Removal of atmospheric nitrous oxide (N_2O) using Photocatalytic Technology

Crop Intellect Ltd

Developer name(s): Dr Apostolos Papadopoulos, Yusuf Khambhati

Email: apostolos@cropintellect.co.uk, yusuf@cropintellect.co.uk,

Phone: +44 (0) 7500 794140

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Abbreviations

Nitrous oxide	N_2O
Greenhouse gas	GHG
Carbon dioxide	CO_2
Tons of Carbon Dioxide equivalent	tCO_2eq
Sources, sinks and reservoirs	SSRs
General Data Protection Regulation	GDPR
Quality assurance and quality control	QA/QC
Quick Response	QR
Deoxyribonucleic acid	DNA
Polymerase Chain Reaction	PCR
Nitrogen	N_2
Oxygen	O_2
Life Cycle Assessment	LCA
Gas chromatography	GC
Hectare	Ha

1. Methodology Overview

1.1 Scope

The proposed methodology is[1] applicable to projects that utilise photocatalysts[1] to breakdown nitrous oxide (N_2O) from the atmosphere. The photocatalysts can be deployed by placing them on any eligible surface i.e., by spraying or embedding into the surface. Any project that enables N_2O breakdown using photocatalysts will be eligible to adopt this methodology.

1.2 Motivation

N_2O is a very potent greenhouse gas (GHG) having global warming potential 273 times greater than that of Carbon dioxide (CO_2) and is responsible for rising global temperatures (IPCC Greenhouse Gas Protocol, 2024). The photocatalytic technology for N_2O removal developed by Crop Intellect Ltd is called R-Leaf and may be deployed on any appropriate surface that can receive and retain the photocatalyst but is especially effective on leaf canopies in agricultural cropland. Agriculture is a major contributor of N_2O emissions generated from synthetic nitrogen fertilisers usage typically applied to soil which is a global farm practice. According to DEFRA National statistics (2022), Chapter 11: Environment (Updated 27 July 2022), Agriculture was responsible for 69% of the overall UK N_2O emissions in 2020 which amounts to 14.5 million tCO_2eq. The use of photocatalysts to remove atmospheric N_2O by using daylight provides a unique opportunity to reduce the impact of N_2O towards climate change at scale.

1.3 Outline

The methodology is applicable to project activities aiming at removing N_2O from the air via deployment of photocatalysts placed on eligible surfaces such as crop leaves. The methodology offers flexibility to project developers to use photocatalytic technologies removing N_2O in their project design, including choosing a project location. The landowners or farmers will apply the photocatalyst that removes N_2O from the atmosphere in their practices i.e., spraying crops. Calculating the impact is performed through N_2O flux and monitoring the parameters that affect its efficacy. The photocatalytic performance and capacity for N_2O breakdown have been quantified through lab experiments and large open-air field trials, however, the parameters that affect its efficacy are specific to the region where the project is set up, therefore they are used to adjust the N_2O removal accordingly. The set up for measuring the N_2O flux and the equations used to adjust the impact of the monitored parameters affecting the N_2O breakdown in terms of tCO_2eq are defined and described in this methodology.

2. Applicability and Conditions

The methodology is applicable in any qualifying land-based project where plants/crops/vegetation are typically sprayed, or such spraying operation can be performed, and the level of N_2O in ambient air is typically over 300ppb. The photocatalyst is applied according to specific guidelines for crop type and growth stage. Monitoring the parameters affecting the efficacy of the photocatalyst is required. The photocatalyst for N2O removal must abide to regional regulatory requirements.

[1] A **photocatalyst** is a substance that accelerates a chemical reaction when exposed to light, without being consumed or altered in the process. Photocatalysts absorb light energy and create reactive species that facilitate the breakdown of pollutants or conversion of substances.

2.1 Eligibility

2.1.1 Geographical Scope

This methodology is globally applicable to land-based projects where spraying can be conducted. The project boundary encompasses agricultural land, including crops or vegetation, where the spraying operation is feasible and appropriate for reducing greenhouse gas emissions. The methodology applies to a variety of regions, provided the local environmental conditions allow for effective spray application and photocatalytic activity.

2.1.2 Project Boundary and Aggregation of Project Areas

The spatial extent of the project boundary includes all areas where photocatalysts are applied. This boundary is defined by the land or farmland directly involved in the intervention. For aggregate projects, multiple project sites within the same geographical region can be grouped together under one umbrella project, provided they experience similar environmental conditions (e.g., temperature, rainfall, sunlight) that influence the photocatalytic efficiency of the intervention.

Aggregate projects may be formed where multiple project locations share comparable climatic, soil, and operational parameters. These aggregated areas must be located within a reasonably defined region to ensure consistency in environmental conditions and the uniform application of the photocatalyst. The aggregation of several project boundaries into one larger project is encouraged for efficiency in measurement, reporting, and verification (MRV) processes, provided that either the geographic proximity ensures uniformity in regional parameters or if different these are measured (project relevant weather stations).

2.1.3 Technology and Equipment Requirements

This methodology is applicable only to projects that have access to photocatalytic technology with demonstrated evidence of its ability to remove N_2O under visible light. Projects must also have the necessary equipment to deploy the photocatalytic material, such as spraying systems or other relevant application methods.

In addition, projects must be equipped with appropriate monitoring tools to track regional environmental conditions (e.g., light, humidity, temperature) that impact the effectiveness of the photocatalytic process. Furthermore, equipment for accurately measuring the removal of N_2O emissions, as outlined in this methodology, is required to ensure that the outcomes can be reliably verified and reported.

2.1.4 Type of surface for photocatalyst application

This methodology applies to any project where photocatalysts for N_2O removal can be sprayed or spread on an appropriate surface. If the surface is permanently shaded (e.g., indoors or lacking light in general), a suitable light source of sufficient intensity relevant to the surface area must be provided to enable photocatalysis.

The most suitable surface for the photocatalyst application would be the canopy of plant leaves either on a crop farm or any other crop area. In this case, the type of crop selected is required to maintain a canopy for at least 4 weeks to ensure adequate impact from the photocatalytic activity. Application of agrochemical input onto a plant canopy by spraying is standard practice in crop production; the photocatalyst for N_2O removal can be mixed with the agricultural inputs (e.g., fungicides) and therefore no further activity than the farm standard would be required.

