone is about 0.5°C while due to carbon dioxide (CO_2) alone is about 0.75°C. As CH_4 emissions will continue growing, in order to limit warming to 1.5°C, some of the most effective strategies are rapidly reducing CH_4 emissions and developing large scale CH_4 removal methods. The aim of this review article is to summarise and propose possible methods for atmospheric CH_4 removal, based on the hydroxyl radical (°OH), which is the principal natural sink of many gases in the atmosphere and on many water surfaces. Inspired by mechanisms of °OH generation in the atmosphere and observed or predicted enhancement of °OH by climate change and human activities, we proposed several methods to enhance the °OH sink by some physical means using water vapour and artificial UV radiation. © 2022 Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: hydroxyl radical; natural sink; methane removal; greenhouse gas removal; negative emissions technology; water vapour; UV light

Introduction

Methane (CH_4), is a potent greenhouse gas (GHG). For a 100-year time horizon, CH_4 has a global warming potential (GWP) 27–35 times higher than that of carbon dioxide (CO_2). It also has a short residence time in the atmosphere with a GWP 84 times higher than that of CO_2 over 20 years.[1]

Currently, CH_4 contributes 0.5°C of warming next to the highest contribution of 0.75°C from CO_2,[2] as shown in Fig. 1(A), according to the latest report from the Intergovernmental Panel on Climate Change (IPCC). By the end of the century, in a baseline scenario, the warming due to CH_4 alone can be as high as 0.9°C, ranging from 0.75°C to 1.5°C.[3]

The tropospheric CH_4 concentration has grown by nearly 2.6 times over its pre-industrial level and growing faster in the recent two decades,[1] as shown in Fig. 1(B). In 2020 and 2021 the annual increases in
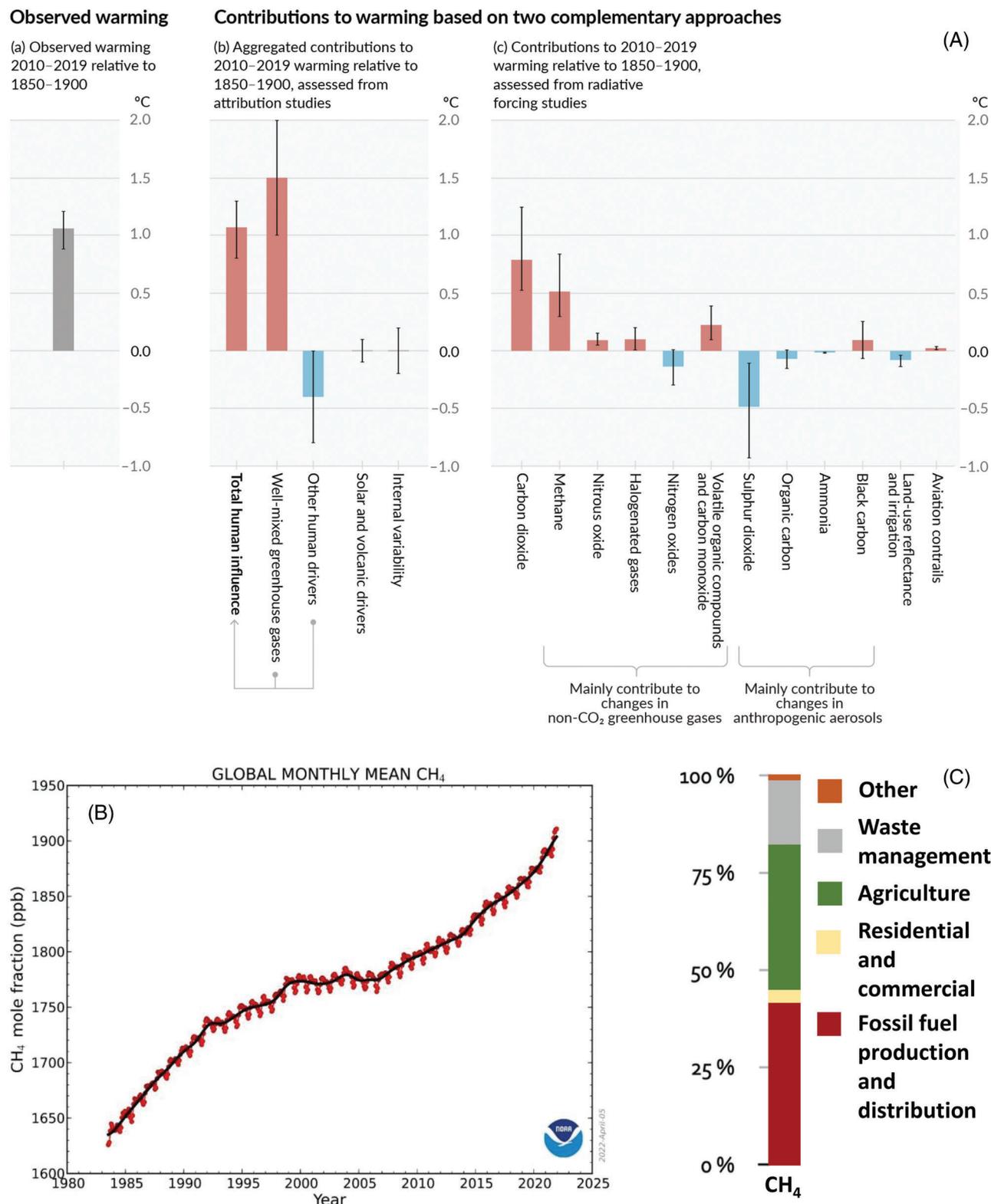
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Figure 1. A) Assessed contributions of various warming factors to observed warming in 2010–2019 relative to 1850–1900. Reproduced with permission.[2] Copyright 2021, IPCC. (B) Globally-averaged, monthly mean atmospheric CH_4 concentration since 1983. (NOAA Global Monitoring Laboratory). (C) Relative sectoral contributions to the anthropogenic emissions of CH_4.[2]Copyright 2021, IPCC.

