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Effects of enhanced rock weathering on soil gas fluxes across UK land uses

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Abstract. Enhanced rock weathering (ERW) is a proposed carbon dioxide (CO_2) removal strategy via the application of crushed silicate rocks to accelerate the natural breakdown of silicate minerals, permanently trapping atmospheric CO_2. Application of rock dust may alter soil properties, such as pH, with potential consequences for soil trace gases fluxes relevant to climate forcing and air quality. However, previous ERW studies have focused mainly on the principal greenhouse gases, while broader trace gas responses remain poorly constrained. This laboratory study presents measurements of nitric oxide (NO), ammonia (NH_3), carbon monoxide (CO), hydrogen (H_2) and volatile organic compounds (VOCs), as well as CO_2, methane (CH_4) and nitrous oxide (N_2O), from control and ERW-treated soils collected from arable, grassland and newly planted broadleaf and conifer forest field trials in the UK. Soils were sieved, repacked and rewetted for laboratory measurements. A dynamic air-flow-through chamber system, equipped with a high-resolution multi-gas analyser and a proton-transfer-reaction mass spectrometer, was used to measure N_2O, NO, NH_3, CO, and VOCs between 5 and 25 °C. CO_2 and CH_4 fluxes were measured online at 20 °C using a closed-loop chamber method, and H_2 fluxes were measured by discrete sampling from static chamber headspace using gas chromatography. ERW-associated differences varied among gases and soils, with no consistent response across all incubated samples. The reported treatment differences included lower CO_2 emissions in both forest soils, greater CH_4 uptake in broadleaf forest soil, higher NO emissions in grassland soil, and changes in CO and hydrocarbon fluxes in forest soils. NH_3 and H_2 fluxes showed no statistically significant treatment responses, and no individual VOC remained significantly different after correction for multiple testing. Overall, rock dust application had limited and inconsistent impacts on trace gas fluxes across the soils examined in this snapshot study. Longer-term measurements at ERW field trials are needed to examine how these responses vary seasonally and evolve as the applied materials continued to weather. These measurements should be accompanied by in-depth soil characterisation and microbial analyses to elucidate the complex relationships between ERW treatment and trace gas fluxes. This evidence is needed to assess the full climate, air-quality and environmental implications of large-scale ERW deployment.

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1 Introduction

Large-scale carbon dioxide (CO_2) removals are required in addition to significant reductions in greenhouse gas (GHG) emissions to meet the Paris Agreement target of limiting global warming to well below 2 °C by the end of the century (IPCC, 2021). One proposed strategy for this is enhanced rock weathering (ERW), in which crushed calcium- and magnesium-rich silicate rocks are spread onto land (usually under agricultural management). As these materials are broken down by natural weathering, calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations are released into the soil. The resulting alkalinity of these basic cations facilitates the conversion of atmospheric CO_2 into bicarbonate ions, which then leach through the soil in a dissolved phase, accumulating over time and remaining in groundwater and oceans for upwards of 10,000 years (Beerling et al., 2018; Hartmann et al., 2013; Renforth and Henderson, 2017).

One of the key effects that ERW has on soil properties is an increase in soil pH (often towards neutrality or alkalinity) (Araujo et al., 2024; Beerling et al., 2024; Dietzen et al., 2018). Soil pH can influence various soil processes, including microbial activity (Bååth and Anderson, 2003; Lauber et al., 2009; Rousk et al., 2010), chemical reactions (Avnimelech and Laher, 1977; Homyak et al., 2017; Yamulki et al., 1997) and physical interactions (Serrano and Gallego, 2006). These processes in turn can influence trace gases fluxes from soil (e.g. Ge et al., 2025; Hénault et al., 2019; Kemmitt et al., 2006; Kusin et al., 2025). These gases include the primary GHGs, CO_2, methane (CH_4) and nitrous oxide (N_2O), which have direct implications for the potential of ERW to mitigate climate change. Other trace gases, including nitric oxide (NO), ammonia (NH_3), carbon monoxide (CO), hydrogen (H_2) and volatile organic compounds (VOCs), may also be affected. Although these gases are present at low atmospheric concentrations, they can influence atmospheric chemistry, GHG lifetimes and ecosystem and human health via air quality effects (Atkinson, 2000; Daniel and Solomon, 1998; Ocko and Hamburg, 2022). Therefore, understanding how ERW affects soil trace gas fluxes is important for assessing both the potential benefits and unintended consequences of large-scale ERW deployment.