2.1.5 Non-standard crop surfaces and associated emissions

If spraying or spreading of the materials is not a standard practice for the surface selected for the photocatalyst for N_2O removal, then the excess emissions due to the spraying or spreading activity are not part of the baseline and need to be accounted for as a part of project activity emissions. Similarly, if an artificial light source is provided, the emissions from electricity or other energy sources used, including the material, must be factored into the overall project emissions.

2.2 Additionality

The projects adopting this methodology to generate certified carbon credits must demonstrate additionality. Any project can be determined as additional based on results of the Barrier Analysis and Common Practice analysis.

2.2.1 Barrier Analysis

When barriers exist that hinder the execution of the project activities, and the project cannot proceed without the benefits provided by carbon certification, the project is considered additional. The Barrier Analysis must be carried out by the Project Developer. The said barriers must be identified and described in the project description document. The possible barriers could be single or multiple, and some examples of the barriers are given below:

- Investment barriers (the technology/product to be used in the project is expensive due to the price of the photocatalyst and the required margin of the distribution network; standard inputs are more affordable and therefore an easy choice).
- Knowledge barriers (accepting the use of a new input in standard practices requires confidence and knowledge on the appropriate use and expected outcomes; the knowledge required to execute the methodology; special training for each crop within a farm).
- Institutional barriers (navigating through the regional policies, regulations and legislations require further work compared to an existing product/technology).
- Technological barriers (use of equipment for implementing the technology i.e., accessing the canopy of trees).
- Regulatory barriers (where for any regulatory specificity the application of the material is prohibited without registration or monitoring).
- Barriers due to regional traditions (regional traditional practices are restricting the use of the technology i.e., protected crops (in greenhouses) or not sprayed).
- Barriers evolving through existing land management practices (regular canopy removal i.e., professionally managed turf).
- Barriers through ecological circumstances (enabling utilisation of areas where spraying is not common practice).

The barriers described above restrict the adoption of the technology, however, through the benefits of the verified carbon credits these barriers can be overcome, and therefore, the technology can be deployed. The Methodological Tool 2: *"Combined tool to identify the baseline scenario and demonstrate additionality"* provides a detailed list of potential barriers (CDM, 2017).

2.2.2 Common Practice Analysis

The project is considered additional only if the project activities are not common practice in the region where the project is established. The Project Developer must carry out the Common Practice Analysis. It is suggested that the Common Practice Analysis be carried out as per CDM Methodological Tool 2: *"Combined tool to identify the baseline scenario and demonstrate"* (CDM, 2017). Any deviation from this method must be acknowledged and documented.

2.3 Principles

The principles outlined in ISO 14064-2:2019 should be adhered to throughout the implementation of this methodology. These principles provide a foundational framework for ensuring the accuracy and reliability of greenhouse gas (GHG) information and guide the methodology's application in its entirety. They are essential for verifying that all GHG-related data and claims are credible and true.

Relevance

Selection of the GHG sources, sinks and reservoirs (SSRs), data and methodologies appropriate to the needs of the intended user.

Completeness

Inclusion of all relevant GHG emissions and removals related to the project, along with all relevant information to support criteria and procedures.

Consistency

Ensure that GHG-related information is presented in a manner that allows for meaningful comparisons over time and across similar projects.

Accuracy

Reducing bias and uncertainties as far as it is practically possible.

Transparency

Disclosure of sufficient and appropriate GHG-related information to allow intended users to make decisions with reasonable confidence.

Conservativeness

Use of conservative assumptions, values and procedures to ensure that GHG emission reductions or removal enhancements are not overestimated.

The above are the extracts of the principles as described in ISO 14064-2:2019 (2019), adopted from Climate Farmers (2022).

2.4 Traceability

To effectively remove N_2O from the atmosphere and achieve the associated environmental benefits that result in carbon offsets being generated, it is crucial to spray the photocatalyst for N_2O removal over the surfaces that enable the photocatalytic reaction to take place. Therefore, it is important to apply the photocatalyst in the field or project area as specified in this methodology. A Quick Response (QR) code system will be utilised to track the movement of the material from production, through the supply chain, to individual landowner/project participant. This will allow the photocatalyst usage to be tracked throughout the distribution process, ensuring the product is received by customers, and photocatalyst usage can be quantified and verified, eliminating the risk of double counting.

Farmers participating in the project will be assigned a unique code that is linked to their specific order. Each pallet/batch of the photocatalyst for N_2O removal from that order will carry a QR code linked to the farmer’s code, the farmer will need to scan the QR code that will confirm that the farmer has received the material assigned to them. The QR code will also be used to track the movement of the photocatalyst through the supply chain along with the delivery information. The data collected from the QR code will be linked to a central database (complying with region’s General Data Protection Regulation (GDPR)), which will include information such as the farmer's name, address, order details, crop to be sprayed, area, equipment, timing and field location. This procedure will be a requirement for every landowner/project participant. They will have the choice of providing the details online, on an application (i.e., mobile app) or by sending a paper form completed.

2.4.1 Data Storage

The data will be predominantly handled according to GDPR requirements by the project developer, who will also be responsible for data management and storage. The following are the guidelines for data storage and handling.

1. Data Storage Location: The data collected during the project, including information on photocatalyst usage, must be stored in a centralized and secure location. This central repository will serve as a reliable source for data verification and analysis. The storage location can be either physical or digital, depending on the project's requirements and available resources.

2. Accessibility: To ensure transparency and collaboration, the data storage system should be accessible to all relevant stakeholders, including project coordinators, researchers, farmers, and regulatory bodies. Controlled access will be provided through secure logins or user authentication to ensure that only authorized personnel can view or modify the data.

3. Security Measures: Implementing stringent security measures is crucial for protecting the integrity and confidentiality of the stored data. The following measures should be implemented:

    - Data Encryption: Utilize encryption techniques to secure the stored data, both during transmission and while at rest. This helps prevent unauthorized access or tampering with sensitive information.
    - Regular Backups: Regularly back up the data to prevent loss or corruption. Maintain redundant copies of the data in secure location to ensure its availability in the event of system failure or data breaches.
    - Access Controls: Implement robust access control mechanisms to restrict data access based on user roles and permissions. This helps maintain the confidentiality of sensitive data and prevents unauthorized modifications.
    - Data Integrity Checks: Perform regular data integrity checks to ensure that the stored information remains accurate, complete, and unaltered. Implement mechanisms to detect any discrepancies or anomalies in the data, which may indicate potential issues or data tampering.
    - Disaster Recovery Plan: Develop a comprehensive disaster recovery plan to address potential data loss scenarios, such as natural disasters, system failures, or cyber-attacks. This plan should include procedures for data restoration and contingency measures to minimize downtime.

