# Improving nitrogen cycling in a land surface model (CLM5) to quantify soil N₂O, NO and NH₃ emissions from enhanced rock weathering with croplands

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**Abstract.** Surficial enhanced rock weathering (ERW) is a land-based carbon dioxide removal (CDR) strategy that involves applying crushed silicate rock (e.g., basalt) to agricultural soils. However, unintended biogeochemical interactions with the nitrogen cycle may arise through ERW increasing soil pH as basalt grains undergo dissolution that may reinforce, counteract, or even offset the climate benefits from carbon sequestration. Increases in soil pH could drive changes in the soil emissions of key non-$CO_2$ greenhouse gases, e.g., nitrous oxide ($N_2O$), and trace gases, e.g., nitric oxide (NO) and ammonia ($NH_3$) that affect air quality, and crop and human health. We present the development and implementation of a new improved nitrogen cycling scheme for the land surface model Community Land Model v5 (CLM5), the land component of the Community Earth System Model, allowing evaluation of ERW effects on soil gas emissions. We base the new parameterizations on datasets derived from soil pH responses of $N_2O$, NO and $NH_3$ of ERW field trial and mesocosm experiments with crushed basalt. These new capabilities involve the direct implementation of routines within the CLM5 N-cycle framework, along with asynchronous coupling of soil pH changes estimated through an ERW model. We successfully validated simulated 'control' (i.e., no ERW) seasonal cycles of soil $N_2O$, NO and $NH_3$ emissions against a wide range of global emission inventories. We benchmark simulated mitigation of soil $N_2O$ fluxes in response to ERW against a sub-set of data from ERW field trials in the U.S. Corn Belt. Using the new scheme, we provide a specific example of the effect of large-scale ERW deployment with croplands on soil nitrogen fluxes across five key regions with high potential for CDR with ERW (North America, Brazil, Europe, India, and China). Across these

regions, ERW implementation led to marked reductions in $N_2O$ and $NO$ (both 18%) with moderate increases in $NH_3$ (2%). While further developments are still required in our implementations when additional ERW data become available, our improved N-cycle scheme within CLM5 has utility for investigating the potential of ERW point-source and regional effects of soil $N_2O$, $NO$ and $NH_3$ fluxes in response to current and future climates. This framework also provides the basis for assessing the implications of ERW for air quality given the role of $NO$ in tropospheric ozone formation, and both $NO$ and $NH_3$ in inorganic aerosol formation.

## 1 Introduction

Drastic and rapid emission reductions and the use of carbon dioxide ($CO_2$) removal (CDR) technologies are essential for meeting the Paris Agreement on Climate and net-zero commitments (IPCC, 2021). Modelled scenarios indicate that 7-15 gigatons (Gt) of $CO_2$ must be removed and safely stored each year to limit warming to 2°C (Riahi et al, 2021). A series of land-based CDR strategies involving the terrestrial biosphere have been proposed, which includes afforestation and reforestation, bioenergy crops, enhanced rock weathering (ERW) and peatland restoration, among others. An overview of these land-based CDR strategies and recommendations for their application have been summarized by independent international expert committees (e.g., National Research Council, 2015, Royal Society, 2018, Smith et al., 2023) as well as the IPCC 2021 report (Canadell et al., 2021). All these reports agree that there are unidentified environmental risks that must be assessed, because they may reinforce, counteract, or even offset the climate benefits from carbon sequestration.

Land-based enhanced rock weathering is a CDR strategy, which involves applying crushed silicate rock (e.g., basalt) to soils to sequester carbon, and is potentially feasible for large-scale deployment with managed croplands and grazing lands. Basalt is an ideal abundant silicate rock for ERW because of its potential co-benefits for crop yields and capacity to reverse soil acidification (Kantola et al., 2017; Beerling et al., 2018) and supply plant-essential nutrients like phosphorus (Goll et al., 2021). The estimated global net CDR potential for ERW deployed on main crop regions worldwide is 0.5–2 Gt $CO_2$ $yr^{-1}$ with extraction costs of US\$80–180 per tonne of $CO_2$ and carbon storage time scales of $\geq$10,000 years (Beerling et al., 2020). However, interactions between ERW, nitrogen (N) cycling, and soil-plant processes lead to changes in the emissions of other greenhouse gases (GHGs), e.g., nitrous oxide ($N_2O$), methane ($CH_4$), and atmospheric pollutants, e.g., nitrogen oxides ($NO_x$=$NO$+$NO_2$) and ammonia ($NH_3$) from soils.

$N_2O$ is an important greenhouse gas and a long-lived stratospheric ozone-depleting substance (Prather et al., 2015). The concentration of atmospheric $N_2O$ has increased by more than 20% during the last centuries and is currently increasing at a rate of 2% per decade (Tian et al., 2020). Agricultural ecosystems are the largest anthropogenic source of $N_2O$, with about 50% of the global emissions (Tian et al., 2020). Agricultural ecosystems are also significant sources of $NH_3$ and $NO_x$, comprising about 80% of global $NH_3$ emissions (Van Damme et al., 2021) and about 10% of global $NO_x$ emissions (IPCC, 2021). Once emitted from soil, $NH_3$ and $NO_x$ species can lead to air pollution, by increasing N deposition as well as production

of other air pollutants, such as ozone ($O_3$) and particulate matter (PM, as $PM_{2.5}$ with particles with an aerodynamic diameter <2.5 µm and $PM_{10}$ with diameter <10 µm), which are harmful to human, ecosystem, and crop health. These nitrogen trace gases can also contribute to water eutrophication, soil acidification and loss of plant species and habitat diversity (e.g., Sutton et al., 2009). In the coming decades, soil nitrogen emissions in croplands are expected to continue to increase because of fertilizer and manure application to meet the growing demand for food, forage, fibre, and energy (e.g., Reay et al., 2012; Davidson and Kanter, 2014; IPCC, 2021).

In agriculture ecosystems, soil $N_2O$ and NO fluxes are driven by two main biochemical processes: nitrification and denitrification, while soil $NH_3$ is driven by volatilization. These three processes are controlled by many environmental factors such as temperature, soil pH, water and oxygen content and N availability (via synthetic fertilizer and manure applications) (e.g., Reay et al., 2012; Tian et al., 2016). Analyses from enhanced weathering field experiments in the U.S. Corn Belt have shown that the application of basalt consistently increases soil pH and reduces soil $N_2O$ fluxes with no effects on soil $CO_2$ emissions (Blanc-Betes et al., 2020). It is expected that increases in soil pH will concurrently produce a decrease in soil $NO_x$ emissions, by decreasing rates of denitrification and nitrification (Parson et al., 2001) and an increase in $NH_3$ volatilization (Mkhabela et al., 2006). Thus, widespread implementation of ERW holds consequences for air quality and human and crop health as well as for climate mitigation that have so far been overlooked. To date, there is no modelling framework that has the capability to fully quantify the changes in biogeochemical processes and atmospheric trace gas emissions from ERW applications.

In this study, we present the development and implementation of a new improved N cycling scheme for the land surface model Community Land Model v5 (CLM5), the land component of the Community Earth System Model, allowing evaluation of ERW effects on soil nitrogen gas emissions. We base the new parameterizations on datasets derived from soil pH responses of $N_2O$, NO and $NH_3$ in ERW field trial and mesocosm experiments with crushed basalt. Finally, we present a case examining the impact of large-scale deployment of ERW on main croplands across the world on $N_2O$, NO and $NH_3$ emissions.

## 2 Methodology

### 2.1 The Community Land Model version 5 (CLM5)

We implemented new parameterizations into the Community Land Model version 5.0.25 (CLM5; Lawrence et al., 2019) to determine $N_2O$ and NO fluxes, and $NH_3$ volatilized from soil due to basalt amendments in crops. CLM is the terrestrial component of the Community Earth System Model version 2 (CESM2; Danabasoglu et al., 2020). CLM5 represents terrestrial carbon and nitrogen cycling with prognostic vegetation and crop growth. The model uses a sub-grid hierarchy in which grid cells are composed of multiple land units, columns, and patches to represent the spatial land surface heterogeneity and the biogeophysical and biogeochemical differences between various land types within a model grid cell. The CLM5 land units are vegetated, lake, urban, glacier, and crop. Vegetation and crops are represented by plant and crop functional types (PFTs and

CFTs), each with its own set of ecophysiological, morphological, phenological, and biogeochemical parameters (Levis et al., 2018). The default PFT distribution of natural vegetation and crops are derived from satellite observations (e.g., MODIS) and

100 agricultural census data (Lawrence and Chase, 2007; Portmann et al., 2010). There are 16 types of natural vegetation (including bare ground) and eight active crops (temperate soybean, tropical soybean, temperate corn, tropical corn, spring wheat, cotton, rice, and sugarcane) (Lombardozzi et al., 2020). In CLM5, natural vegetation and croplands are treated on separate columns and isolate particular management practices, i.e., natural vegetation is handled in single unmanaged soil columns sharing a single pool of water and nutrients, whereas each crop has a dedicated column (Drewniak et al., 2013).

105 For crops, CLM5 provides nutrients from the mineral N pool in the soil, which is supplied through organic matter decomposition, N deposition, N fixation and fertilization. The interactive N fertilization scheme in CLM5 simulates fertilization by adding N directly to the soil mineral $NH_4^+$ pool to meet crop N demands using both synthetic fertilizer and manure application. Fertilizer is applied to each crop for 20 successive days uniformly as soon as the crops enter the leaf emergence phase and is added in each layer from ground surface to 0.4 m depth according to the model-defined soil profile

110 (Lawrence et al., 2019). CLM5 simulates the beginning of plant growth stages (seedling, leaf emerging, and grain filling) as well as crop sowing dates and planting durations based on the cumulative warm-enough hours at the beginning of spring. Crops are harvested once they reach maturity or a predefined maximum growing days (typically 150–165 days) (Lawrence et al., 2019; Lombardozzi et al., 2020).