The emission and uptake of soil trace gases are controlled by a combination of biological and abiotic processes that may respond to ERW-induced changes. Soil CO_2 emissions originate from respiratory processes in the soil, such as plant root respiration and microbial decomposition of soil organic matter (Abalos et al., 2020), while N_2O and NO fluxes are driven primarily by microbial denitrification and nitrification, with additional contributions from abiotic processes such as chemonitrification (Butterbach-Bahl et al., 2013). Soil CH_4 fluxes are controlled by a balance between methanogenesis under anaerobic conditions and CH_4 oxidation by methanotrophic bacteria (Conrad, 2009; Nazaries et al., 2013), while emission of NH_3 from soil depends on NH_3 volatilisation and is governed by the pH and temperature-dependent partitioning of total ammoniacal nitrogen between ammonium (NH_4^+) and NH_3 (Hidalgo et al., 2026; Zhenghu and Honglang, 2000). Soil can also uptake or emit CO through microbial and abiotic processes (van Asperen et al., 2015; Conrad and Seiler, 1980; King and Weber, 2007) and generally act as a sink for H_2 primarily through microbial oxidation (Hou et al., 2025). Similarly, various physical, chemical and biological soil processes control the uptake and emission of VOCs, including microbial production, consumption and decomposition of organic matter, as well as VOC sorption to soil particles (Peñuelas et al., 2014; Tang et al.,

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2019; Trowbridge et al., 2020). As many of these processes are sensitive to pH and the associated changes in microbial activity and nutrient availability, ERW has the potential to alter both the magnitude and direction of soil trace gas fluxes.

Despite the potential effects on soil gas fluxes, previous ERW studies have primarily focused on quantifying CO_2 (or CO_2 equivalent) removal or mitigation potential, with gas flux measurements restricted to CO_2, CH_4 and N_2O (e.g. Anthony et al., 2025; Chen et al., 2025; Dietzen et al., 2018; Kantola et al., 2023; Li et al., 2025; Milliken et al., 2025; Vienne et al., 2024; Yan et al., 2023). The reported responses of these gases to ERW treatment to date are variable. For example, Chiaravalloti et al. (2023a) and Anthony et al. (2025) observed decreased N_2O emissions from agricultural and grassland soils after ERW treatment, while Chen et al. (2025) reported increased in N_2O emissions from a tropical forest soil. These varying observations suggest that the impact of ERW on soil gas fluxes is not universal and may vary with land use, plant cover, soil management, microbial associations and edaphic properties. Ultimately, the effects of ERW on a broader suite of soil trace gases remain poorly constrained.

In the UK, GHG removal is expected to play an increasing role in meeting net zero targets as current government targets are to remove 21.8 $MtCO_2e$ per year by 2035 (Department for Energy Security and Net Zero, 2025), and land-based approaches such as ERW are being recommended within these carbon removal pathways (Climate Change Committee, 2025). Kantzas et al. (2022) have estimated that ERW could remove 6–30 $MtCO_2$ per year in the UK by 2050, while also mitigating the potent greenhouse gas N_2O, reversing soil acidification, and reducing fertilizer costs. However, as large-scale ERW deployment involves costs, logistical constraints and in-built carbon emission of its own (mining, crushing, grinding, and transportation), it is essential to understand not only the CO_2 removal potential of ERW, but also its wider effects on soil trace gas fluxes, including possible risks and co-benefits for climate mitigation, air quality, and environmental and human health. This study investigates the effects of ERW on a suite of soil trace gas fluxes across different soil types and land uses in the UK under controlled laboratory conditions.

2 Methodology

2.1 Site descriptions

Soils were collected from ERW field trials on three different land uses: arable, grassland and forest (broadleaf and conifer). Key descriptors of the sites and their soil properties are provided in Table 1.

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Table 1. Descriptions of site locations, climate and soil properties. The methodologies for measuring soil pH and elemental composition are described in S1.1. The meteorological data is obtained from Met Office MIDAS Open: UK Land Surface Stations Data (1853-current) (2026), using the average across 2022–2023 for the grassland site and 2021–2024 for the arable and forest sites; forest data is from the nearest weather station to site (Sennybridge), arable and grassland data are from on-site weather stations.

		Arable	Grassland	Forest (broadleaf)	Forest (conifer)
Latitude, longitude (degrees)		51.81, -0.38	50.77, -3.90	52.06, -3.74	
Mean annual temperature / °C		10.9	11.4	9.2	
Annual precipitation / mm		752	997	1605	
Texture		52 % silt	50 % silt	40 % silt	
		20 % clay	38 % clay	24 % clay	
		28 % sand[a]	12 % sand[b]	36 % sand[c]	
pH	Control	6.83 ± 0.19	5.41 ± 0.03	5.36 ± 0.24	6.40 ± 0.01
	ERW	7.68 ± 0.02	5.95 ± 0.06	6.12 ± 0.38	7.01 ± 0.06
Total carbon / %	Control	1.76 ± 0.00	3.56 ± 0.05	6.47 ± 0.08	6.07 ± 0.15
	ERW	1.60 ± 0.08	3.60 ± 0.01	6.20 ± 0.27	6.23 ± 0.22
Organic carbon / %	Control	1.41 ± 0.07	2.94 ± 0.22	5.43 ± 0.19	4.99 ± 0.42
	ERW	1.52 ± 0.09	3.00 ± 0.08	5.29 ± 0.18	5.08 ± 0.24
Nitrogen / %	Control	0.18 ± 0.01	0.38 ± 0.01	0.65 ± 0.01	0.63 ± 0.02
	ERW	0.16 ± 0.01	0.38 ± 0.01	0.62 ± 0.03	0.61 ± 0.01

[a] Described in Desmalles et al. (2025). [b] Obtained from Rothamsted Research (2018). [c] Described in Jones et al. (2025).