As an additional security measure to deter fraudulent claims, for instance, product being re-sold, used at lower rate, on a different crop or at different dose, a Deoxyribonucleic acid (DNA) based tracing technology or similar (biomarker) will be incorporated into the product. The DNA-based traceability method involves the addition of a unique DNA sequence to the product contents, this would be a plant-based DNA of a different type of typical farmed crop. This allows for easy and reliable confirmation of the photocatalyst deployment during the project. A subsample check will be performed to ensure the product has been used within each project. The added DNA sequence will be a random, non-coding sequence that poses no risk of gene transfer or harmful contamination to food or the environment. To confirm the presence of the photocatalyst for N_2O removal, a Polymerase

Chain Reaction (PCR) test will be performed on the leaf samples collected from the farms using primers specific to the added DNA sequence. This test will confirm the presence of the photocatalyst supplied. Sampling a sprayed crop will entail collecting leaves from three points in the field representing three different sections of that field appropriate for its size. These sampling points will be selected randomly by a third-party verifier, and the sampling will be done at any random time after the photocatalyst application date. The leaf samples will be from 5-10 plants in each sampling point and adequate to perform PCR analysis. The PCR test will be from a composite sample for the field and depending on the size of the project, an acceptable subsample to conform with statistical representation will be performed. The PCR test will be performed according to standard PCR protocols, Lorenz (2012) can be used as guidance. Instead of DNA tracing, any other method of achieving the same result can be incorporated according to availability and requirements.

Overall, the use of QR codes and DNA markers offers a safe and reliable option for tracing the deployed photocatalyst. This method can be easily implemented to ensure product traceability and confirm the application of the photocatalyst as specified by the methodology.

2.5 Project Description

The deployment of the photocatalyst for N_2O removal will be performed through spraying using typical and existing farm equipment. The photocatalyst will be tank mixed and sprayed with other agricultural inputs, which are already a standard practice, and hence the deployment of the photocatalyst will not require additional activities or change of practice.

Different types of plants/crops/vegetation have different sowing and harvesting time periods which also depend on the part of the world they are grown in. Due to this, the deployment times and rate of the photocatalyst can be different, resulting in varying project durations for different types of plants/crops/vegetation. The residual time of the photocatalyst on the leaves should be at least 4 weeks, and hence it can only be deployed on crops that maintain full leaves for a minimum of 4 weeks. The photocatalyst for N_2O removal resides on leaves for a duration of 4-12 weeks. It is recommended to deploy further layers as deemed required to maintain a certain level of efficiency. This typically relates to the crop growth and development. Therefore, a minimum of two sprays of the photocatalyst (1 kilogram/hectare) during the growth period will be typically required. The period of the residence time of the photocatalyst on the suitable surface defines the duration of the project.

In cases where two different crops are grown one after another on the same land over a year/season, each crop will be considered separately regarding its impact, but can be included under the same project, and each will receive photocatalyst applications. These applications will still align with agricultural inputs which is the standard farm practice.

In case thatthe project includes vegetation that does not require harvesting, for example, grasslands or evergreen trees, then the maximum project duration will be one year, and a new project will commence each year. As such, projects will have vegetation that maintains canopy or leaves year-round, the photocatalyst application will we done every 4-12 weeks throughout the year.

The by-products of N_2O breakdown are Nitrogen (N_2) and Oxygen (O_2), they are not required to be monitored. As the project area is an open system (i.e., farmland), N_2O degraded by the photocatalyst will be replaced by atmospheric N_2O (background level). The atmospheric N_2O concentration throughout the project site can be assumed to be uniform given that background levels of N_2O are consistent. Other methods to measure N_2O concentration that give similar end results can be adopted based on requirements and availability.

2.6 Quality Management

The project description document is prepared for every project by the Project Developer. This document confirms the eligibility of the project as per methodology requirements and it establishes consistency with regards to verification and validation. This document describes the specifications of the project and serves as the basis for third-party verification and validation.

The project description document must include the data quality management approach with appropriate clarifications. It should detail the quality assurance and quality control (QA/QC) protocols to ensure following factors:

- Accurate data collection
- Completeness (assessment of whether the data set is comprehensive and contains all the necessary data points or records)
- Independent checks of analysis results
- Trackable data archiving methods, including any anticipated updates to electronic files
- That data is archived electronically and kept for 5 years after the end of the last project crediting period
- Data protection
- A transparent uncertainty assessment
- A statement on how version control (of applied models, methodologies, tools, etc.) is handled

Guidance for evaluation of the quality standards can be taken from the ISO 8000 series which provides a comprehensive framework for data quality management. ISO 8000-1:2022 (2022), ISO 8000-2:2022 (2022), and ISO 8000-61:2016 (2016) are specific standards in this series that focus on data quality concepts, data quality models, and data quality measurement, respectively. ISO/IEC 25012:2019 (2008) is a standard specifically focused on data quality metrics. It provides guidance on the selection and use of data quality metrics for evaluating and assessing data quality. Guidance or specifications for uncertainty assessment can be found in ISO/IEC Guide 98-3:2008 (2008). This international standard provides guidance on evaluating and expressing measurement uncertainties. It covers principles, methods, and practical examples for uncertainty estimation.

2.7 Project validation

Third-party validation shall be carried out for all projects at their start, or at the time of the first project verification. The third-party validator checks the compliance of the project specifications with the project description document along with the correct implementation in line with this methodology. Relevant project data and documentation must be provided for a desk-based review. A validation report documenting the findings shall be produced.