**2.2 Updates and implementations in the soil nitrogen scheme**

115 Figure 1 summarizes the main processes of the terrestrial N cycle in CLM5, following the 'holes-in-a-pipe' concept (e.g., Firestone and Davidson, 1989; Davidson and Verchot, 2000; Inatomi et al., 2019), highlighting the main implementations in this work. The model tracks N content in soil, plants, and organic matter as a series of distinct N pools, with biogeochemical processes acting as N exchange fluxes across them. Soil N transformations occur in vertically resolved soil profiles in each soil column following a Century-like implementation of soil biogeochemistry (Koven et al., 2013; Lawrence et al., 2019).

120 Plant uptake, microbial immobilization, N mineralization, nitrification, and denitrification compete for soil mineral nitrogen ($NH_4^+$ and $NO_3^-$) based on the relative demand from each process. The release of $N_2O$ as byproduct of nitrification and denitrification, and the leaching of soil nitrate ($NO_3$) result in N losses from terrestrial ecosystems, which are replaced through fertilization, atmospheric N deposition, and biological N fixation (both symbiotic and asymbiotic). In this study, we modify CLM5 to better simulate the terrestrial nitrogen cycle by implementing soil NO fluxes and $NH_3$ from volatilization, integrating

125 regulating functions of soil pH that allows to evaluate the potential impact of basalt amendments on soil nitrogen gas fluxes, and a weathering option to modify the soil pH.

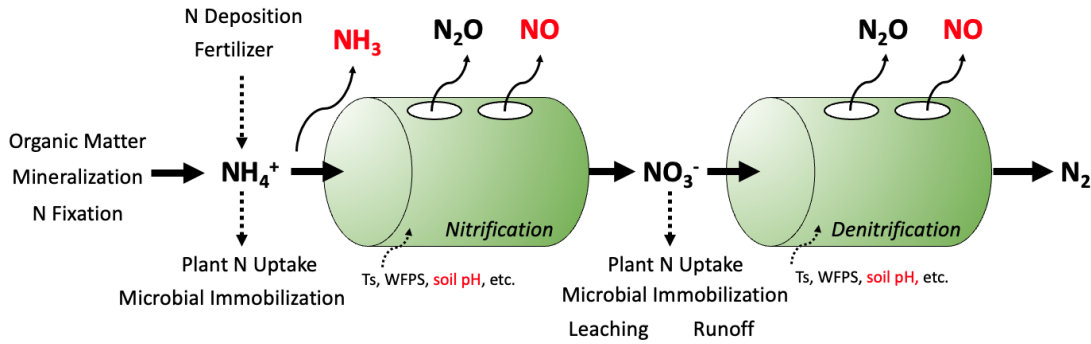



**Figure 1: Conceptual diagram of nitrogen cycle and the "holes-in-a-pipe" approach. Parameters in red are new additions in the default model. Ts is soil temperature; WFPS is water-filled pore space; and N is nitrogen.**

130 **2.2.1 Inorganic N transformations, soil N₂O fluxes and soil pH**

Nitrification and denitrification processes in CLM5 are based on the process-based biogeochemical model DAYCENT (Parton et al., 1996; Del Grosso et al., 2000; Del Grosso et al., 2006). For nitrification fluxes, we included the dependency of N mineralization-based term on potential nitrification rates that was implemented in Parton et al. (2001), which was missing from previous versions of CLM5 (Nevison et al., 2022a). Under this scheme, 20% of mineralized nitrogen is nitrified.

135 CLM5 assumes a constant fraction to be N₂O produced from nitrification ($fN_2O_{nit} = 6 \times 10^{-4}$; Li et al., 2000). However, this N₂O production depends on environmental conditions like soil temperature, water content and pH (Inatomi et al., 2020 and references therein). Considering an independent N₂O emission fraction linked to environmental conditions provide better estimates of N₂O emissions. To incorporate the effect of basalt addition on nitrification N₂O fluxes via regulating soil pH, we adopted a modified pH-based function ($fN_2O_{nit}$) proposed by Inatomi et al., (2020) based on a meta-analysis:

140
$$fN_2O_{nit} = 721.86 \times e^{-2.387 \times pH}$$

The updated $fN_2O_{nit}$ function made the nitrification rate in CLM5 go from the global constant average of 0.06% to 0.3% and increased the global N₂O nitrification/denitrification ratio from 1% to 14%, more accordingly to previous estimates (Inatomi et al., 2020). It should be noted that $fN_2O_{nit}$ values at typical soil pH levels in croplands (5.8 to 6.2) fall within a relatively narrow range of 3 to 7 × 10⁻⁴, which is not significantly different from the original 6 × 10⁻⁴ implemented in the model. Small

145 variations in $fN_2O_{nit}$ (e.g., ±20%) have a negligible impact on the total soil N₂O fluxes, with changes ranging 0.04 to 0.3%. However, further work is needed to evaluate the sensitivity of the model to this specific parameterization under other soil conditions, as well as to incorporate the influence of other environmental factors, such as water content and temperature.

As CLM5 uses a fixed pH value of 6.5 across all soils (Lawrence et al., 2019), we implemented the global soil pH from the Harmonized World Soil Database (FAO, 2012; Wieder et al., 2014). This dataset provides global spatial distribution of soil

pH and other soil properties for surface (0 to 30cm) and deeper soils (30 to 100 cm) at 0.05-degree spatial resolution, and regridded to the CLM5 resolution (0.9x1.25) for the nominal year of 2000 (Fig. S1 in Supplementary Material (SM)). We further distributed the topsoil and subsoil soil pH values through the CLM5 soil layers accordingly.

Denitrification also produces $N_2O$ as a byproduct (Fig. 1). To model the effect of basalt addition on $N_2O$ fluxes from denitrification, we included the updated denitrification scheme of Blanc-Betes et al., (2020). As in CLM5, Blanc-Betes et al., (2020)'s scheme is a modified version of the DAYCENT denitrification subroutine (Parton et al., 1996; Del Grosso et al., 2000) with the difference that it incorporates the effects of soil pH on gross denitrification rates ($N_2 + N_2O$) and on the stoichiometry of denitrification end products ($R_{N_2:N_2O}$ ratio).

For the total N loss during denitrification, the pH effect function ($f_{pH}$) was based on Liu et al. (2010) and Rochester (2003):

$$f_{pH} = 0.0016e^{1.006 \times pH}$$

For the $N_2$ to $N_2O$ ratio of the end products, we included the pH effect function ($f_{pH}$) adapted from Wagena et al. (2017) with adjusted thresholds:

$$f_{pH} = \begin{cases} 0.001 & \text{for pH} \leq 4 \\ 0.001 + \dfrac{pH - 4}{3} & \text{for } 4 < pH < 7 \\ 1.0 & \text{for pH} \geq 7 \end{cases}$$

More information about the scheme, model calibration and validation with basalt observations in crops is provided by Blanc-Betes et al (2020).

## 2.2.2 Soil NO fluxes

In addition to the modifications in the $N_2O$ scheme, we implemented a new parameterization to calculate NO released as by-products of nitrification and denitrification. We used the ratio of NO to $N_2O$ to account for the emission of NO during nitrification and denitrification based on Parton et al., (2001) and Zhao et al., (2017):

$$R_{NO:N_2O} = 15.2 + \frac{35.5 \tan^{-1}[0.75\pi(10D_r - 1.86)]}{\pi},$$

where $D_r$ is the soil relative gas diffusivity in soil with respect to air and is calculated as a function of air-filled pore space (AFPS) of soil (Davidson and Trumbore, 1995):

$$D_r = 0.209 AFPS^{\frac{4}{3}},$$

where AFPS is $1 - \dfrac{\theta_V}{\theta_{V,sat}}$ and $\theta_V$ and $\theta_{V,sat}$ are instantaneous and saturated volumetric soil water content (in $m^3\ m^{-3}$), respectively.

175    NO emitted from soils is quickly oxidized to $NO_2$ by $O_3$ near the canopy, and the formed $NO_2$ may be deposited onto the plant canopy (Bakwin et al., 1990; Jacob and Wofsy, 1990). To account for the loss of NO to plant canopy, we applied a canopy reduction scaling factor (CRF; Fig. S2 in SM) based on Yan et al (2005):

$$CRF = \frac{e^{-K_S \times SAI} + e^{-K_C \times LAI}}{2},$$

where SAI and LAI are stomatal area index and leaf area index, respectively, and $k_s$ and $k_c$ are 11.6 and 0.32, respectively. The
180    corresponding SAI was derived from the SAI:LAI ratio of Yienger and Levy (1995). NO captured from the atmosphere is taken up by the plant system either by direct incorporation into the leaf tissues or by the roots after absorption into the soil (Yoneyama et al., 1980). Since the precise mechanisms underlying these two routes is uncertain and fall outside the scope of this study, we assumed that all captured NO is returned to the soil directly as $NH_4^+$.

We also included a rain pulse factor to the base NO flux associated with nitrification to simulate the rapid increase of NO
185    fluxes following rain onto a previous dry soil period (e.g., Parton et al., 2001; Yan et al., 2005; Hudman et al., 2012) as:

$$P_{peak} = 13.01 \ln (l_{dry}) - 53.6 \times e^{-ct},$$

where $P_{peak}$ represents the magnitude of the peak flux relative to the pre-wetting flux and the value of $l_{dry}$ is the antecedent dry period in hours. The $c$ is a rate constant representing the rise/fall time of the pulse (0.068 $h^{-1}$) and $t$ is time-step in hours. $P_{peak}$ depends logarithmically on the length of the antecedent dry period and the condition for a pulse is a change in soil moisture.
190    To test for pulsing potential, we employed the two-part condition as in Yan et al., (2005). Dry soil is defined as soils with a moisture content below 17.5% (v/v). To trigger a pulse, an increase of more than 0.5% (v/v) in the moisture content of soil that experiences dry conditions for at least 3 days is required. This increase of 0.5% (v/v) in 7 cm of surface soil is equivalent to about 3.5 mm of rainfall, which is the rainfall amount previously reported to cause a pulse (e.g., Johansson and Sanhueza, 1988; Martin et al., 1998).

