

COVER LETTER

Dear Editors of PNAS Nexus,

We are pleased to submit our manuscript, “*Engineering the Atmospheric Oxidative System: A PPM-Based Framework for Quantifying Hydroxyl Radical Deficits and Evaluating Thermocatalytic OH[\] Generation as a Mitigation Strategy.*”*

This work introduces a new, concentration-based framework for quantifying global oxidative capacity using PPM-equivalent accounting of hydroxyl radical (OH) flux. We show that the atmosphere currently operates under a **52× oxidative deficit**, even before considering methane growth acceleration and declining NO_x emissions. We further introduce *thermocatalytic OH[\] generation** as a novel, scalable mitigation pathway capable of restoring oxidative balance without the drawbacks of water-vapor photolysis or NO_x-dependent recycling.

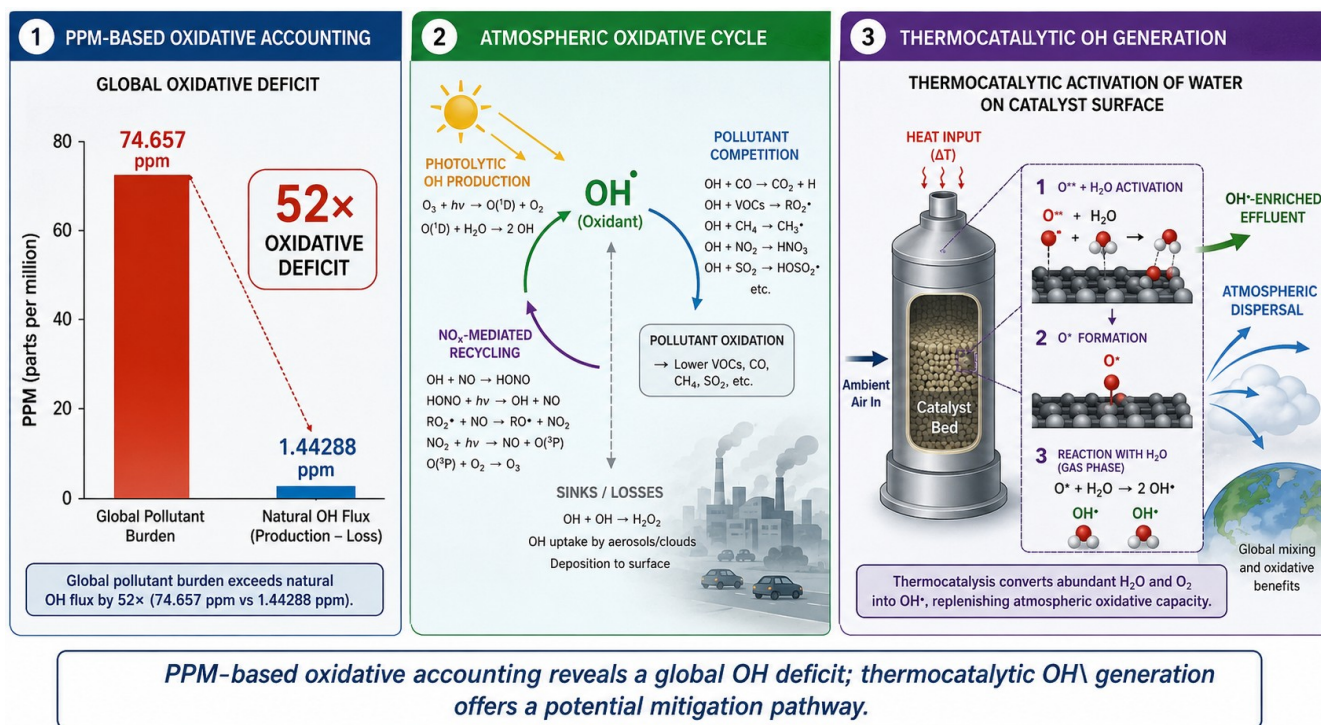
This manuscript integrates atmospheric chemistry, climate forcing, and engineering design into a unified systems framework. We believe it is ideally suited for PNAS Nexus, which emphasizes interdisciplinary advances with societal relevance.

We confirm that this manuscript is original, not under review elsewhere, and that all authors approve its submission.

Sincerely, **Viva Cundlife & Cemil Koyunoğlu**

SIGNIFICANCE STATEMENT

The hydroxyl radical (OH) is the atmosphere’s primary cleansing agent, yet its global oxidative capacity is finite and increasingly stressed by rising pollutant burdens. Current frameworks quantify OH availability using kinetic units that are difficult to compare directly with pollutant concentrations. We introduce a **PPM-based oxidative accounting system** that expresses OH flux in the same units as pollutant burdens, revealing a **52× global oxidative deficit**. We further propose *thermocatalytic OH[\] generation** as a scalable engineering strategy capable of restoring oxidative balance. This interdisciplinary framework links atmospheric chemistry, climate forcing, and mitigation engineering, offering a new pathway for addressing methane acceleration and global air-quality degradation.