atmospheric CH_4 (respectively 15.3 ppb and 17 ppb) were the largest annual increases ever recorded since systematic measurements began.[4]

CH_4 sources are widely spread from natural sources (e.g. tropical wetlands, thawing permafrost and submarine CH_4-clathrates, lakes and reservoirs) and anthropogenic emissions (e.g. rice paddies, landfills, fossil fuels, livestock, agriculture, wildfires and biomass burning, hydroelectric installations, as shown in Fig. 1C).[5] Global emissions of CH_4 are increasing by shale gas fracking, venting, flaring, fugitive emissions of global gasoline and diesel,[6] as well as by leaks in extraction,[7] distribution and use.[8] The emissions of CH_4 from the fossil fuel industry are 25–40% higher than previous estimates.[9]

To limit global warming to less than 2°C or below 1.5°C as targeted by the Paris agreement, the most effective strategy would be to rapidly reduce CH_4 emissions. Therefore, a recent United Nations report proposes to reduce the human-caused CH_4 emissions by 45% in this decade to keep the current warming level (about 0.5°C) more or less the same by the end of the century.[10] In November 2021, during the 26th conference of parties (COP26) in Glasgow, UK, more than 100 countries signed the Global Methane Pledge committing to reduce anthropogenic CH_4 emissions by 30% in 2030 compared to the 2020 level.[11]

A complementary strategy to CH_4 emission mitigation is CH_4 removal from the atmosphere (i.e. CH_4 remediation).[12] Scientists proposed numerous mitigation methods for CH_4,[13–15] in different sectors such as agricultural soil[16] and animal operations.[17] But remediation proposals for CH_4 already present in the atmosphere are still scarce.[18–22] The main proposals consist of enhancing natural heterogeneous reactions with semi-conductor metal oxides in dusts,[23] by photocatalysis[18] or by thermal catalysis,[22] as well as by enhancing the Cl atom natural sink of CH_4.[19,24]

The aim of this review is to summarise and propose some possible methods for atmospheric CH_4 removal, based on the hydroxyl radical (°OH), which is the principal natural sink of CH_4 (and also many other gases) in the atmosphere and on many water surfaces.