195    Following Parton et al., (2001), total NO emissions from soils and released above canopy are thus calculated as a function of the simulated $N_2O$ fluxes, the $R_{NO:N_2O}$ function, the factor to account for rain pulses in NO emission initiated by precipitation events (P) and the CRF:

$$Soil\ NO_{soil} = N_2O_{denit} \times R_{NO:N_2O} + N_2O_{nit} \times R_{NO:N_2O} \times P$$

$$Soil\ NO_{above-canopy} = Soil\ NO_{soil} \times CRF$$

200    ### 2.2.3 Soil $NH_3$ volatilization

For $NH_3$ volatilization, we used the scheme implemented by Fung et al., (2022) and embedded within the CLM5 N cycle. This scheme is derived from the DeNitrification-DeComposition (DNDC) biogeochemical model (Li et al., 2012) and includes a further parameterization to account for released $NH_3$ that is captured in the plant canopy. As in the soil NO scheme, we assumed

all captured NH$_3$ returns to the soil directly as NH$_4^+$. In this scheme, NH$_3$ is very sensitive to soil pH, as it grows exponentially
with pH, in the order of $10^{pH}$. As shown by Fung et al., (2022), the use of a spatially distributed soil pH database is not feasible as it overestimates NH$_3$ fluxes in alkaline soils (pH > 6.5). This is a well-known limitation in current NH$_3$ schemes (e.g., Sutton et al., 2013; Vira et al., 2020), where functions are not parameterized for global applications, and further work is needed for global models to accurately describe soil pH effects on NH$_3$ fluxes. In this work, we kept the soil pH constant to 6.5 to estimate a consistent NH$_3$ flux baseline and added a unit factor ($f_{pH}$) as a function of soil pH to model the effect of basalt addition on NH$_3$ fluxes. The new regulating $f_{pH}$ function is based on previous observations of NH$_3$ and soil pH from lime (Mkhabela et al., 2006), biochar (Kim et al., 2021) and basalt applications (Chiaravalloti, 2023) (Fig. S3 in SM):

$$f_{pH} = \begin{cases} 0.6 & \text{for pH} < 5 \\ 0.6 + \dfrac{0.4}{3} \times (\text{pH} - 5) & \text{for } 5 \geq \text{pH} \leq 8 \\ 1.0 & \text{for pH} > 8 \end{cases}$$

This function is a first approximation, which allows releasing some NH$_3$ in very acidic crop soils (pH < 5.5), whereas increasingly NH$_3$ volatilization losses occur in higher soil pH with a saturation at relatively high soil pH levels (>8). Observations on the magnitude of soil pH in controlling NH$_3$ volatilization fluxes from basalt applications are very scarce. However, our proposed changes in $f_{pH}$ are fairly consistent with soil pH effects in NH$_3$ volatilization observed in field measurements in a marshland soil with lime application (Mkhabela et al., 2006), experimental measurements from basalt application (12.5 t rock ha$^{-1}$) in a greenhouse setting (Chiaravalloti, 2023) and chamber experiments with 3% biochar and liquid fertilizers (Kim et al., 2021). Further observations of NH$_3$ volatilization rates from basalt application under wider range of soil pH conditions are urgently needed to verify the actual effect of soil pH.

## 2.2.4 Weathering

To simulate the impact of basalt addition on soil N$_2$O, NO, and NH$_3$ fluxes, we introduced a weathering option into CLM5, in which. This approach involves incorporating annual or monthly changes in soil pH estimated by an ERW model (Beerling et al., 2020; Kantzas et al., 2022) into the CLM5 N cycle. The coupling of soil pH in CLM5 and the ERW model occurs asynchronously (Kantzas et al., 2022). In the first phase, the ERW model dynamically calculates soil pH using alkalinity mass and flux balances with an adaptive time-step controlled by mineral dissolution rates. The alkalinity balance accounts for net acidity input during crop growth for removed biomass cations, and secondary mineral precipitation of calcite. Additionally, the N cycle's influence on soil acidity is considered. For that, each nitrogen transformation (e.g., nitrification, denitrification, volatilization) is associated with hydrogen ions production or consumption, leading to stoichiometric acidity fluxes to each nitrogen flux within the ERW model. These calculations begin with initial soil pH values and nitrogen fluxes provided by CLM5 to the ERW model, run individually at each grid cell. Subsequently, in the second phase, spatially distributed changes in soil pH (i.e., delta pH) estimated by the ERW model are integrated into CLM5. This process enables CLM5 to adjust the

initial soil pH values accordingly. Detailed descriptions of the soil pH calculations are provided in Beerling et al., (2020) and Kantzas et al., (2022).

## 2.3 CLM5 ERW simulations

We performed single-point simulations at the Energy Farm field site (University of Illinois, U.S.) to examine the model sensitivity to basalt applications in maize and soybean crops and soil and climate conditions. We spun-up the model for about 600 years, so that all the state variables in the model, especially total ecosystem soil carbon and soil $N_2O$ reached equilibrium. Then, the same initial condition was used for both the soybean and the corn single-point present-day spin-up simulations because a uniform soil condition was achieved for both crop systems. The present-day spin-up was based on a historical simulation 1850–2014, using historical N and aerosol deposition and atmospheric $CO_2$ forcing (Lawrence et al., 2019), with soil texture and soil pH values based on onsite measurements in Control and ERW plots at the Energy Farm (Blanc-Betes et al., 2020). The meteorological forcings were from the Global Soil Wetness Project (GSWP3 version 1; http://hydro.iis.u-tokyo.ac.jp/GSWP3/), with forcing data available from 1901 to 2014 and cycled from 1901 to 1920 for years prior to 1901.

Following the historical simulation, the Energy Farm simulations were run from 2015 to 2019 with meteorological forcing data retrieved from the North American Land Data Assimilation System (NLDAS) forcing dataset (Xia et al., 2012), and initial conditions starting in 2015 for the two single-point simulations, without basalt ('Control' Run) and with basalt ('ERW' Run) application. The use of two different atmospheric forcings, GSWP3 (1901-2014) and NLDAS (1999-2020), was necessary in this study due to their distinct time coverage. Although this approach has the potential to introduce biases and changes in soil dynamics, we conducted a comparison for a coincidental period (2001-2014) and found no significant impacts on vegetation, soil nitrogen fluxes and soil dynamics (Fig. S4 in SM).

In addition to single-point simulations, we performed global simulations to validate the new implementation at large scale and assess the regional effects of basalt treatments to soil direct agricultural N fluxes. We first spun-up CLM5 with the new implementations to steady state in 1850 using an accelerated decomposition procedure and fixed pre-industrial $CO_2$, land use, and atmospheric N deposition (Lawrence et al., 2019). The accelerated decomposition spin-up was for about 1200 years as the total soil organic matter carbon in the Arctic regions required a longer time frame to reach equilibrium; we considered the model fully spun-up when the land surface had more than 97% of the total ecosystem carbon in equilibrium. After the historical spin-up, we initialized CLM5 simulations for 2000 using fully spun-up conditions. As in the single-point simulations, the present-day spin-up was based on a historical simulation 1850–2014, using historical N and aerosol deposition, atmospheric $CO_2$ forcing, land use change and meteorological forcings from GSWP3 (Lawrence et al., 2019).

To include the effect of ERW on the $N_2O$, NO and $NH_3$ fluxes from soil, we considered the soil pH changes as well as application locations across five key regions with high potential for CDR with ERW (North America, Brazil, Europe, India, and China) required to remove 2Gt $CO_2$ per year (Beerling et al., 2020). Thus, in the "Control" Run soil pH is kept constant

to the nominal values provided by Harmonized World Soil Database, whereas in the "ERW" Run is modified following the
265  ERW model projection. To test the new scheme at a global scale, we used changes in annual soil pH (Fig. 2 and Fig. S5 in
SM); dynamic changes of soil pH in monthly timesteps were tested in a regional study for the UK (Kantzas et al., 2022).

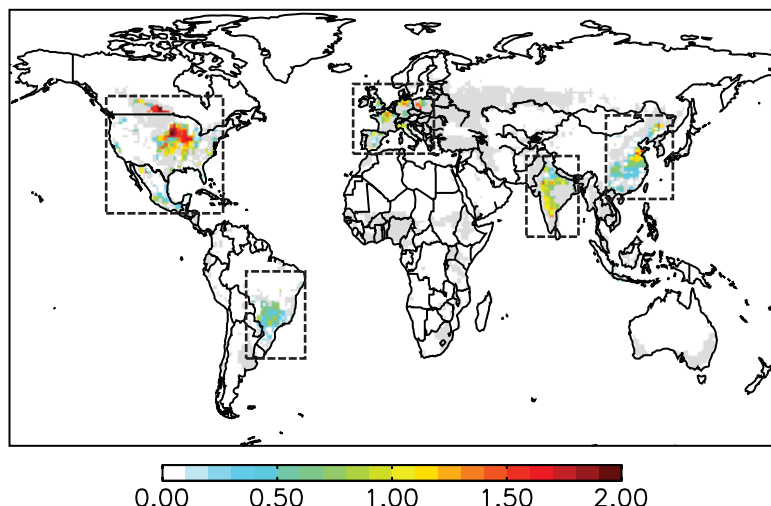



**Figure 2: Changes in soil pH after annual basalt applications in a 25-year timeframe to remove 2 Gt $CO_2$ (Beerling et al., 2020). Delimited are the five agriculture regions considered in this study; shaded in grey are grid cells with crops**
270  **(> 10%), in which basalt was not applied. A close-up view for each region is in Figure S5 in SM.**

Simulations were completed at a resolution of 0.9° latitude by 1.25° longitude and with a 30-min time step. We used the mean
and standard deviation of the last 5 years (2010–2014) of the historical simulations as an approximation of present-day
conditions of the modelled N cycle, for a Control Run (without basalt) and an ERW Run (with basalt). In both simulations,
synthetic fertilizer application was prescribed by crop type on the Land Use Model Intercomparison Project (Hurtt et al., 2011)
275  and manure fertilizer was applied at a fixed rate for all crops (20 kg N ha$^{-1}$ yr$^{-1}$; Lombardozzi et al., 2020).