2.8 Verification

Third-party project verification shall be carried out after project implementation has commenced and before the first tCO_2eq reduction or removal credits are issued. The following aspects shall be assessed during verification (see Sections 2.5, 4, 5 and 7):

- The extent to which project activities have been implemented in accordance with the project description,
- The extent to which monitoring procedures have been implemented in conformance with the monitoring plan,
- The reliability of the evidence for the determination of tCO_2eq reductions and removals, as presented in the monitoring report,

- The correct application of the formulas and methods set out in the project description for calculating baseline emission and project emissions,
- The accuracy of the calculated tCO_2eq emission reductions and removals in accordance with the project description and applied methodology.

2.9 Uncertainty Analysis

A complete quantitative uncertainty analysis associated with parameters, model variables and results of emission or removals will be performed according to IPCC protocols (IPCC, 2019). As stated in those protocols, when a variable cannot be statistically quantified, a pedigree matrix assessment will be performed, and the result included in the total uncertainty for the intervention. To combine the uncertainties of the different parameters, a propagation of error approach will be used in accordance with IPCC 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Volume 1, Chapter 3 Uncertainties (IPCC, 2019). A report explaining the importance of the parameter uncertainties will be provided as well as any peer reviewed document used in the uncertainty evaluation.

3. Boundaries

3.1 Project Boundary

This methodology can be applied globally on any land-based projects where plants/crops/vegetation are typically sprayed, or such deployment operation can be performed. The spatial extent of the project boundary encompasses the land (or farmland) included in the project. All the surfaces, including crops, sprayed with the photocatalyst are included in the project. Aggregate projects may be set up if the project locations are in the same region and are subjected to similar environmental conditions and parameters. Hence, the project area can include several project boundaries aggregated into one project. Since the by-products of N_2O breakdown are N_2 and O_2, they are not required to be monitored. The N_2O concentration will be measured with analysis conducted on air samples collected in the field using special air sampling bags. The project boundary ensures that key parameters such as day light length and sprayed area will not vary significantly.

The greenhouse gases included in or excluded from the project boundary are shown in Table 1 below.

Table 1. *Emissions sources or sinks included in or excluded from the project boundary*

Scenario	Source / Sink	Gas	Included	Justification
Baseline scenario	N_2O generated from agricultural activities (application of synthetic fertilizer) is a source in the baseline scenario	CO_2	No	Not significant through this activity
		CH_4	No	Not significant through this activity
		N_2O	Yes	Part of Farm carbon footprint
	Farming activities are a source of direct or indirect CO_2 emissions	CO_2	Yes	Part of Farm carbon footprint
		CH_4	No	Not significant through this activity
		N_2O	No	Not significant through this activity
Project	Photocatalyst	CO_2	No	Not significant through this activity

scenario	application is a N_2O sink in the project scenario	CH_4	No	Not significant through this activity
		N_2O	Yes	Important sink for emissions
	Manufacturing, processing, packaging, storage, and delivery of the photocatalyst is a source of direct or indirect CO_2 emissions	CO_2	Yes	Important source of emissions
		CH_4	No	Not significant through this activity
		N_2O	No	Not significant through this activity
	Farming activities are a source of direct or indirect N_2O and CO_2 emissions (this won't change from baseline as the photocatalyst application does not increase farming activities)	CO_2	Yes	Part of Farm carbon footprint
		CH_4	No	Not significant through this activity
		N_2O	Yes	Part of Farm carbon footprint

3.2 Temporal boundaries

The time frame of the project is specified before the commencement of the monitoring, and it is included in the Project Description Document (PDD). The PDD includes the start and end date of the project activity, the start and end date of the crediting period and reporting milestones including set reporting periods.

The following guidelines define the reporting period and establishment of the time limits:

- The project length shall be generally one growing cycle or one year, depending on the type of plants/crops/vegetation the photocatalyst is applied on, as described in Section 2.5.
- The project is detailed in PDD at the beginning of the project period.
- Throughout the duration of the project, the necessary data points/parameters shall be monitored during time periods described in Sections 5 and 7 of this methodology.
- The project developer shall record data on activities, change in practices and any other relevant details to the specific project area along with tCO_2eq emission.
- Throughout the duration of the project, the necessary data points/parameters shall be monitored during time periods described. A document shall be created that outlines the project's progress using a traceable scoring procedure and includes the number of assessed credits.
- Modifications to the project timeline can be made for justified reasons, such as extreme weather events. Any changes shall be documented and described.

4. Baseline Emissions

Continuation of pre-project N_2O emissions and no means of removing that N_2O is the most plausible baseline scenario. The project activities will remove the ambient N_2O that is released from the agriculture or other sources.

The use of synthetic nitrogen fertilisers is the standard practice in farming. These nitrogen inputs get converted to N_2O through nitrification and denitrification processes taking place in the soil. The N_2O is released into the atmosphere, thereby making agriculture a source of greenhouse gas emissions. The other farming activities also contribute to emissions; these emissions along with N_2O make up the carbon footprint of a farming operation. The carbon footprint of the field/farms included in the project is taken as the baseline. The greenhouse gas (GHG) emissions generated by standard agricultural practices without the application of the photocatalyst for N_2O removal will be compared to the N_2O removals achieved through the application of the photocatalyst. The photocatalyst application itself does not impose changes on standard farming practices as it is tank-mixed with other agricultural inputs already being sprayed. This makes the comparison straightforward and reflective of real-world farm conditions.

The background N_2O concentration before commencement of the project activities will also be measured (before photocatalyst application) in the project field. As the project area is an open site where air moves freely, the N_2O concentration is assumed to be the same within the project boundary. The project baseline activity will be demonstrated using the latest version of CDM Methodological Tool 2: “Combined tool to identify the baseline scenario and demonstrate” (CDM, 2017).

5. Quantification of GHG Emission Removals

It is essential to determine the amount of N_2O removed by the application of the photocatalyst to determine the GHG removal in terms of tCO_2eq. As the end products of the photocatalytic reaction (i.e., N_2 and O_2) are not stored but released into the atmosphere, the GHG removal cannot be determined through soil or crop sample analysis as in carbon sequestration methodologies, which sets this methodology apart. Hence, the N_2O quantification is done using flux calculations and considering the parameters that affect it.

5.1 N_2O Breakdown Equation

The equation for calculating N_2O breakdown integrates the interaction of key factors, with a focus on measuring the most significant variables. By leveraging established knowledge and validated assumptions, we can accurately estimate reaction rates, ensuring reliable and practical calculations.