Enhancing the tropospheric °OH sink of CH_4

Why °OH?

In the troposphere, the major oxidizing agent is the °OH. It is generated naturally and is considered as the

Table 1. Global emission of some trace gases in the troposphere and the estimated percent of removal by °OH.[26]

Gas	Global emission rate (Tg year^{-1})	Removal by °OH (%)
CO	2,800	85
CH_4	530	90
C_2H_6	20	90
Isoprene	570	90
Terpenes	140	50
NO_2	150	50
SO_2	300	30
$(CH_3)_2S$	30	90

detergent of the atmosphere converting about 3.7 gigatons of trace gases into CO_2 each year,[25] including several GHGs and many gases involved in stratospheric ozone (O_3) depletion (man-made hydrofluorocarbons [HFCs] and hydrochlorofluoro-carbons [HCFCs], biogenic chloromethane and bromomethane), volatile organic compounds (VOCs) and urban air pollution. Accordingly, the °OH concentration determines their atmospheric lifetimes.

As shown in Table 1, Prinn et al.[26] summarised some of the principal trace gases in the troposphere, their global emission and the estimated °OH role in their removal (°OH has no effect on CO_2 and N_2O).
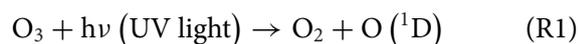
While the global natural oxidative capacity of the atmosphere seems to be stable,[27] on a wide variety of space and timescales the levels of °OH in the atmosphere do not remain steady but change rapidly. The °OH sinks increase with pollution emissions of reduced gases (e.g., SO_2, NO, CO). The °OH sources are turned off when UV radiation is absent (night time, polar winter), or decrease by lowering UV radiation (e.g. increasing cloudiness, the recovery of the stratospheric O_3 layer). The °OH sources also decrease for instance by lowering NO_x emissions, decreasing humidity (winter, altitude, droughts, deserted regions…), etc.[26]

Mechanisms of °OH generation in the atmosphere

The concentrations of °OH depend on numerous factors: concentrations of O_3, relative humidity, temperature, ultraviolet radiation, emissions of VOCs,

carbon monoxide (CO), nitrogen oxides (NO$_x$),[28] and some other factors.[29]

An important source for °OH during daytime comes from the UV photolysis of O$_3$ which generates oxygen and excited atomic oxygen O(^{1}D), which then reacts with water (H$_2$O) to produce two OH radicals as in reactions R1 and R2:

$$O_3 + h\nu \, (\text{UV light}) \rightarrow O_2 + O\left(^1D\right) \quad \text{(R1)}$$

$$O\left(^1D\right) + H_2O \rightarrow 2\,^{\circ}OH \quad \text{(R2)}$$

These reactions show that O$_3$, H$_2$O and UV radiation in the wavelength range between 310 and 350 nm[30,31] are essential in the troposphere to produce °OH.

As °OH generation is triggered by O$_3$, UV and humidity, its concentration shows strong day/night cycles and seasonal variations, its concentration shows strong day/night cycles, seasonal variations, and correlation with height due to decreased H$_2$O concentration with lower temperatures in altitude. In the tropics, as the humidity is high and the solar radiation is intense, the concentrations of tropospheric °OH are the highest.

UV levels vary mainly with the height of the sun in the sky, the time of day (higher around solar noon), and the time of year (higher in summer), but also with latitude, as the closer to the equator the shorter the distance to travel through the atmosphere and the lower the amount of the UV radiation which is absorbed by the atmosphere. For the same reason, UV levels increase by approximately 10% with every 1 km in altitude.