**2.6 Datasets for model validation**

We used observational data collected at the University of Illinois Energy Farm in 2016–2019. The Energy Farm is in central
Illinois (40.06° N, 88.19°W) and the historic land use is corn-soy agriculture (Cheng et al., 2020; Blanc-Betes et al., 2020). In
the spring of 2016, a pilot ERW experimental study was conducted using twenty, 2 x 2 m plots in a field of maize; a field-
280  scale experiment was initiated in 2017.  This large-scale field experiment consists of several ERW experimental plots of 3.8
ha (200x200 m) each in size, with control and basalt-treated plots, each instrumented with an eddy covariance system at the
centre of the plot to measure surface energy, water, and carbon fluxes (Zeri et al., 2011).  Soil pH is measured through surface
soil samples (0–10 and 10–30 cm) and N$_2$O fluxes were monitored through static chambers atop PVC collars during the
planting season (Blanc-Betes et al., 2020).

We also compared our global simulation results with available observations and emission inventories. Simulated CLM5 nitrogen emissions are compared with multiple emission inventories, including the Copernicus Atmosphere Monitoring Service (CAMS; Bennouna et al., 2020), Community Emissions Data System (CEDS; Hoesly et al., 2018), Emission Database for Global Atmospheric Research (EDGAR; Crippa et al., 2018) and Harmonized Emissions Component (HEMCO; Lin et al., 2021). For $N_2O$, we also used results from the global $N_2O$ Model Intercomparison Project (NMIP; Tian et al., 2018), and estimates from Wang et al., (2020) and the CarbonTracker Lagrange North American Regional Inversion Framework (Nevison et al., 2018). Details of all these datasets are presented in Table 1. The datasets were regridded to match our model resolution of 0.9 by 1.25 using bilinear interpolation. It is important to note that our CLM5 model-inventory comparison should be considered as an approximation because our simulations do not match the meteorological years of the inventories and because actual manure and synthetic fertilizer usage in CLM5 may differ from what was assumed in the inventories.

**Table 1. Summary of observations and emission inventories used in this study for model comparison and validation.**

| Name and Reference | Coverage | Resolution | Period | Notes |
| --- | --- | --- | --- | --- |
| CAMS (Granier et al., 2018) | Global | 0.1º x 0.1º Monthly | 2010–2019 | NO and $NH_3$ from agricultural soils and nitrogen deposition |
| CEDS (Hoesly et al., 2018) | Global | 0.01º x 0.01º Monthly | 2005–2015 | NO and $NH_3$ from agricultural soils with both synthetic and manure fertilizers |
| EDGAR (Crippa et al., 2018) | Global | 0.1º x 0.1º Monthly | 2010 | $N_2O$, NO, $NH_3$ from agricultural soils with both synthetic and manure fertilizers |
| HEMCO (Lin et al., 2021) | Global | 0.5º x 0.625º Monthly | 2005-2017 | NO soil emissions weighted by CLM5 gridded crop area |
| NMIP (Tian et al., 2018) | Global | 0.5º x 0.5º Annual & Monthly | 2000-2015 | Modeled $N_2O$ fluxes in crops from the global $N_2O$ Model Intercomparison Project |
| Wang et al., (2020) | Global | 0.1º x 0.1º Annual | 2010-2014 | Modeled $N_2O$ fluxes in crops with an empirical upscaling method using site-level observations spatially distributed |
| Nevison et al., (2018) | USA | 1º x 1º Daily | 2008–2015 | $N_2O$ fluxes from an inversed model with atmospheric $N_2O$ observations |

**3 Validation**

CLM5 simulations have been extensively evaluated by comparison with observations on a global scale (e.g., Lawrence et al., 2019; Lombardozzi et al., 2020; Nevison et al., 2022b) as well as in specific field sites (e.g., Chen et al., 2020, Nevison et al., 2022a). We focus our evaluation on soil $N_2O$ fluxes from croplands at the Energy Farm, continental U.S., and agriculture 300 $N_2O$, $NO_x$ and $NH_3$ emissions at a global scale and the response of the simulated soil $N_2O$ to changes in soil pH from basalt applications.

**3.1 Soil $N_2O$ at the Energy Farm and continental U.S.**

Figure 3 compares modeled soil $N_2O$ in our single-point simulations with available observations at the Energy Farm pre-trail (maize) in 2016 and trial rotation crops (maize, maize, and soybean) in 2017–2019, for control and basalt-treated plots. For 305 daily soil $N_2O$ fluxes (Fig. 3a), we found that simulated daily $N_2O$ showed generally good agreement with the limited daily observations at the Energy Farm, simulating larger averaged soil $N_2O$ fluxes during the growing season in maize (37.2–51.7 gN ha$^{-1}$ day$^{-1}$) than soybean (5.4 gN ha$^{-1}$ day$^{-1}$), similar to what was observed in the field trails (18.8–62.3 gN ha$^{-1}$ day$^{-1}$ for maize and 6.2 gN ha$^{-1}$ day$^{-1}$ for soybean). As shown for DAYCENT by Blanc-Betes et al., (2020), CLM5 also simulates well the increases in $N_2O$ fluxes following fertilization and precipitation events at the Energy Farm, although with daily fluxes 310 peaking slightly earlier in the growing season compared to observations due to yearly differences in planting schedule and fertilization. We note that in this project CLM5 has not been tuned specifically for the Energy Farm conditions or across the U.S., rather used as in the released version as the objective is to use the model at a global scale, across many crops, regions and for future climate projections. As a result, the land management practices, such as planting and harvesting times, as well as fertilizer application frequency and rates, employed in our simulations may not precisely match those implemented at the 315 Energy Farm. To facilitate a more direct comparison for soybean, we made an exception and turned off synthetic and manure fertilizers in the soybean simulation because the Energy Farm does not apply nitrogen fertilizers to this crop.

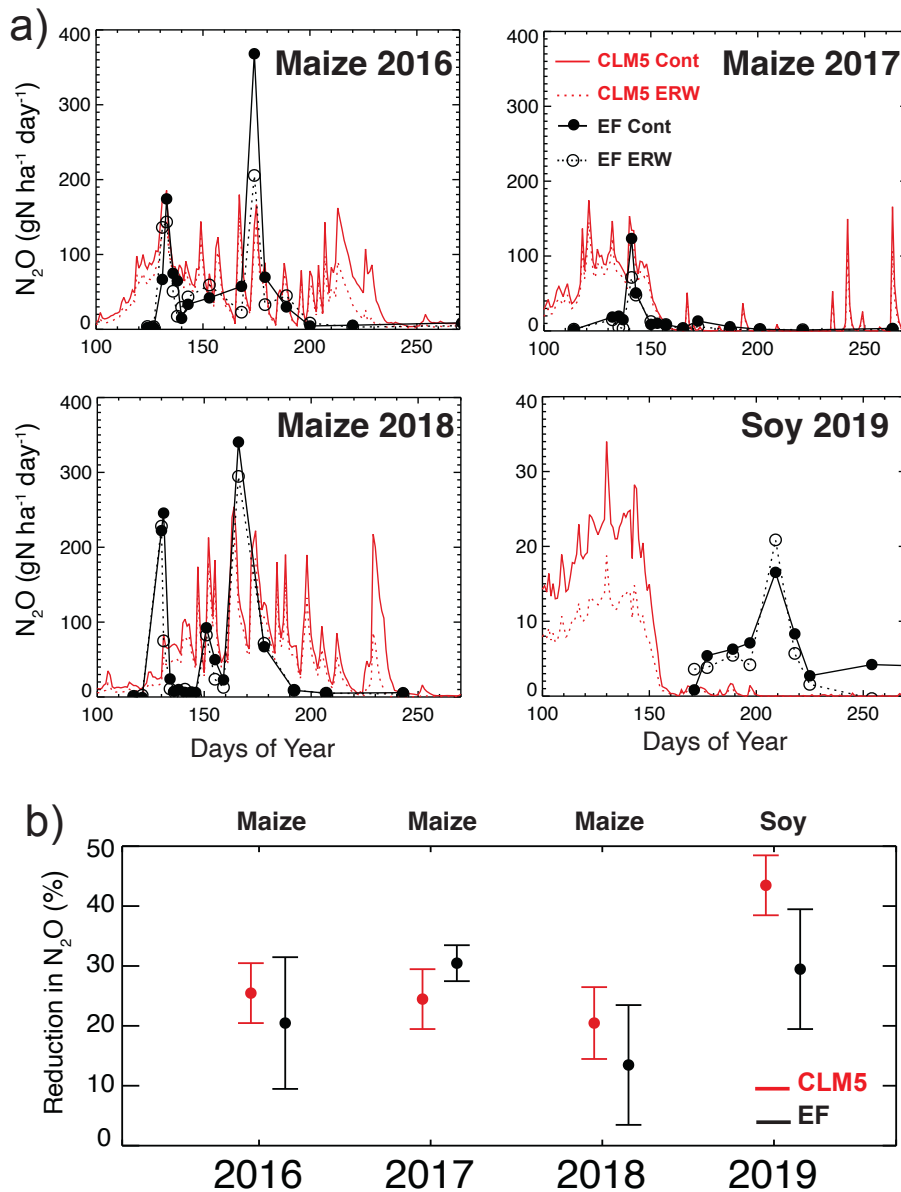
To determine if CLM5 simulates soil $N_2O$ changes due to basalt amendments, we compared the relative changes in $N_2O$ in the basalt-treated plots with respect to the control plots for each year, at the Energy Farm and simulated by the model in Fig. 3b. The changes in $N_2O$ were obtained by comparing the cumulative $N_2O$ at the end of the growing season using the measured 320 and simulated $N_2O$ flux at the time of the discrete measurements. For the basalt amendment run in CLM5, we considered the same increases in soil pH observed in the field experiments (section 2.3; Blanc-Betes et al., 2020). We found that CLM5 effectively reproduces the decrease in soil $N_2O$ in the basalt-treated plots with soil $N_2O$ fluxes 21–25% (maize) and 44% (soy) smaller than control plots, in line with the observed decreases of 12–32% and 31% at the Energy Farm.