5.1.1 Scientific Background

Within a closed laboratory environment, the change in N_2O concentration is directly related to the amount of N_2O that is converted by the photocatalyst. However, in the open-air vicinity of the field , any change in N_2O is related to gradients in its concentration close to the plants and that arises from uptake by the photocatalyst. Well above the plants, the concentration will be unchanged.

Specifically, the amount of N_2O converted by the photocatalyst (the vertical flux (*F*) of N_2O towards the plants, in units of mass per unit area per second) is given by:

$$F = \overline{w'c'} \qquad [Eq.\ 1]$$

where *w'* is the vertical velocity fluctuation due to turbulence and *c'* is the fluctuation in the N_2O concentration around the mean concentration *C* (mass per unit volume). The overbar represents the mean value of this quantity (the covariance), which can be measured directly using suitable instrumentation, this is known as the eddy covariance method.

An approximate representation of *Eq. 1* is to express the flux of N_2O in terms of mean quantities as follows:

$$F = K.dC/dz \qquad [Eq.\ 2]$$

where *K* is the exchange coefficient which depends on the magnitude and length scales of the atmospheric turbulence and *z* is the height above ground. The length scales of the turbulence increase with the height above the ground *z*, and so, for constant flux, *dC/dz* decreases with *z* and hence the most easily measurable changes in *C* are likely to be quite close to the plants (for example, within a few meters).

5.1.2 N_2O breakdown calculation from N_2O flux

To calculate the N_2O flux, it is important to determine the exchange coefficient. The exchange coefficient *K* depends on the atmospheric turbulence and height above ground. Hence, it can be represented in terms of the wind friction velocity *u**, von Karman's constant *κ* and representative height *z*. It is calculated using *Eq. 3*.

$$K = \kappa.z.u^{*} \qquad [Eq.\ 3]$$

The value of von Karman's constant *κ* is 0.4.

The wind friction velocity *u** is calculated using the following equation:

$$u^{*} = z_u\,\kappa/\ln(U_{(10)}/z_0) \qquad [Eq.\ 4]$$

Where,

*u** Wind friction velocity (m/s)

z_u Height of wind measurement (taken as 10m)

κ Von Karman's constant (0.4)

$U_{(10)}$ Average wind speed at 10m height (m/s)

z_0 Surface roughness (taken as 0.1m for most crops)

The representative height for exchange coefficient is calculated using the following equation:

$$z = (z_1 + z_2)/2 \quad [Eq.\ 5]$$

Where,

z Representative height (m)

z_1 Height of canopy measurement (m)

z_2 Height 1m above canopy (m)

(Please note that z_2 may change as appropriate to over 1m above the canopy based on further field experiments).

Assuming that the concentrations over the untreated field represent the background concentration and that this concentration is reached 1m above the canopy, the flux may then be estimated using *Eq. 2* and *Eq. 3* as follows:

$$F = \kappa . z . u^{*} . dC/dz \quad [Eq.\ 6]$$

Where,

F Flux of N_2O from the atmosphere to canopy (ppb.m/s)

The gradient in N_2O concentration between the two measurement heights (in ppb/m) is represented by *dC/dz* and it can be calculated using following equations:

$$dC = C_2 - C_1 \quad [Eq.\ 7]$$

$$dz = z_2 - z_1 \quad [Eq.\ 8]$$

Where,

C_1 N_2O concentration at canopy height (ppb)

C_2 N_2O concentration 1m above canopy (ppb)

z_1 Height of canopy measurement (m)

z_2 Height 1m above canopy (m)

Flux of N_2O is converted into the unit $\mu g_{N2O}/m^2/s$ by using the following equation:

$$F_{N2O} = F . MW_{N2O}/V_g \quad [Eq.\ 9]$$

Where,

F_{N2O} Flux of N_2O from the atmosphere to canopy ($\mu g_{N2O}/m^2/s$)

F Flux of N_2O from the atmosphere to canopy (ppb.m/s)

MW_{N2O} Molecular weight of N_2O (44 g/mol)

V_g Volume (approx.) of 1 mole of gas (22.4 L)

The Equivalent CO_2 flux (F_{CO2}) is calculated using the Global Warming Potential of N_2O, which is 273 times greater than that of CO_2 (IPCC Greenhouse Gas Protocol, 2024):

$$F_{CO2} = F_{N2O}.273 \quad [Eq.\ 10]$$

Where,

F_{CO2} The Equivalent CO_2 flux ($\mu g_{CO2}/m^2/s$)

The Equivalent CO_2 is converted to the unit g/ha/day using the following equation:

$$F'_{CO2} = F_{CO2}.\left(\frac{1}{1000000}\right).10000 \times 3600 \times 24 \quad [Eq.\ 11]$$

It was previously estimated the loss of efficiency of a suitable photocatalyst over time to be 0.08%/day (0.93 factor), hence, the Equivalent CO_2 removal per hectare for a 90-day active period (assuming 13 hours of daylight every day during the project period) in terms of tCO_2eq is

$$F_{tCO2eq} = F'_{CO2}.48.\times 5 \times 0.93/1000000 \quad [Eq.\ 12]$$

Where,

F_{tCO2eq} The Equivalent CO_2 removal (tCO_2eq/ha)

This value will be multiplied by the total area of application of the photocatalyst for N_2O removal (in ha) to obtain total GHG removal in terms to tCO_2eq.

5.2 Sampling and Analysis

The Flux calculation described in Section 5.1 requires N_2O concentration data at canopy height and at least 1m over the canopy. To obtain this data, air sampling in the field at two heights vertically over each other needs to be conducted, and then analysed for N_2O.

The air samples can be collected in multilayer foil sampling bags or Tedlar sampling bags, and using manual or electric pumps. The samples are to be collected from the field where the photocatalyst for N_2O has been sprayed, the first sample is to be collected between 1 to 5 days after application. Further samples should be taken after 5 days of application (three sets of samples recommended at collection interval of 3 to 5 days) to get a more robust data set.

A uniform and portable setup is required to take samples at two heights (see *Figure 5.2.1*). A tube will be attached to the pump's inlet and the other end of the tube will be moved to the desired height, instead of the pump being moved. This will be done for all the pumps used for the sample collection. A stick with uniform markings will be set up in the field at the measuring points. Two pumps are required at each measuring point to collect air samples at two heights. The tube inlet of the first pump will be attached to the stick at canopy height and inlet of the second pump attached at least 1m above canopy. Both pumps will be operated simultaneously. The bags will be attached to the pump outlets via tubes.