°OH can also be formed through the reaction between O$_3$ and some terpenes during the entire 24-hour cycle,[32,33] as well as from hydrogen peroxide H$_2$O$_2$ by Fenton reaction.[34] The in-situ generation of H$_2$O$_2$ can be divided into three categories: chemical, photochemical, and electrochemical pathways that activate O$_2$.[35] The photochemical activation is the most likely process that happens in the atmosphere, where the photocatalytic activation of O$_2$ is usually achieved by photoelectrons from catalysts under light irradiation.[36] The in-situ produced H$_2$O$_2$ is catalytically breakdown to generate °OH in this unique Fenton/Fenton-like process.[37,38]

Observed or predicted enhancement of °OH atmospheric concentration by climate change and human activities

The primary sources of tropospheric °OH are reactions R1 and R2 starting with the photo-dissociation of O$_3$ by solar UV radiation, and in a warmer climate as projected under future global warming characterised by increased amounts of water vapour, the °OH abundance (as well as of other tropospheric oxidants such as HO$_2$°) is expected to be enhanced in the troposphere. Photolysis rates influence °OH (Reaction R1), and hence variations in the cloud and stratospheric O$_3$ also have an impact on the concentration of °OH.[39]

Lamarque et al.,[40] showed that under reduced aerosol emissions, a warmer and moister climate significantly increases global °OH concentration which illustrates the importance of the humidity concentration and distribution. Some studies estimate that in a warmer climate with doubled tropospheric CO$_2$, the annual global mean °OH concentration would increase by 12.5%[41] or 7%.[42]

Regional phenomena should also be noted, such as a 10-fold decrease for °OH in the Tropical West Pacific in relation to the surrounding area and increases in the South Atlantic and East Pacific.[43] Coupled climate chemistry models found that about 85% of CH$_4$ oxidation by tropospheric °OH occurs between 40° South and 40° North.[44]

There are not yet publications proposing methods for enhancing the tropospheric °OH sink for CH$_4$ (as well as of other less concentrated GHGs). But from the above, it can be deduced that if human activities change the humidity levels (e.g., in hot and dry regions with high UV radiation index), the amounts of °OH generated will increase and thus °OH sink for CH$_4$ will be enhanced.

As an example, in some regions of Australia, Saudi Arabia, India or the United States, anthropogenic humidity changes already occur, for instance when irrigation for agriculture is made using river flows, fossil groundwater, or sometimes desalinated seawater. Several studies have shown that irrigation can increase relative humidity by 9–20%, and can have significant impacts on local meteorological fields.[45] It is estimated that irrigation in California increases humidity in

southwestern US states (Arizona, Colorado, New Mexico, Utah and Wyoming).[46]

The modelization made in early 2010s estimates that from 16.7 km^3 of irrigation water used in the summer months over the 52,000 km^2 of irrigated area in Californian Central Valley, evapotranspiration amounts to 14.7 km^3 which benefits the southwestern United States by water vapor export strengthening the regional hydrological cycle. The moisture is blown over the Sierra Nevada, initiating an anthropogenic loop, with a 15% increase in summer precipitation in the other states, and this additional rain in return causes the Colorado River stream flow to experience a 28% boost.[46]

Due to the global increasing population rates (expected to rise to 9.8 billion by 2050 and 11.2 billion in 2100[47]) significant expansion of irrigated land in developing countries will continue.

One possible path to fight global warming is "planting a trillion trees". If this path becomes reality, in order to avoid competition for fertile agricultural land, some arid regions would need to be transformed and that requires irrigation and implies increasing evapotranspiration and more humidity, which in turn will generate more humidity transfer to adjacent regions.