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**Figure 3: Soil N₂O fluxes at the Energy Farm for the pilot study (maize; 2016) and the large field trials (rotation crops as maize, maize and soybean; 2017–2019). Shown is simulated (red) and observed (black) daily N₂O fluxes (g N ha⁻¹ day⁻¹) at the control (solid lines or solid circles) and basalt-treated plots (dotted lines or open circles) (a) and reductions in N₂O emissions (%) in the basalt-treated plots compared to the control plots for the simulated by CLM5 (red) and**

330 **measured at the field experiments (black) (b). Error bars represent variability in the reduction (%) estimated using propagation of errors.**

We used observations of $N_2O$ from agricultural fields summarized in published studies (e.g., Stehfest and Bouwman, 2006; Shcherbak et al., 2014; Wang et al., 2018), including the Energy Farm, and $N_2O$ emissions estimated across North America using the Carbon Tracker-Lagrange regional inversion framework (Nevison et al., 2018) to assess how well CLM5 captures agriculture $N_2O$ emissions in the U.S., an important agricultural region suitable for large-scale ERW deployment (Beerling et al., 2020) (Fig. 4).
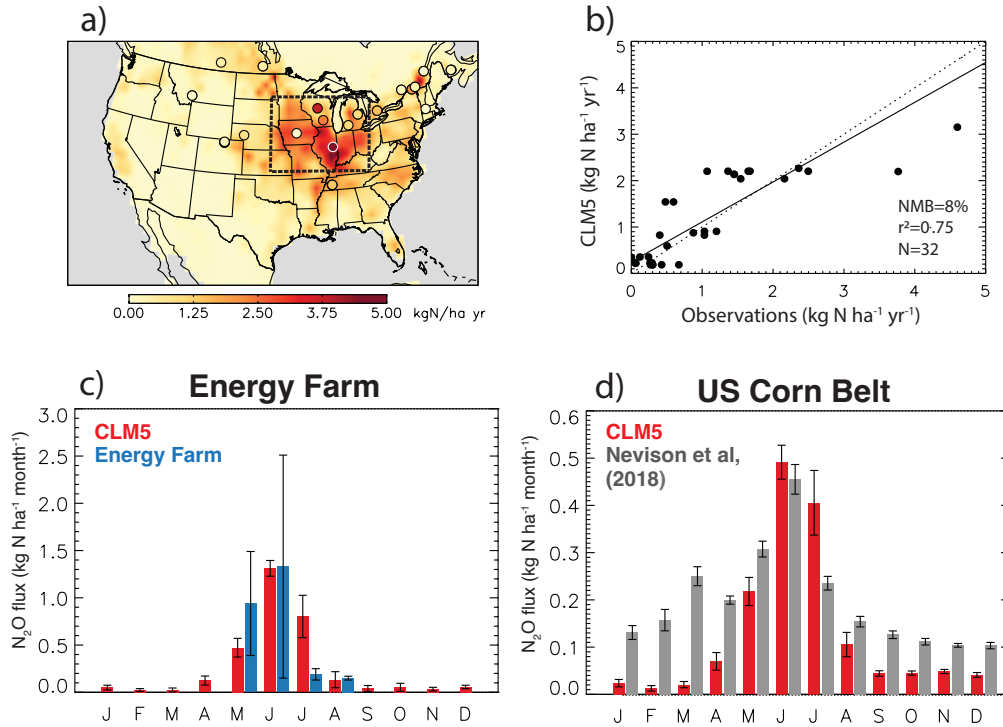
**Figure 4: Soil $N_2O$ fluxes in U.S. with modelled and observed values at individual measurement sites (a), the scatter plot with modelled and observed values at the individual sites (b), seasonal variability of monthly soil $N_2O$ at the location of the Energy Farm (c) and across the US Corn Belt (d). Observations are means from published measurements, including the Energy Farm (2017-2019; Blanc-Betes et al., 2021) or averaged monthly fluxes from the Carbon Tracker-Lagrange regional inversion model (2008-2014; Nevison et al., 2018). The squared-correlation coefficient ($r^2$), nominal mean bias (NMB, %) and number of observations (N) are shown in the inset. Reduced major axis-regression lines (solid) for croplands and the 1:1 line (dashed) are also shown. The US Corn Belt is represented with a dashed box and location of Energy Farm (40.07 N, 88.2 W) with a white border circle in the CLM5 map. Error bars represent the standard deviation of the annual totals.**

For our studied period, CLM5 estimates a total $N_2O$ emission across continental U.S. croplands of 0.59±0.06 Tg $N_2O$-N $yr^{-1}$, with more than 50% emitted in the U.S. Corn Belt. Our soil $N_2O$ emissions fall well within the range of previous estimates for

direct agriculture emissions in the U.S. (0.3–1.1 Tg N yr$^{-1}$) reported by the U.S. Environmental Protection Agency (EPA), bottom-up inventories, and other processed-based land models (e.g., Tian et al., 2019; Lu et al., 2021; U.S. EPA, 2022). Similar to other studies, our modelled estimates are lower than those reported from top-down N$_2$O studies (1.6–2.6 Tg N yr$^{-1}$; Miller et al., 2012; Nevison et al., 2018) as they consider more N$_2$O source types than direct agriculture emissions, e.g., fossil fuel combustion, industry non-combustion processes, biomass burning, and solid waste and sewage water. For the U.S. Corn Belt, dominated by agriculture sources, our annual flux (0.31±0.04 Tg N$_2$O- N yr$^{-1}$) is comparable to that from top-down estimates (0.32–0.42 Tg N yr$^{-1}$; Griffins et al., 2013; Chen et al., 2016; Nevison et al., 2018) as well as previous estimates with process-based models (0.26–0.60 Tg N yr$^{1}$ (e.g., Li et al., 1996; Del Grosso et al., 2006; Lu et al., 2021).

We synthetized a consistent set of field observations representative of long-term means for different croplands across North America and identified a total of 32 observations gathered from 1998 to 2016 (Figs. 4a-b). We summarized the comparison between the model and observations using the normalized mean bias (NMB=$\frac{\sum(M_i - O_i)}{\sum O_i}$, where $M_i$ and $O_i$ are modelled and observed) and the squared-correlation coefficient ($r^2$). We found that the model captures well the spatial distribution of soil N$_2$O in croplands across the U.S.. Simulated soil N$_2$O fluxes show good agreement with the mean observations over croplands ($r^2$=0.75) although they are slightly overestimated (NMB=8%).

We also evaluated the seasonal variability of our simulated soil agriculture N$_2$O fluxes in the U.S. (Figs. 4c-d) using averaged field observations at the Energy Farm (Blanc-Betes et al., 2020) and regionally averaged monthly fluxes in the Corn Belt from the Carbon Tracker-Lagrange regional inversion framework (Nevison et al., 2018). Figure 4a shows the location of the Energy Farm and the approximate limits of the U.S. Corn Belt. We found that the model represents reasonably well the seasonal variability of soil N$_2$O fluxes across the Corn Belt as well as at the Energy Farm in Illinois, with direct agriculture N$_2$O emissions peaking up early in the growing season (April–May), which coincides with addition of fertilization, as in the observations.

### 3.2 Global soil NO, N$_2$O and NH$_3$

We also evaluated soil NO, N$_2$O and NH$_3$ emissions simulated by CLM5 in the global control simulation. Figure 5 presents the total annual global N$_2$O, NO and NH$_3$ agriculture emissions averaged over 5 years (2010–2014) in our simulations. Soil NO and NH$_3$ emissions are at above-canopy (sections 2.2.2 and 2.2.3). We also compared our soil gas nitrogen emissions with the available estimates reported in a wide range of global emission inventories (CAMS, CEDS, EDGAR, HEMCO) and previously modeled agriculture fluxes (NMIP, Tian et al., 2018 and Wang et al., 2020) (Table 1). NH$_3$ emissions were extensively evaluated in Fung et al., (2020) and we included here a follow-up and simpler validation to assess our small updates in the parameterization (section 2.3.3).

Emission inventories provide monthly estimates from several agriculture sources, such as synthetic and organic fertilizers, manure management, indirect nitrogen losses, among others and, in some cases, emissions from soils in natural ecosystems.

To be able to compare the emissions directly with the CLM5 estimates, we extracted monthly emission estimates and selected the sources to represent as best as possible direct agriculture emissions from synthetic and manure fertilizers. In the case of HEMCO, which provides soil NO emissions from both natural and agricultural soils, we weighted their emissions by the fraction of cropland covering each grid-cell in CLM5. For $NH_3$, we considered that one-third of the total agricultural $NH_3$ emission reported by CAMS, CEDS and EDGAR is attributed to fertilizers, which aligns with the fraction reported in previous studies and environmental assessments (e.g., Paulot et al., 2014; National European Environment Agency, 2013; Fung et al., 2022). We conducted a spatial comparison of the annual $N_2O$, NO and $NH_3$ emissions from CLM5 and each inventory (grid-cell by grid-cell) by computing the normalized mean bias (NMB) and the Pearson's correlation coefficient ($r$). Table 2 shows the annual totals and a summary of these statistics. Spatial distribution of annual-total $N_2O$ emission estimated by the inventories and differences with CLM5 are shown in Figs. S6–S8 in SM.
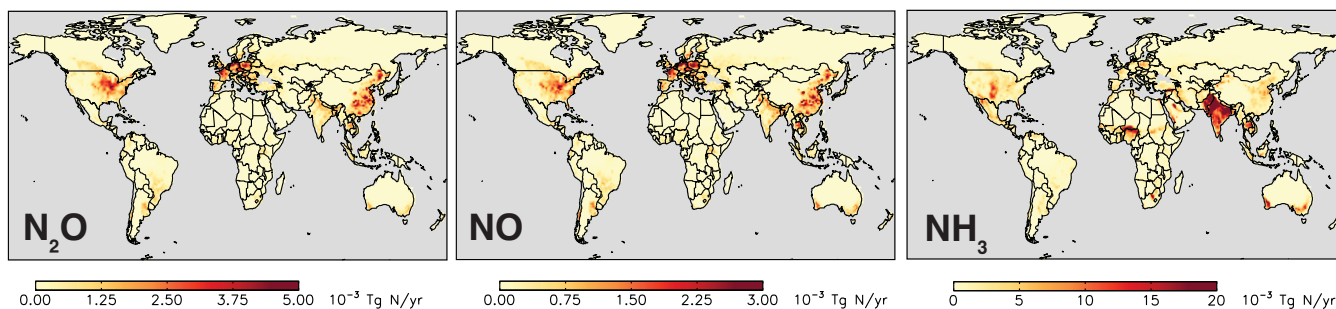
**Figure 5: Simulated global soil agriculture $N_2O$, NO and $NH_3$ emissions in CLM5 without basalt ('Control Run').**