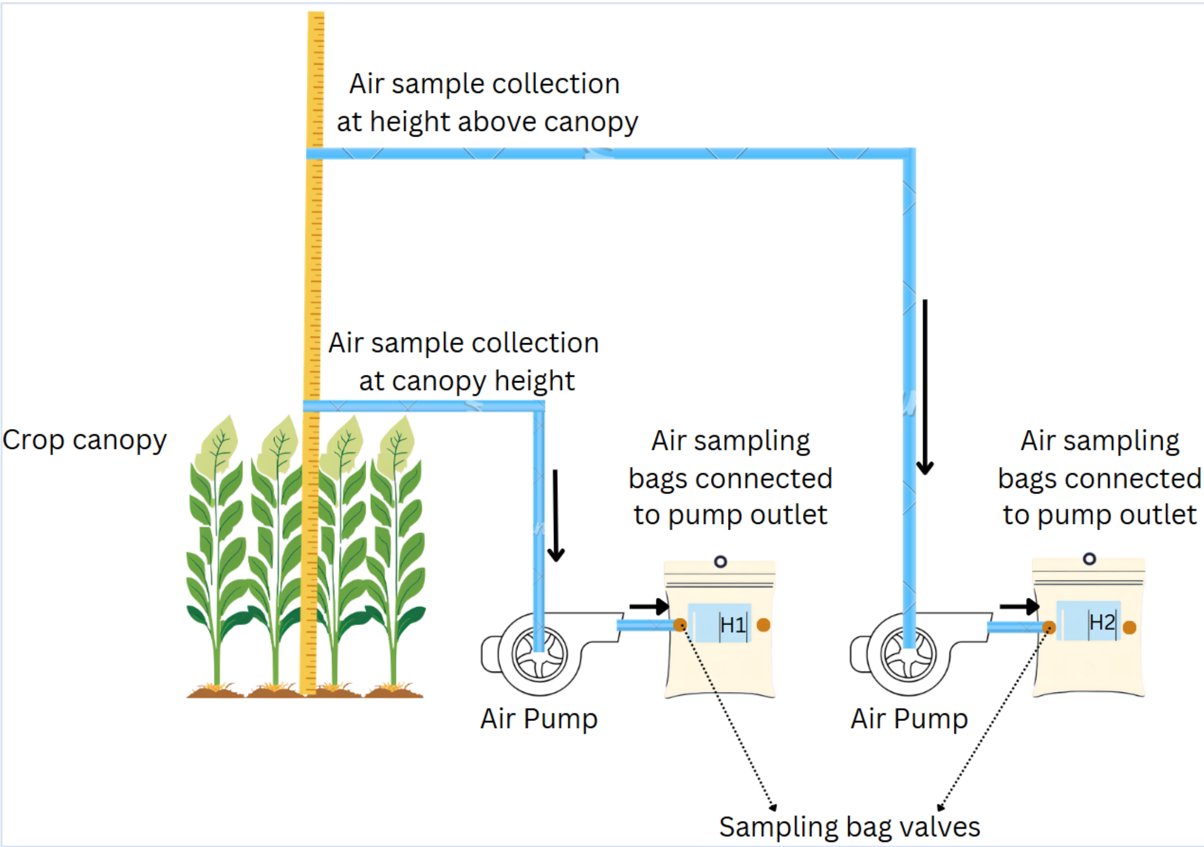

Figure 1. Setup for air sampling in the field

The air samples are collected following the steps below:

- Connect the valve of the bags to the outlet of the pumps.
- Open connected valve of both bags (for both heights) and start the pumps.
- To account for short time fluctuations in N_2O concentrations, the bag should represent a composite sample of 1-2 minutes of environmental activities, i.e., the flow of the pump should be controlled so that bag is full in 1-2 minutes.
- Once full, close the bag valves and detach from the pump.
- Connect the next set of bags and repeat the procedure.
- Collect 8 to 10 set of bags.

The sampled air will be analysed using gas analysers such as LI-COR LI-7820 N2O/H2O Trace gas analyser (analysers with ability to detect N_2O changes at ppb levels) or more commonly used gas analysis techniques such as Gas Chromatography (GC). The output of the analysis should be the N_2O concentration in ppb which needs to be averaged and applied to *Eq. 7* and *Eq. 8* as *C1* and *C2*.

A detailed sampling and analysis procedure used in practice is available in Appendix A.

6. Project Activity Emissions

The Project Activity Emissions are the emissions that arise from the operations required to implement, run, monitor, and conclude the project. As these activities release the GHGs into the atmosphere which would not have occurred in the absence of the project, they need to be accounted for and deducted from the GHG removal claims in the project.

As mentioned in Section 2.1.4, the implementation of the project in crop farming will not affect the standard farming practices as spraying is already an operation performed regularly. Therefore, the emissions from the standard agricultural practices are not part of the project activities, and hence will not be deducted from the GHG removal claims.

The activities resulting from procurement of raw materials, manufacturing processes, packaging and transportation for the production and supply of the photocatalyst for N_2O removal will generate emissions. These emissions ought to be calculated as part of full Life Cycle Assessment (LCA) of the photocatalyst, and then be deducted from the GHG removal claims in the project.

The emissions from other project activities like monitoring and measurements will be considered and deducted from the total GHG removal claim, unless they can be described as negligible.

Therefore, the Net GHG removal claimed by the project will be the Project Activity Emissions deducted from the tCO_2eq N_2O removed.

7. Monitoring

Table 2 details the parameters that will be monitored during the project.