Another example of human activity enhanced evaporation in dry regions is the hydroelectric reservoirs. Several dams have been built in dry regions and among them, one of the world's largest reservoirs is Lake Nasser in Egypt, almost 500 km long and with an average width of about 12 km covering about 6000 km^2 and having a storage capacity of about 162 km^3 of fresh water. The evaporated water loss is estimated to range between 12 and 16 km^3 every year.[48-50] Since temperatures and the UV index are high, there is no doubt that the enhancement of the relative humidity also enhanced the °OH generation.

Human activities can contribute in one more unexpected way. The reasons why the 2020 and 2021 CH_4 concentrations were the highest ever recorded[51] are multifactorial, but one of them is probably due to Covid-19 pandemic lockdowns, as at the global scale the emissions of NOx decreased, leading to a decrease in the levels of tropospheric O_3,[52,53] even if locally in many cities the O_3 burden increased due to other factors.[54] This reduction of NOx emissions and O_3 generation lead to a decrease in the atmospheric CH_4 oxidation due to lower levels of °OH, estimated to be

1.6 to 2% with an atmospheric chemistry transport model.[55] This reduced °OH generation is in turn partially responsible for the record increase of the atmospheric CH_4 concentration in 2020 and 2021.

Last but not the least, man-made °OH generators are commercially available and have been proposed for the removal of some pollutants at point sources.[56,57] °OH generators are becoming cheaper thanks to the development of long life-time UV-LEDs, whose use has exploded for UV-disinfection or sterilization following the SARS-CoV-2 pandemic. But such systems have not yet been suggested for large scale CH_4 removal.

Table 2 summarises the observed or predicted enhancement of °OH atmospheric concentration by climate change and human activities.

Further enhancement of °OH atmospheric concentration by water vapour

Water vapor is a key link between physical climate and °OH. The previous sections of this paper have focused on the discussion related to why more water vapor in hot dry places will generate more °OH. In very dry regions the tropospheric level of °OH is low. By adding humidity to the local atmosphere, which is very sunny and UV rich, °OH will be generated according to reactions R1 and R2.

A device was developed in Israel to generate huge amounts of humidity in very dry regions: it is named the downdraft energy tower (DET). It is a power plant that generates electricity by using sea water and solar energy stored in hot, dry desert air.[58] As demonstrated in Fig. 2, DET[59] includes a high downdraft evaporation tower, pumps, pipes, turbines and water reservoirs. The DET must be located inland, in the driest possible area, because moisture reduces the yield; yet, DET should not be too distant from the ocean, since seawater is required and piped through ducts to the DET. Then, sea water is pumped to the top of the DET and sprayed with a slew of nebulizers. Water droplets fall and evaporate, creating a downward flow of cold air that is denser than the ambient air. To ensure humidity saturation, the tower is relatively big and tall (usually 400 m in diameter and 1.4 km in height). The strong artificially generated cold wind powers turbines at the base of the tower. Only about a third of the electricity generated is required to pump the seawater to the top

Table 2. Observed or predicted enhancement of °OH atmospheric concentration.

| By climate change	Influences	Ref.
Solar UV radiation	Photo-dissociation of O_3	39
Cloud and stratospheric O_3	Photo-dissociation by UV	39
Humidity concentration and distribution	Regional phenomena	40–42
By human activities	**Influences**	
Irrigation for agriculture	Enhanced evaporation	46
Hydroelectric reservoirs	Enhanced evaporation	48–50
Emissions of NO_x	Changing the lifetime of CH_4	55
°OH generators	Direct °OH generation	56, 57
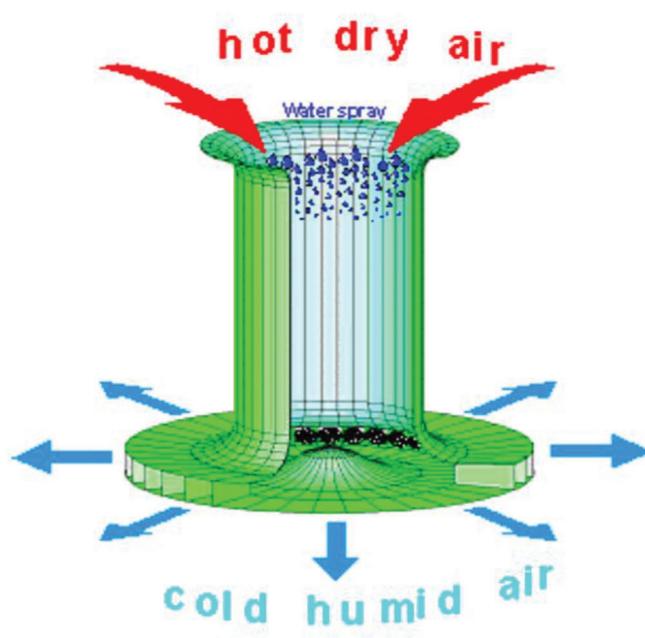
Figure 2. Schematic illustration of the energy tower, Reproduced with permission.[60] Copyright Czisch and Technion - Israel Institute of Technology.