410 **Table 2. Summary of agriculture N$_2$O, NO and NH$_3$ fluxes. Reported is the total global emission (average ± standard deviation of the annual totals), nominal mean bias (NMB) and Pearson's correlation coefficient (r).**

| Emissions | N$_2$O | | | NO | | | NH$_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Total (Tg N yr$^{-1}$) | NMB (%) | r | Total (Tg N yr$^{-1}$) | NMB (%) | r | Total (Tg N yr$^{-1}$) | NMB (%) | r |
| CLM5 | 3.12±0.12 | – | – | 2.17±0.06 | – | – | 15.18±0.39 | – | – |
| CLM5*[a] | 4.19±0.15 | – | – | – | – | – | – | – | – |
| CAMS | – | – | – | 2.05±0.02 | 6 | 0.6 | 11.78±0.40 | 38 | 0.5 |
| CEDS | – | – | – | 1.38±0.06 | 57 | 0.4 | 11.40±0.30 | 34 | 0.6 |
| EDGAR[b] | 3.03 | 3 | 0.3 | 1.00 | 117 | 0.4 | 10.3 | 46 | 0.5 |
| HEMCO | – | – | – | 2.27±0.10 | -5 | 0.4 | – | – | – |
| NMIP | 3.30±1.20[c] | -7 | 0.4 | – | – | – | – | – | – |
| Wang et al., | 2.56±0.03 | 22 | 0.3 | – | – | – | – | – | – |

[a]CLM5* is the default version, without any implementation.
[b]Only monthly data are available for 2010. Reported mean of 2010.
[c]Reported mean ± standard deviation of seven models

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For N$_2$O, CLM5 estimates global direct agriculture emissions of 3.1 Tg N$_2$O-N yr$^{-1}$, which is in line with previous annual estimates for agriculture sources (1.7–5.8 Tg N yr$^{-1}$; e.g., Del Grosso et al., 2006; Syakila and Kroeze, 2011; Saikawa et al., 2014) and the IPCC 2021 reported values for 2007–2016 (3.8 Tg N yr$^{-1}$) (Canadell et al., 2021). Our updates in the CLM5 N-cycle did not significantly alter the global soil N2O flux in agriculture systems compared to the default CLM5 version (4.2 Tg

420 N$_2$O-N yr$^{-1}$). In addition, our estimate is similar to the widely used EDGAR emission inventory (3.03 Tg N yr$^{-1}$) and falls within the range of modeled estimates (2.6–3.3 Tg N yr$^{-1}$; Tian et al., 2018; Wang et al., 2020). The global *r* values range between 0.3 and 0.4 across the inventory and models, suggesting that CLM5 does not exactly replicate the spatial patterns reported on the emission inventories. The global NMB values are small and range between -7 to 25%, showing a good agreement with the reported estimates overall.

425 For global agriculture NO emissions, CLM5 estimates 2.2 Tg NO-N yr$^{-1}$, which is in line with previously reported fertilizer-induced soil NO emissions (0.4–3.5 Tg N yr$^{-1}$ e.g., Stehfest and Bouwman, 2006; Crippa et al., 2018; Bennouna et al., 2020; Lin et al., 2021). Our global *r* values lie between 0.4–0.6 across all inventories, indicating a fair correlation. Our estimate is higher than two emission inventories (CEDS and EDGAR) with a global NMB value between 57 and 117%, but close to the CAMS (NMB=6%) and the adjusted HEMCO (NMB=-5%) estimates.

430    Global fertilizer-induced $NH_3$ emissions in CLM5 are 15.2 Tg $NH_3$-N $yr^{-1}$. This estimate is close to estimates (from synthetic and manure fertilizers) reported by Fung et al., (2020) (14 Tg N $yr^{-1}$) and Vira et al., (2020) (18 Tg N $yr^{-1}$) for $NH_3$ schemes also implemented in CLM5. It is important to note that despite using Fung et al., (2020) $NH_3$ parameterization in CLM5, our estimate is not exactly as that work because we updated the nitrification and denitrification schemes as well as implemented a dependance on soil pH (section 2.2.3). As indicated by Fung et al., (2020), the CLM5 estimates are slightly higher than three

435    widely used global emissions inventories (10–12 Tg N $yr^{-1}$; CAMS, CEDS and EDGAR). The global $r$ values are 0.5–0.6, indicating a fair correlation between CLM5 in all three emission inventories. The high bias in CLM5 is indicated by global NMB values of approximately 34–46% between CLM5 and the emission inventories.

In CLM5 as well as other models and emission inventories, the largest agricultural emissions are found over major cropland regions (Fig. 5 and Figs. S6-S8). However, their spatial distribution differs mostly due to differences in fertilization rates and

440    application patterns adopted by the models and emission inventories and in some cases, spatial distribution of soil pH. Table 3 summarizes the regional emission totals in our five studied agricultural regions. These areas are major food-producing regions and are responsible for most of the agriculture $N_2O$ (75%), NO (61%) and $NH_3$ (55%) emissions with respect to the global total. In CLM5, major crop $N_2O$ emitters are Europe (0.68 Tg N $yr^{-1}$), China (0.63 Tg N $yr^{-1}$) and North America (0.59 Tg N $yr^{-1}$), each with about 19–22% of global emissions. Our modifications to the CLM5 N-cycle did not result in significant

445    regional-scale changes in agriculture soil $N_2O$ compared to the default version, although led to lower $N_2O$ emissions over India (0.18 vs. 0.36 Tg N $yr^{-1}$). Soil NO losses are similar, with Europe (0.49 Tg N $yr^{-1}$; 23%), North America (0.37 Tg N $yr^{-1}$; 17%), and China (0.40 Tg N $yr^{-1}$; 18%) as the largest agriculture sources.  As reported by Fung et al (2020), major fertilizer-induced $NH_3$ emissions in CLM5 are from India (3.47 Tg N $yr^{-1}$; 23%), followed by North America (1.77 Tg N $yr^{-1}$; 12%) and China (1.25 Tg N $yr^{-1}$; 8%). Emission inventories show a similar regional distribution of emissions, with a higher proportion of

450    agriculture emissions in China and India. For example, for $NH_3$ emissions, CAMS, CEDS, and EDGAR indicate that India is the largest emitter, accounting for 23–30% of global emissions, followed by China with 16–17%.

Figure 6 shows the seasonality of $N_2O$, NO and $NH_3$ emissions in these five main crop regions for CLM5 and global inventories and NMIP. In this analysis, for NMIP $N_2O$ fluxes we considered the average of only two models as not all seven provided monthly outputs (Hanqin Tian, Auburn University, personal communication, 2019). In CLM5, each crop has fertilizer applied

455    (as $NH_4^+$) evenly over the course of 20 days beginning with leaf emergence (section 2.1). The addition of $NH_4^+$ in the soil accelerates plant uptake, microbial immobilization, denitrification, nitrification and $NH_3$ volatilization, which explains why $N_2O$, NO and $NH_3$ emissions peak mostly in spring (March–May) in North America, Europe, China and India and in the fall (October–November) in Brazil. Soil $N_2O$ and NO fluxes are also strongly dependent on environmental conditions (e.g., precipitation), which mainly drive the smaller secondary peaks later in the season in North America, Europe and China. All

460    global emission inventories and NMIP estimates show similar emission variability, with springtime peaks in the Northern hemisphere (North America, Europe, China, and India) and fall peaks in the southern hemisphere (Brazil).  For soil $N_2O$, the seasonality in CLM5 is consistent with that given by the NMIP models although significantly lower in magnitude for Brazil

and China. However, annual estimates in CLM5 for Brazil (0.12 Tg N yr$^{-1}$) and China (0.63 Tg N yr$^{-1}$) are in line with the average from the seven-model ensemble (0.20 Tg N yr$^{-1}$ and 0.80 Tg N yr$^{-1}$, respectively) (Table 3).