Table 2. *Parameters monitored throughout each project, a) Average wind speed at 10m height, b) Height of canopy, c) Height at least 1m above canopy, d) N_2O concentration at canopy height, e) N_2O concentration at least 1m above canopy height.*

(a)	
Data / Parameter	Average wind speed at 10m height ($U_{(10)}$)
Data unit	m/s
Description	Refers to average wind speed at the height of 10m above the ground, for the project duration.
Equations	Eq. 4

Source of data	Meteorological station readings/weather reports
Justification of choice of data or description of measurement methods and procedures applied	This parameter is important to determine wind friction velocity for flux calculations. The project developer will be responsible to gather this data. The data should be noted daily.
Purpose of Data	Quantification of GHG emission removal
Comments	N/A

(b)	
Data / Parameter	Height of Canopy (z_1)
Data unit	m
Description	Refers to the height of crop canopy
Equations	Eq. 5 and Eq. 8
Source of data	Field measurements
Justification of choice of data or description of measurement methods and procedures applied	This parameter is important to determine the exchange coefficient and gradient of N_2O for flux calculations. The project developer will be responsible to gather this data. The data should be noted during air sampling in the field.
Purpose of Data	Quantification of GHG emission removal
Comments	N/A

(c)	
Data / Parameter	Height at least 1m above canopy (z_2)
Data unit	m
Description	Refers to the height at least 1m over the crop canopy from where the air sample are collected
Equations	Eq. 5 and Eq. 8

Source of data	Field measurements
Justification of choice of data or description of measurement methods and procedures applied	This parameter is important to determine the exchange coefficient and gradient of N_2O for flux calculations The project developer will be responsible to gather this data. The data should be noted during air sampling in the field.
Purpose of Data	Quantification of GHG emission removal
Comments	N/A

(d)	
Data / Parameter	N_2O concentration at canopy height (C_1)
Data unit	ppb
Description	Refers to the N_2O concentration at canopy height, analysed from the air samples collected from the field.
Equations	Eq. 7
Source of data	Field measurements
Justification of choice of data or description of measurement methods and procedures applied	This parameter is important to determine the gradient of N_2O for flux calculations. The project developer will be responsible to gather this data. The data should be collected at least once during the project, three times recommended.
Purpose of Data	Quantification of GHG emission removal
Comments	N/A

(e)	
Data / Parameter	N_2O concentration at least 1m above canopy height (C_2)
Data unit	ppb
Description	Refers to the N_2O concentration at height at least 1m above canopy, analysed from the air samples collected from the field.

Equations	Eq. 7
Source of data	Field measurements
Justification of choice of data or description of measurement methods and procedures applied	This parameter is important to determine the gradient of N_2O for flux calculations. The project developer will be responsible to gather this data. The data should be collected at least once during the project, three times recommended.
Purpose of Data	Quantification of GHG emission removal
Comments	N/A

References

BALLARI, M., HUNGER, M., HUSKEN, G., BROUWERS, H., (2010). Modelling and experimental study of the NOx photocatalytic degradation employing concrete pavement with titanium dioxide. *Catalysis Today*. **151**, 71-76. DOI: 10.1016/j.cattod.2010.03.042.

CDM, (2017). Tool 2: Combined tool to identify the baseline scenario and demonstrate additionality. *EB 96 annex 3* (Version 07.0). Available: https://cdm.unfccc.int/Reference /tools/index.html Accessed 22nd October 2024]

Climate Farmers, (2022). Methodology 01: Adoption of Regenerative Land Management (Version 01) [PDF]. Available: https://www.climatefarmers.org/wp-content/uploads/2022/09/Methodology_Adoption-of-Regenerative-Land-Management_v01.pdf [Accessed 23rd June 2023]

DEFRA National statistics, (2022). Chapter 11: Environment. GOV.UK. Available: https://www.gov.uk/government/statistics/agriculture-in-the-united-kingdom-2021/chapter-11-environment#:~:text=Agriculture%20is%20the%20major%20source,dioxide%20emissions%20in%20the%20UK. [Accessed 15th February 2023]

HUFSCHMIDT, D., BAHNEMANN, D., TESTA, J.J., EMILIO, C.A., LITTER, M.I., (2002). Enhancement of the photocatalytic activity of various TiO2 materials by platinisation. *Journal of Photochemistry and Photobiology A: Chemistry*, **148**(1-3), 223-231.

IPCC Greenhouse Gas Protocol, (2024). IPCC Global Warming Potential Values, Version 2.0. Available: https://ghgprotocol.org/sites/default/files/2024-08/Global-Warming-Potential-Values%20%28August%202024%29.pdf. [Accessed 11th October 2024]

IPCC, (2019). 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Available at: https://www.ipcc.ch/report/2019-refinement-to-the-2006-ipcc-guidelines-for-national-greenhouse-gas-inventories/ [Accessed: 25 October 2024]

ISO 14064-2:2019, (2019). Greenhouse gases - Part 2: Specification with guidance at the project level for quantification, monitoring and reporting of greenhouse gas emission reductions or removal enhancements

ISO 8000-1:2022, (2022). Data quality — Part 1: Overview. Available: https://www.iso.org/standard/81745.html. [Accessed 14th September 2023]

ISO 8000-2:2022, (2022). Data quality — Part 2: Vocabulary — Amendment 1. Available: https://www.iso.org/obp/ui/#iso:std:iso:8000:-2:ed-5:v1:en. [Accessed 14th September 2023]

ISO 8000-61:2016,(2016). Data quality — Part 61: Data quality management: Process reference model. Available: https://www.iso.org/standard/63086.html. [Accessed 14th September 2023]

ISO/IEC 25012:2008, (2008). Software engineering — Software product Quality Requirements and Evaluation (SQuaRE) — Data quality model. Available: https://www.iso.org/standard/35736.html. [Accessed 14th September 2023]

ISO/IEC Guide 98-3:2008, (2008). Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995). Available: https://www.iso.org/standard/50461.html. [Accessed 14th September 2023]

KOCI, K., RELI, M., TROPPOVA, I., (2017). Photocatalytic decomposition of N2O over TiO2/g-C3N4 photocatalysts heterojunction. *Applied Surface Science*. **396**, 1685-1695. DOI: 10.1016/j.apsusc.2016.11.242.

KUDO, A., SAKATA, T., (1992). Photocatalytic Decomposition of N2O at Room Temperature. *Chemsitry Letters*. **21**, 2381-2384. DOI: 10.1246/CL.1992.2381.

LORENZ, T.C., (2012). Polymerase chain reaction: basic protocol plus troubleshooting and optimization strategies. *J Vis Exp. (Journal of Visualized Experiments)* ;(63):e3998. DOI: 10.3791/3998.