of the tower and from the ocean. For this technology, the higher the temperature differential between water and ambient air, the higher the energy efficiency. The energy required is collected from the air, that is, the ultimate source is the sun. This means that it can be considered as a form of solar power generation.[58]

In comparison with many other renewable energy systems, the temporal behavior of the DET is particularly beneficial. As dry air is accessible 24 hours a day, the daily fluctuations are minimal. The ideal

areas are along the desert belts' coastlines, where Passat Winds, for example, supply hot dry air. There are no transportation or elevation losses for bringing water to the chimney's foot there. About 41 m³s⁻¹ of water are evaporated, representing 15 g of water per kg of air processed[61] and about 1.3 km³ per year: ten such downdraft towers evaporate nearly the same quantity of water than due to irrigation in California or to Lake Nasser evaporation losses.

The daily amount of °OH generated by a DET can be calculated via the following equation, based on reaction R1 and R2:

$$N\left(^\circ OH\right) = 2N\left(O_3\right) = 2 \times N\left(air\right) \times c\left(O_3\right)$$

$$= 2 \times c\left(O_3\right) \times \frac{Q\left(air\right)}{22.4 L/mol}$$

$$= 2 \times c\left(O_3\right) \times \frac{tvS}{22.4 L/mol}$$

where, $c(O_3)$ means the concentration of O_3 in the atmosphere (approximately 1ppm at 1.4 km); t represents the time (24×3600 s); v is the air velocity at the tower's bottom (17.8 m/s[15]) and S is the bottom surface area of the tower. As a result, it is about 1.724×10^7 mol.

As we mentioned earlier, DET is a power plant that generates electricity by using sea water and solar energy stored in hot, dry desert air.[58] Herein, the water vapour is generated from this process as a by-product, which does not require additional energy. Take the cooling tower built by Abdelsalam et al. as an example, the tower generates 409 MWh of gross energy annually. 40% of that (164 MWh) is utilised to power the pumps that elevate the water to the top of the chimney. System

losses consume 20% of the gross energy (82 MWh). As a result, the net benefit is 40% (164 MWh) of usable energy.[63]

Further enhancement of °OH atmospheric concentration by artificial UV radiation

The atmospheric concentration of °OH can also be enhanced by artificial UV-B radiation to generate both O_3 (via photolysis of O_2)[64] and °OH in locations or at times where their concentration is low and when the risks are minimal both for fauna and flora.

Several types of UV lamps are commercially available such as conventional ones with Hg vapour inside, economy bulbs (without the coating transforming the UV into visible light) and light emitting diodes (LEDs). Their lifetimes and efficiencies increase in the order cited, while their energy consumptions and prices decrease. The wavelength specificity was generally good and is still improving for both visible LEDs and UV-LEDs, which are more and more used in horticulture (some higher plants and green algae have a UV-B photoreceptor named UV-R8[65]) and for analytical purposes, for instance, diode array detectors coupled with chromatographic apparatus[66] equip almost all modern laboratories. Selective UV reflecting mirrors[67] allow directing the radiation in the desired direction.