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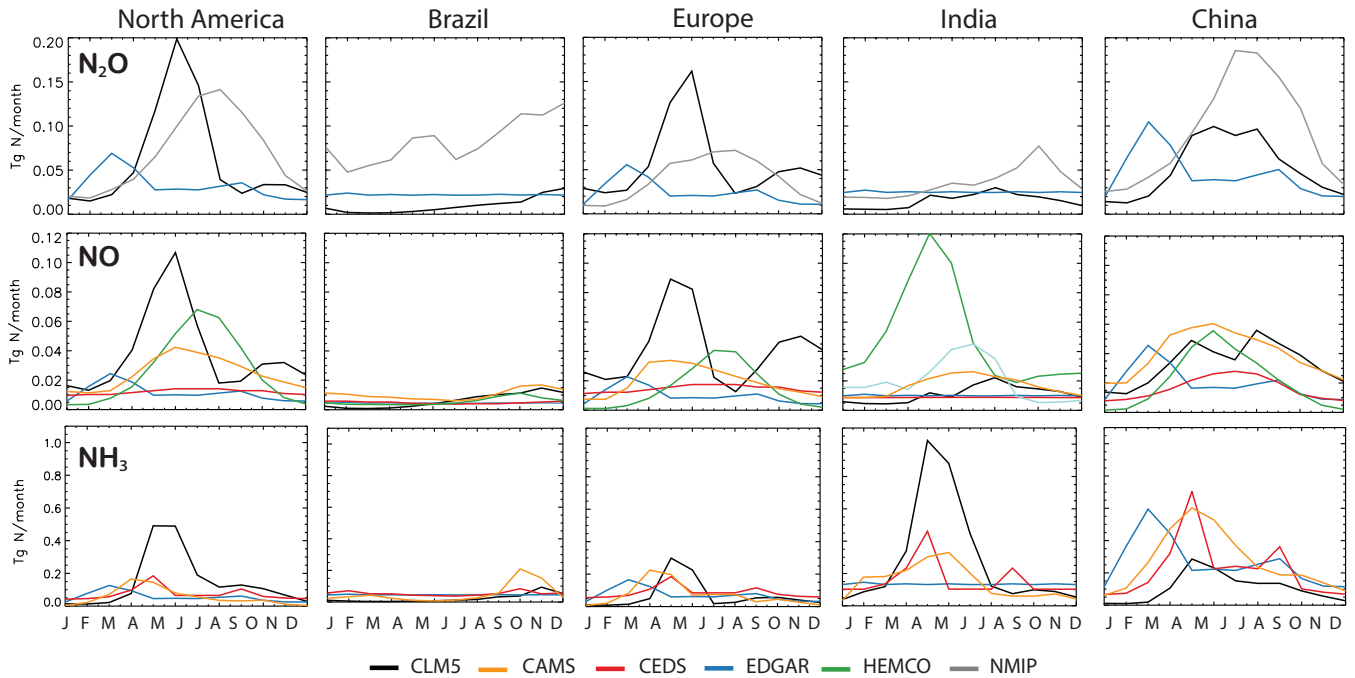
**Figure 6**: **Monthly agriculture N$_2$O, NO and NH$_3$ emissions in the main crop regions considered in the study (North America, Brazil, Europe, India, and China) estimated by CLM5, CAMS, CEDS, EDGAR, HEMCO and NMIP (Table 1). Soil NO emissions in HEMCO were weighted by cropland fraction; soil N$_2$O in NMIP is the average of only two**
470 **models that provided monthly output.**

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**Table 3. Summary of regional agriculture N₂O, NO and NH₃ fluxes in CLM5 and emission inventories.**

| Emissions | North America | Brazil | Europe | India | China |
|---|---|---|---|---|---|
| $N_2O$ (Tg N yr$^{-1}$) | | | | | |
| CLM5 | 0.59 | 0.12 | 0.68 | 0.18 | 0.63 |
| CLM5*[a] | 0.69 | 0.09 | 0.66 | 0.36 | 0.91 |
| EDGAR | 0.30 | 0.27 | 0.29 | 0.30 | 0.55 |
| NMIP | 0.30 | 0.20 | 0.30 | 0.50 | 0.80 |
| NO (Tg N yr$^{-1}$) | | | | | |
| CLM5 | 0.37 | 0.07 | 0.49 | 0.13 | 0.40 |
| CAMS | 0.12 | 0.20 | 0.15 | 0.24 | 0.25 |
| CEDS | 0.11 | 0.06 | 0.17 | 0.11 | 0.20 |
| EDGAR | 0.10 | 0.05 | 0.12 | 0.12 | 0.24 |
| HEMCO | 0.25 | 0.07 | 0.18 | 0.58 | 0.26 |
| $NH_3$ (Tg N yr$^{-1}$) | | | | | |
| CLM5 | 1.77 | 0.26 | 0.82 | 3.47 | 1.25 |
| CAMS | 0.66 | 0.63 | 0.86 | 1.76 | 3.24 |
| CEDS | 0.88 | 0.64 | 1.04 | 1.89 | 2.61 |
| EDGAR | 0.66 | 0.55 | 0.86 | 1.61 | 3.11 |

[a]CLM5* is the default version without any implementation.

485 It is important to acknowledge that substantial differences among emission inventories also exist in terms of their magnitude, spatial distribution and seasonality. For example, soil N₂O, NO and NH₃ emissions in EDGAR always peak about one month earlier in the season than the other emission inventories and CLM5; soil NH₃ emissions in CEDS have two seasonal peaks compared to CAMS, CLM5 and EDGAR. As discussed by Fung et al., (2020), these disparities are primarily caused by differences in the planting season and length of fertilization considered within the inventories as well as the agriculture sources

490 included (e.g., synthetic and/or manure application, manure management, etc). In addition, there are systematic uncertainties in the global inventories (e.g., emission factors, environmental conditions, fertilizer types and rates, etc) (Hoesly et al., 2018; Fung et al., 2020). Here we did not intend to understand these differences, rather use the model-inventory comparison to assess the CLM5 performance. We concluded that CLM5 provides a reasonable representation of the magnitude and seasonality of direct agriculture nitrogen emissions across the major hotspot regions (North America, Brazil, Europe, India, and China),

495 which are relevant for our study. We note that there may be some limitations and uncertainties associated with the model's performance as well as current emission inventories in capturing the full complexity of these emissions. Further investigations and validation efforts are warranted to enhance our understanding of regional variations in agricultural nitrogen emissions.

## 4 Effect of basalt application on soil nitrogen gas emissions

We assessed the regional impact of amending cropland soils with basalt by estimating changes in the nitrogen cycling. We performed this case study by using the soil pH increases after 25 years of repeated annual basalt application as well as optimized deployment locations required to remove 2Gt $CO_2$ $yr^{-1}$ projected by the ERW Model in Beerling et al., (2020) (Figs. 2 and S5). Figure 7 shows the changes in soil $N_2O$, NO and $NH_3$ emissions due to large-scale deployment of ERW with croplands and summarizes the regional changes across the five agricultural regions (North America, Brazil, Europe, India, and China). A close-up view of changes in these five regions are included in Fig. S9 in SM; regional emissions in the Control and ERW runs are summarized in Table 4.

**Table 4. Soil $N_2O$, NO and $NH_3$ fluxes in the control and basalt treatment CLM5 runs on main cropland regions. Reported is total emission as average ± standard deviation of the annual totals.**

| Region | $N_2O$ (Tg N $yr^{-1}$) | | NO (Tg N $yr^{-1}$) | | $NH_3$ (Tg N $yr^{-1}$) | |
|---|---|---|---|---|---|---|
| | Control | ERW | Control | ERW | Control | ERW |
| North America | 0.59±0.06 | 0.40±0.03 | 0.37±0.04 | 0.27±0.03 | 1.77±0.25 | 1.83±0.25 |
| Brazil | 0.12±0.01 | 0.10±0.01 | 0.07±0.01 | 0.07±0.01 | 0.26±0.03 | 0.27±0.03 |
| Europe | 0.68±0.06 | 0.60±0.05 | 0.49±0.04 | 0.43±0.03 | 0.82±0.05 | 0.85±0.06 |
| India | 0.18±0.02 | 0.15±0.02 | 0.13±0.02 | 0.11±0.01 | 3.47±0.29 | 3.53±0.29 |
| China | 0.63±0.03 | 0.53±0.02 | 0.40±0.02 | 0.33±0.01 | 1.25±0.04 | 1.26±0.04 |
| Total | 2.20±0.09 | 1.78±0.07 | 1.46±0.06 | 1.21±0.05 | 7.57±0.38 | 7.74±0.39 |
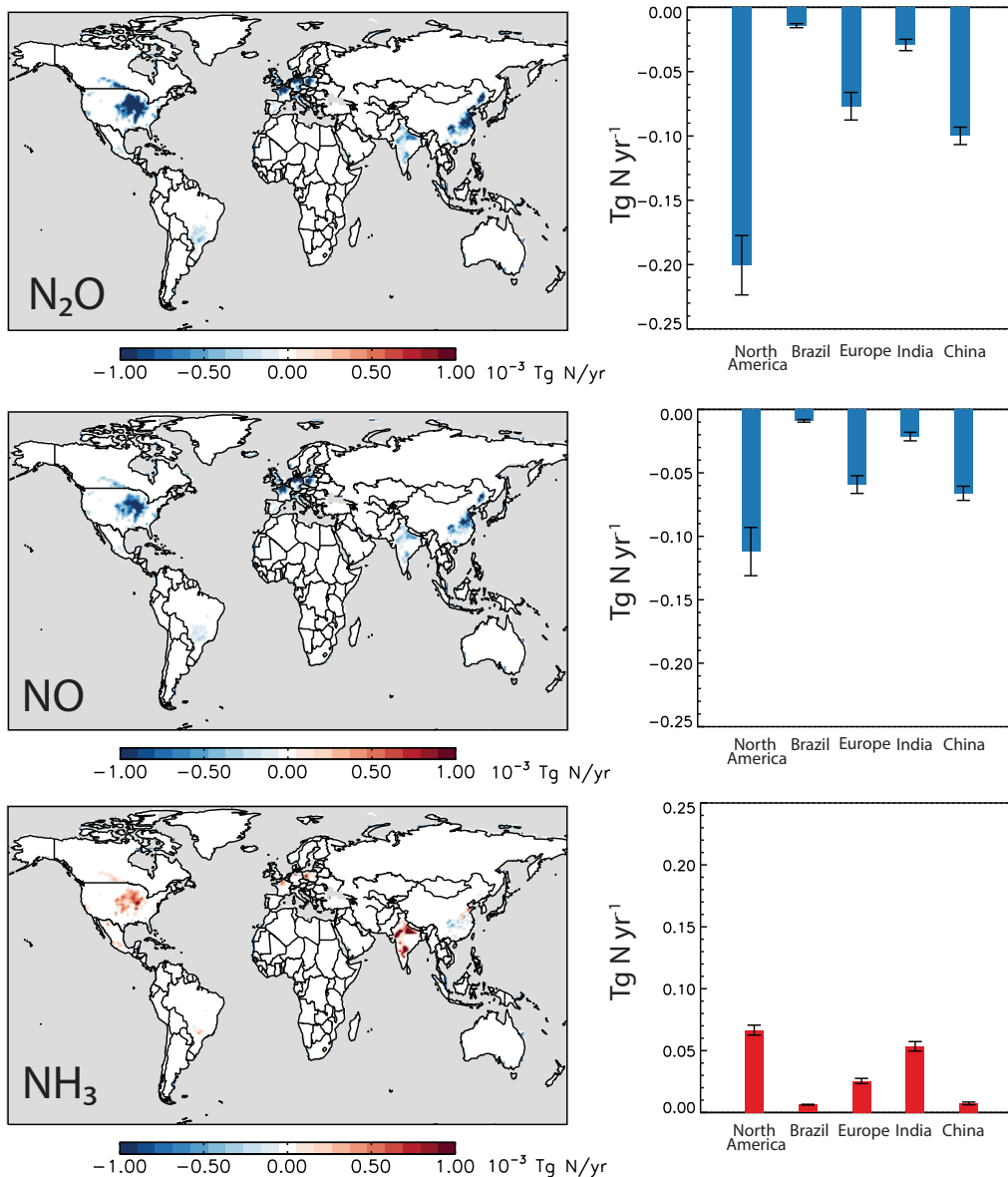
**Figure 7: Changes in annual soil N₂O, NO and NH₃ fluxes across the main five agriculture regions (North America, Brazil, Europe, India, and China) based on increases in soil pH resulting from basalt treatment required to sequester 2 Gt CO₂ yr⁻¹ (Figure 2). Shown is the spatial distribution of changes in soil N₂O, NO and NH₃ (Δ ERW-Control) and the summary of the regional changes (Tg N yr⁻¹). Error bars indicate the standard deviation of the annual total changes.**