LYU, X., WANG, T., SONG, X., *et al*., (2021). Reducing N2O emissions with enhanced efficiency nitrogen fertilizers (EENFs) in a high-yielding spring maize system. *Environmental Pollution*. **273**, 116422. DOI: 10.1016/j.envpol.2020.116422.

MATUSZKO, D., (2012). Influence of the extent and genera of cloud cover on solar radiation intensity. *International Journal of Climatology*. **32**, 2403-2414. DOI: 10.1002/joc.2432.OBALOVA, L., RELI, M., LANG, J., (2013). Photocatalytic decomposition of nitrous oxide using TiO2 and Ag-TiO2 nanocomposite thin films. *Catalysis Today*. **209**, 170-175. DOI: 10.1016/j.cattod.2012.11.012.

SI, H., ZHOU, M., FANG, Y., HE, J., YANG, L., WANG, F., (2021). Photocatalytic concrete for NOx degradation: Influence factors and durability. *Construction and Building Materials*. **298**, 123835. DOI: 10.1016/j.conbuildmat.2021.123835.

UNFCCC, (2017). CLEAN DEVELOPMENT MECHANISM TOOL02: Methodological tool Combined tool to identify the baseline scenario and demonstrate additionality (Version 07.0) [PDF]. Available: https://cdm.unfccc.int/methodologies/PAmethodologies/tools/am-tool-02-v7.0.pdf [Accessed 23rd June 2023]

ZHANG, J., VIKRANT, K., KIM, K.H., DONG, F., CHUNG, M.W., WEON, S., (2022). Unveiling the collective effects of moisture and oxygen on the photocatalytic degradation of m-Xylene using a titanium dioxide supported platinum catalyst. *Chemical Engineering Journal*, **439**, p.135747. DOI: 10.1016/j.cej.2022.135747.

Appendix A

Sampling and data analysis procedures

1. Materials and Equipment

- **Air Sampling Bags**: main type of air sampling bag used:
  - **Two-valve multilayer foil sampling bags** (5-liter capacity): Comprised of four layers (nylon, polyethylene, aluminium foil, and polyethylene). These bags were preferred due to their capability to loop analysis, creating stabilized conditions and ensuring consistent results.
- **Pumps**:
  - **Manual electric pumps**: These were found more efficient, capable of filling bags in 20-30 seconds, reducing variations between sample points. Models included pumps with built-in batteries (e.g., D Cell Electric Air Pump Powertouch™), which allowed for quicker and simultaneous sampling at multiple heights.
- **Other Equipment**:
  - **Tubes** for connection.
  - **UV Light Meter**: To measure the UV intensity during sampling.
  - **Weather station**: To record environmental conditions, such as wind speed and direction.

2. Field Setup and Sampling Procedure

- **Field Selection and Preparation**:
  - Measurement points were selected in treated and control fields based on factors such as wind direction and field shape. Fields sprayed with R-Leaf were confirmed to have visible product coverage on the leaves.
  - It was ensured that the measurement points were far from roads or obstructions to reduce external influences on N2O readings.
  - Geo-locations of all measuring points were marked for consistency for repeated visits.
- **Sampling Heights**:
  - Samples were collected at two heights: canopy level and 1 meter above the canopy. This was performed in a treated and an appropriately identified representative control (No R-Leaf) field. This dual-height approach and corelation with untreated, recommended by CERC, aimed to measure vertical fluxes accurately, resulting in measuring the impact of the photocatalyst on N_2O breakdown.
- **Procedure**:

- Each bag was filled using manual pumps. The bags were purged or vacuumed before use to remove any residual air.
- Bags were filled over approximately 2 minutes with controlled air flow for consistency.
- A total of 6-8 sets of bags were collected sequentially from both the treated and control fields. The control and treated field measurements were ideally conducted simultaneously to account for changing environmental conditions.

- **Sampling recommendations by CERC:**
  - Conducting air sample collection at multiple points and heights within the same field would improve data reliability and reduced uncertainty.
  - Sampling under various weather conditions (e.g., sunny, overcast) would provide insights into how these factors influence R-Leaf's performance.

3. Sample Analysis with LI-COR LI-7820 N2O/H2O Analyzer

- **Analyzer Setup**:
  - The Licor analyser uses Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) for precise, sub-ppb N2O measurements.
  - The equipment was powered either by batteries or connected to an external power source.
- **Analysis Procedure**:
  - Air sample bags were attached to the analyser using specialized compression fittings (e.g., Swagelok fittings).
  - Each sample was analysed for 10 minutes, with the first minute considered as a purging period.
  - Bags were looped for continuous analysis when necessary, ensuring no air leaks occurred.
- **Data Export**:
  - Data was exported from the Licor in '.data' format, with files labelled to correspond to specific sample bags. The exported data was then processed in Excel.

4. Data Processing and Statistical Analysis

- **Data Organization**:
  - Raw data from '.data' files was imported into Excel. A custom computer program was utilized to organize data efficiently into time and N2O concentration columns.
- **Outlier Identification**:

- Outliers were identified using the interquartile range (IQR) method. The quartile function in Excel was used to determine Q1 and Q3, with a stricter IQR multiplier (1.25) to enhance sensitivity.

- **Outlier Filtering**:
  - Data flagged as outliers was excluded from the statistical analysis to improve the accuracy and reliability of the results.

- **Descriptive Statistics**:
  - Mean and standard deviation of the filtered data were calculated using Excel's data analysis tools. These statistics provided a foundational understanding of the N_2O concentration changes observed.

- **Application of the CERC Model**:
  - The Cambridge Environmental Research Consultants (CERC) model was used to calculate vertical N_2O flux, considering environmental data and N_2O concentration gradients between the two heights.
  - The model output was converted into CO_2 equivalents using standard conversion factors, considering R-Leaf's active period and efficiency.

5. Comparison and Interpretation of Results

- **Data Comparisons**:
  - N_2O flux data from treated and control fields were compared. Positive flux indicated N_2O removal attributed to R-Leaf.
  - Control field concentrations served as a baseline for background N_2O levels, essential for distinguishing R-Leaf's impact.

- **Variability**:
  - Results often varied due to factors such as wind speed, time since photocatalyst application, and light/UV intensity. High UV conditions correlated with more effective N2O removal, consistent with the behaviour expected from a photocatalyst. More data eventually will allow model the impact with reduced uncertainty.