Safest locations for generating tropospheric O_3 and °OH by artificial UV light

To not increase the surface O_3 burden over polluted cities, the UV light generators should be located in unpopulated areas, preferably at sources of CH_4 emissions, such as Siberia, the Arctic, coal mines, open pit mines, regions of shale gas extraction by fracking, rice paddies, wetlands, etc.

The UV radiation is either directed upwards to the outer space, in order to protect plants and animals from possible damage; or is used in a closed environment such as the ventilation system of a coal mine.

Other possible locations are over the oceans on fixed floating platforms or moving marine vessels in the Southern Oceans far from populated areas.
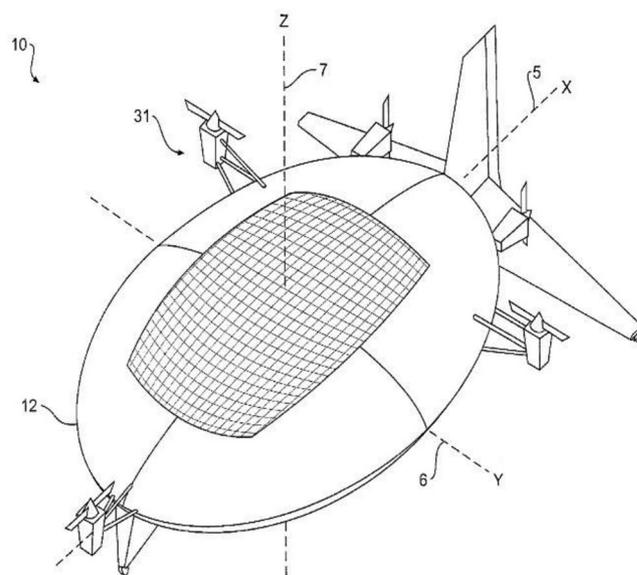

Figure 3. A possible lighter than air platform for solar energy collection, reproduced with permission.[74] Copyright 2014, United States Patent.

The main idea is that the O_3 will be generated locally and rapidly consumed to generate °OH and oxidize CH_4 and other VOCs.

Using balloons, airships, aerostats or flying kites for both holding the UV lamps and power generation

Electrical power generated at altitude, as described in numerous articles[68,69] and patents,[70] can be designed to light UV lamps.

Collecting solar and wind energy is ideal in altitude as winds and solar radiation are more regular and intense. Several types of devices (e.g., aerostats, platforms with PV panels[71] and kites with wind turbines[72]) have been proposed for such applications. Several studies show that, compared to a typical ground-based system, locating them in altitude might bring a significant advantage for the electrical power production.[73]

The feasibility and viability of such techniques which have been studied are not included in this review article, but as an example, the collection of solar energy at altitudes of 6–12 km with the help of a device shown in Fig. 3 could produce four to six times more electricity than on grounds.[73] As a matter of fact, because reaction R1 requires H_2O and O_3 to generate °OH, altitudes lower than 612 km are necessary. Also, the weight of UV lamps (UV LEDs) needs to be taken into consideration when designing those devices.

Ocean based platforms, kites or artificial islands for both holding the UV *lamps* and power generation

When the wind is blowing from land to sea, offshore wind turbines are used to power UV lamps. Several types of alternative power generating devices are described, such as kite-surf plants,[75] sailing wind farms,[76] and artificial floating islands or platforms[77] with multiple renewable energy sources including other marine energies.

During peak load, 100% of electricity produced can be sent to the grid. Before and after the peak of consumption, almost all electricity production could be devoted to the UV lamps. At night some base-load electricity production from the grid, or "excess" wind energy which often costs zero or even has a negative price can be used.