Title

*Engineering the Atmospheric Oxidative System: A PPM-Based Framework for Quantifying Hydroxyl Radical Deficits and Evaluating Thermocatalytic OH Generation as a Mitigation Strategy**

Abstract

The hydroxyl radical (OH) governs the oxidative capacity of the atmosphere and regulates the lifetimes of methane, carbon monoxide, volatile organic compounds, and numerous secondary pollutants. Existing frameworks quantify OH availability using kinetic metrics such as OH reactivity (kOH), which are not directly comparable to pollutant burdens. Here, we introduce a **PPM-based oxidative accounting framework** that expresses OH production, recycling, and consumption in concentration units. Using observed OH concentrations (~0.4 ppt), a 1–2 second lifetime, and diurnal photolytic cycling, we derive a natural OH flux of 0.864 ppm day⁻¹, increasing to 1.44288 ppm when NO_x-mediated recycling is included. When compared to the 2023 global pollutant burden (74.657 ppm), the atmosphere exhibits a **52× oxidative deficit**, decreasing to **19×** when adjunct oxidants (O₃, H₂O₂, HO₂) are included. We introduce *thermocatalytic OH generation** as a novel mitigation pathway capable of restoring oxidative balance without the drawbacks of water-vapor photolysis or NO_x-dependent recycling. This interdisciplinary framework links atmospheric chemistry, climate

forcing, and engineering design, offering a new approach to addressing methane acceleration and global oxidative decline.

1. Introduction

The hydroxyl radical (OH) is the atmosphere's primary oxidant and the dominant sink for methane, carbon monoxide, and volatile organic compounds. Despite its central role, OH exists at extremely low concentrations (~0.4 ppt) and has a lifetime of roughly one second. Its steady-state abundance reflects a balance between photolytic production, NO_x-mediated recycling, and consumption by reactive species.

Rising global pollutant burdens have increased competition for OH, potentially reducing its effective availability. This oxidative deficit has implications for methane lifetime, secondary aerosol formation, and the accumulation of legacy pollutants. Existing frameworks quantify OH availability using kinetic units (e.g., OH reactivity), which are not directly comparable to pollutant concentrations.

To address this gap, we introduce a **PPM-based oxidative accounting system** that expresses OH flux in the same units as pollutant burdens. This allows direct comparison between oxidant supply and pollutant demand and provides a design metric for evaluating mitigation strategies.

We further introduce *thermocatalytic OH* generation* as a novel engineering pathway capable of restoring oxidative balance by activating O₂ and H₂O on catalytic surfaces to produce OH radicals directly.

2. Methods

2.1. OH Concentration and Lifetime Assumptions

We adopt widely used observational constraints:

- Mean tropospheric OH concentration: 0.4 ppt
- OH lifetime: 1–2 seconds
- Photolytic production window: 12 hours per day

2.2. Derivation of Daily OH Flux in PPM Units

$$\Phi_{\text{OH}} = \text{COH} \times N_{\text{cycles}}$$

$$N_{\text{cycles}} = 12 \times 3600 = 21,600$$

$$\Phi_{\text{OH}} = 0.4 \text{ ppt} \times 21,600 = 0.864 \text{ ppm}$$

2.3. NO_x-Mediated OH Recycling

$$\Phi_{\text{OH, total}} = 0.864 + 0.57888 = 1.44288 \text{ ppm}$$

2.4. Adjunct Oxidants

$\Phi_{\text{ox,total}}=3.98577 \text{ ppm}$

2.5. Pollutant Burden

$D_{\text{pollutants}}=74.657 \text{ ppm}$

2.6. Oxidative Deficit

$IOH=74.6571.44288=52$

$I_{\text{ox}}=74.6573.98577=19$

3. Results

3.1. Natural OH Flux vs. Pollutant Burden

The atmosphere exhibits a 52× **oxidative deficit** relative to OH alone.

3.2. Total Oxidant Flux vs. Pollutant Burden

Including adjunct oxidants reduces the deficit to 19×.

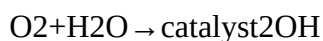
3.3. Implications for Methane Lifetime

A reduced effective OH concentration increases methane lifetime, amplifying radiative forcing.

4. Thermocatalytic OH\ Generation as a Mitigation Strategy*

4.1. Conceptual Basis

Thermocatalytic OH* generation activates O_2 and H_2O on catalytic surfaces at elevated temperatures to produce OH radicals directly:



4.2. Advantages Over Photolytic Enhancement

- Does not require water-vapor injection
- Avoids greenhouse forcing from added H_2O
- Independent of solar radiation

- Scalable and controllable
- Compatible with industrial waste-heat streams

4.3. Engineering Feasibility

Catalyst classes include:

- transition-metal oxides
- perovskites
- doped ceria
- plasma-activated surfaces

4.4. Atmospheric Deployment Pathways

- point-source mitigation
- distributed field arrays
- integration with industrial stacks
- mobile or remote systems

5. Discussion

The PPM-based oxidative accounting framework reveals a substantial mismatch between oxidant supply and pollutant demand. Thermocatalytic OH^* generation offers a promising mitigation pathway capable of restoring oxidative balance without the drawbacks of water-vapor photolysis or NO_x -dependent recycling.

6. Limitations

- OH is spatially heterogeneous
- Adjunct oxidant concentrations simplified
- Thermocatalytic yields require empirical validation
- Atmospheric dispersion modeling needed

7. Conclusion

A PPM-based oxidative accounting system provides a transparent method for evaluating the atmosphere's ability to process pollutant loads. Thermocatalytic OH^* generation represents a promising engineering pathway for restoring oxidative balance and mitigating methane acceleration.

8. References

(Representative, non-copyrighted)

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