Large-scale basalt application consistently decreases soil $N_2O$ and NO emissions over the five main agriculture regions, with a total decrease of 0.42 Tg $N_2O$-N yr⁻¹ and 0.25 Tg NO-N yr⁻¹. These changes are substantial and correspond to 19% for $N_2O$

and 17% for NO of the total agricultural emissions in those five regions, with 13% for $N_2O$, and 12% for NO of the global total. Major reductions in $N_2O$ and NO occurred in North America (28% for $N_2O$ and 24% for NO), followed by China (16% and 18%) and Europe (13% and 12%).

Our new modeling framework only simulates changes in direct soil $N_2O$ emissions in croplands. Indirect soil nitrogen emissions occur through degassing of $N_2O$ from aquifers and surface waters, via the leaching and runoff of applied N ($NO_3$ and $NH_4$) in aquatic systems, and the volatilisation of applied N as $NH_3$ and $NO_x$ followed by deposition of $NH_4$ and $NO_x$ on soils and water (Nevison, 2021). ERW field trials in the U.S. have reported nitrogen losses (in the form of $NO_3$ and $NH_4$) to leaching in the basalt-treated plots that are substantially larger than the control plots in maize (40%) and miscanthus (17%) (Blanc-Betes et al., 2020). However, this indirect contribution to the overall emissions is expected to be small, given that indirect emissions account for less than 5% of total agricultural $N_2O$ emissions (Nevison, 2021; Lu et al., 2022).

Basalt applications increased soil $NH_3$ emissions as expected, with a total increase of 0.17 Tg $NH_3$-N $yr^{-1}$, which is about 2% of agriculture emissions in our five regions and 1% of the global total. The increasing effect on $NH_3$ is not as consistent across all soils as for $N_2O$ and NO and some grid cells with acidic soils (pH < 5.5) displayed decreases in $NH_3$, especially in regions across Brazil and China (Fig. S8). Increases in soil pH favours nitrification and subsequent denitrification processes (Parton et al., 1996), which reduces N in the $NH_4^+$ form in the soils available for $NH_3$ volatilization. Overall, relatively major increases in $NH_3$ occurred in North America, Brazil and Europe (3–4%), followed by India (1.5%) with marginal increases in China (0.8%). Regions with more neutral and alkaline soils have more significant increases (8–12%), such as croplands in the U.S. with soil pH ranging 6.5–7.5, which showed increases up to 10%.

**5 Conclusions**

We present the development and implementation of new updates and schemes for the CLM5 nitrogen cycle to evaluate the potential impact of ERW with croplands. In particular, new updates in $N_2O$ focus on the gross denitrification and denitrification end products rates described by Blanc-Betes et al., (2020) based on observations on ERW field trials in the US, and the $N_2O$ nitrification rate. In addition, we implement a new parameterization to calculate NO release from nitrification and denitrification processes, considering rain pulses in nitrification and loses of NO to plant canopy. Finally, for $NH_3$ we use the volatilization scheme (Fu et al., 2020), with a regulating pH function based on observations of basalt, lime, and biochar applications.

Using our global simulations, we successfully validated simulated 'control' (i.e., no ERW) seasonal cycles of soil $N_2O$, NO and $NH_3$ emissions against a wide range of global emission inventories and previously reported estimates. For $N_2O$, we also use results from the $N_2O$ Model Intercomparison Project, the Carbon-Tracker Lagrange North American Regional Inversion Framework and a compilation of long-term observations in different croplands across North America. We also benchmarked simulated mitigation of soil $N_2O$ fluxes in response to ERW against a sub-set of data from ERW field trials in the U.S. Corn

550 Belt with single-point simulations at Energy Farm in Illinois (U.S.) and provide a case study of the effect of large-scale ERW deployment with croplands on soil nitrogen fluxes across five key regions with high potential for CDR with ERW (North America, Brazil, Europe, India, and China).

We acknowledge the need for further improvement in the CLM5 nitrogen cycling representation and the ERW parameterization. In a comprehensive evaluation of CLM5 nitrification and denitrification processes, Nevison et al. (2022b)
555 emphasized that the nitrification:denitrification ratio (2:1) in CLM5 is likely to be unrealistically low, even when considering the missing N mineralization term in potential nitrification (Section 2.2.1). Consequently, CLM5 underestimates the fraction of gross mineralization leading to nitrification and overestimates $NH_4^+$ uptake by plants. Additionally, CLM5 underestimates $NO_3$ assimilation by immobilizing bacteria. To enhance the confidence in our land model simulations, it is thus crucial to gather more experimental data from ERW field trials as well as observational constraints on soil nitrogen fluxes and flux ratios.

560 Our study represents a first implementation of an ERW parametrization in a land model N cycling, which has enabled us to understand the implication of large-scale deployment of ERW with croplands on direct soil nitrogen trace gas emissions. Our modelling framework simulates important reductions in both $N_2O$ (19%) and NO (17%) and moderate increases in $NH_3$ (2%) across five main cropland regions, using the soil pH increases that would occur after 25-year basalt application to remove 2Gt $CO_2$ per year projected (Beerling et al., 2020). Reductions are most marked over North America, with decreases of 28% in
565 $N_2O$ and 24% in NO and increases of about 10% in $NH_3$ (for neutral and alkaline agriculture soils).

Given agricultural $N_2O$ emissions account for more than 50% of the total $N_2O$ emissions (Tian et al., 2020) and these emissions are expected to continue to grow due to increases in fertilizer usage (IPCC, 2021), regional decreases in $N_2O$ emissions from basalt amendments in croplands are significant and may impact stratospheric ozone. Our study highlights the additional potential of ERW for climate change mitigation through reducing emissions of a non-$CO_2$ greenhouse gas.

570 Simulated decreases in soil NO emissions and moderate increases in $NH_3$ from basalt treatments in our five cropland regions has further implications for regional air quality. Once emitted from soil, $NH_3$ undergoes rapid reactions in the atmosphere forming inorganic $NO_3^-$ and $NH_4^+$ aerosols, which contributes to $PM_{2.5}$ formation. Agriculture $NH_3$ emissions are responsible for 30% of all $PM_{2.5}$ in the U.S., 50% in Europe and 20% in China (e.g., Wyer et al., 2022). Similarly, soil NO is rapidly oxidized, generating tropospheric $O_3$ and secondary organic aerosols (SOA). Ozone is a strong oxidant, which causes harm to
575 human health and to crops, and SOA also contributes to $PM_{2.5}$. These past decades, significant government attention has been focused on regulating $NH_3$ emissions as a strategy for reducing $PM_{2.5}$ (e.g., U.S. EPA, 2004; UK DEFRA, 2019). However, in future emission projections, it is unclear whether controlling $NH_3$ may be an effective strategy for reducing $PM_{2.5}$ particularly given that $NO_x$ can also act as the primary limiting precursor for the formation of secondary $NH_4^+$ aerosols (e.g., Vieno et al., 2016). Our study thus provides a scientific modelling tool to aid stakeholders in evaluating global and regional ERW proposals
580 as an additional strategy to mitigate climate change and ensuring a clean and sustainable environment.

**Code and data availability**: CLM5.0 is publicly available through the Community Terrestrial System Model (CTSM) git

repository (https://github.com/ESCOMP/ctsm). Results presented in this paper were obtained using CLM5.0.25 with an updated version of the nitrogen cycling scheme, which is publicly available through the Zenodo repository (https://doi.org/10.5281/zenodo.8111541). All emission inventory and published observational data used in the study are available from the provided references. Unpublished soil $N_2O$ fluxes from the Energy Farm ERW field trials and CLM5 output data and metadata to recreate the analysis are available through the Zenodo repository (https://doi.org/10.5281/zenodo.8119634).

**Author contribution**: MVM developed and implemented the new code, performed the modelling experiments, and analyzed the output. EBB, KMF, LLT, LKE, WRW and APKT provided input for the model development. MVM, EK and DJB designed the modelling experiment. IBK, MDM, EHD, IC and NJP provided observations collected in ERW field experiments. MVM prepared the manuscript with contributions from all co-authors.

**Competing interests**: The authors declare that they have no conflict of interest.

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855