The use of batteries to store PV generated electricity for night use is probably not necessary because this will unnecessarily increase the costs of the GGR method proposed. CH_4 is a well-mixed GHG and has many types of natural and anthropogenic sources all over the planet, so any excess of electricity produced in the night or even during the daytime could immediately be used for GGR.

Further discussions

Limitations in tropospheric O_3 concentrations

If tropospheric O_3 concentrations become the bottlenecks for °OH generation and more tropospheric O_3 is needed, O_3 generation can be considered far from populations in altitude, or over high seas. Because surface O_3 has detrimental effects on vegetation, animals and humans.[78] Another possibility is commercially available °OH generators (described earlier at the end of Section 3) which do not rely on tropospheric O_3 concentrations.

°OH also reacts with other gases and may generate secondary pollutants

Therefore, a rigorous atmospheric chemistry evaluation of rates and mixing is needed for further quantitative analysis of efficiency, costs, environmental and life cycle impacts, etc. This is a knowledge gap in the research field as great diversity exists among different atmospheric chemistry models which predict °OH variability, distribution and trends. This diversity has been primarily attributed to the following factors: differences in chemical mechanisms that result in differences in the chemical drivers of °OH, differences in meteorology across models that arise either because models produce their own meteorology or are forced by reanalyzed meteorological fields. The quantitative analysis would only be possible once a robust atmospheric model becomes available. Alternatively, some semiquantitative and scenario-based analyses can be attempted to partially bridge this gap.

Water vapor also has a greenhouse effect and absorbs UV

The average residence time of water vapor in the atmosphere is much shorter than that of CH_4 (4–9 days[79,80]), therefore, if CH_4 oxidation is enhanced, it is expected that the climate benefits should be higher, but this has to be quantified by further atmospheric chemistry modelling, which adds more complexity for the development of atmospheric models. Water vapor and artificial UV rays will not offset each other. Artificial UV is only proposed above oceans, or at altitude in locations that do not require adding additional water vapor. Increasing water vapor using downdraft towers is suggested in hot dry deserts where the natural UV levels are quite high and the use of artificial UV is not required.

Co-benefit of CH_4 removal

Some recent modelling work reveals that CH_4 removal provides great benefits for regional surface O_3 reduction in locations where it has detrimental effects, and thus plays a critical role in improving air quality.[81]

Life cycle assessments of all methods proposed

In order to assess if the methods proposed have overall negative emissions, or if the production and deployment of the devices proposed generate more GHGs than they remove, life cycle assessments will be performed in future work. In particular, for devices that only remove CH_4 without any associated co-benefit, the amount of operation time needed to equalize the pollution associated with the manufacture and construction process has to be determined. For devices also producing renewable energy or other co-benefits, more complicated assessments are needed to account for all contributors.

Concluding remarks

There are different approaches to develop the much-needed negative emissions technologies. In this review paper, we discussed some strategies to remove atmospheric CH_4 by enhancing the natural °OH sink.

Inspirations can be found in observed or predicted enhancement of °OH atmospheric concentration by climate change and human activities. Change of humidity and introduction of artificial UV radiation are the two main topics here, which we believe deserve more attention from the scientific community to help evaluate their potential risks, impacts, costs and public acceptability.

It is worth pointing out that those strategies may be expensive and have externalities, so careful assessments (e.g., techno-economic analysis, life cycle assessment) will be required to compare the proposed schemes versus CH_4 emission mitigation approaches. We believe that one of the main knowledge gaps for such assessments is the great diversity among different atmospheric chemistry models which predict °OH variability, distribution, and trends.

If the knowledge gap closes and evaluations prove those proposed schemes are viable, together with GHGs mitigation and CO_2 removal, large-scale CH_4 removal methods can help win time to fight climate change by slowing down warming and thus meet the targets of the Paris Agreement with limited temperature overshoot.

Acknowledgements

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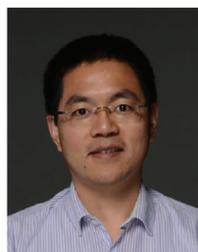
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