2.1.1 Arable

Soil was collected from an arable field site in Harpenden in south-east England, managed by Rothamsted Research. The soil is a silty clay loam of the Batcombe series, corresponding to a profundic chromic endostagnic luvisol (IUSS Working Group WRB, 2022). The ERW field trial was established in 2021 within a long-term liming field trial. A basalt ERW feedstock was used, with majority labradorite (44.4 %), augite 13.5 %, chlorite (11.2 %) and smectite (9.2 %) mineralogy, obtained from a quarry in Middleton-in-Teesdale, Country Durham in the UK. Further details of the feedstock are described in Desmalles et al. (2025). The basalt was applied at a rate of 40 t ha^{-1} each autumn from 2021–2024, prior to crop sowing. Fertiliser was applied in spring 2023 (140 kg N ha^{-1}, 54 kg SO_3 ha^{-1}), summer 2023 (30 kg N ha^{-1}), winter 2024 (61 kg N ha^{-1}) and spring 2024 (90 kg N ha^{-1}). Winter bean, winter barley and winter oil seed rape were grown in 2022, 2023 and 2024, respectively. Winter barley was planted at the end of 2024, but this crop failed due to waterlogging. The trial consists of six 24 x 24 m subplots (three with basalt application, three control) within the field. Soil subsamples were collected from the top 10 cm of soil in each subplot in February 2025 and combined into one composite ERW sample and one composite control sample.

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2.1.2 Grassland

Soil was collected from a grassland field site in North Wyke, also managed by Rothamsted Research, near Okehampton in south-west England. The soil is a clayey pelo-stagnogley of the Hallsworth series, corresponding to a clayic eutric stagnosol (IUSS Working Group WRB, 2022). The same basalt as used in the arable field trial was applied in April 2022 and 2023, at a rate of 40 t ha^{-1}. Fertiliser was applied in spring 2022 and 2023 (50 kg N ha^{-1}, 65 kg P_2O_5 ha^{-1} and 80 kg K_2O ha^{-1}) and summer 2022 and 2023 (after vegetation cut; 25 kg P_2O_5 ha^{-1} and 90 kg K_2O ha^{-1}). Vegetation was cut in early summer and early autumn in both 2022 and 2023. The trial consists of six 10 x 34 m subplots (three with basalt application, three control) within a field. Soil subsamples were collected from the top 10 cm of soil in each subplot in December 2023 and combined into one composite ERW sample and one composite control sample.

2.1.3 Forest (broadleaf and conifer)

Soil was collected from Glandwr Forest, established and managed by The Carbon Community, near Llandovery, south Wales. The soil is well-draining fine loam of the Manod series, corresponding to a chromic mollic endoskeletic umbrisol (IUSS Working Group WRB, 2022). The site was historically used as upland sheep pasture, and in the 20 years prior to tree planting, only farmyard manure was used as fertiliser. Tree saplings were planted in June 2021 as part of a large experimental field trial in a random block design replicated eight times across 11.52 ha. Plots within the field trial include basalt-treated monocultures of Sitka spruce (hereafter referred to as 'conifer') and basalt-treated mixtures of native broadleaf species, as well as the corresponding forest types with no soil amendments. A metabasalt feedstock obtained from Builth Wells Quarry in Wales was used for the ERW trial, with mineralogy of plagioclase (61–83 %), chlorite (12–18 %), calcite (1–14 %) and trace vermiculite and quartz. Further details of the feedstock and field trial are found in Jones et al. (2025) and Waring et al. (2026). The feedstock was applied in November 2020 (40 t ha^{-1} with < 4 mm particle size) and June 2023 (24 t ha^{-1} with < 2 mm particle size). Samples of the top 10 cm soil were collected in February 2025 from the central 20 x 20 m of the 40 x 40 m plots; the broadleaf soils were sampled from one experimental block whereas the conifer soils were sampled from three blocks and pooled into one sample each of ERW and control soils.

2.2 Soil preparation

Soil samples were air-dried prior to sieving to 2 mm. Sub-samples of sieved soil were oven-dried at 105 °C to determine gravimetric water content (GWC). One to three days prior to gas flux measurements (01 April 2025–03 April 2025), 750 to 850 g (dry mass) soil was added to Perspex chambers (19.3 cm diameter, 10 cm height; 3 chambers prepared per site and per soil treatment from the pooled soil samples, i.e. 24 chambers total) and wetted to GWC 60 % with deionised water, gently mixed and then smoothed to ensure a flat surface. Throughout the gas flux measurement period (02 April 2025–28 April 2025), soil chambers were stored at 20 °C in a temperature-controlled laboratory with loose covers to minimise drying. GWC was

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monitored throughout and was similar between control and ERW chambers for a given site. Any vegetation shoots that started growing in the chambers throughout the experimental period were gently removed.

2.3 Dynamic chamber flux measurements

Measurements of VOCs, N_2O, NO, NH_3 and CO were conducted using the dynamic air-through flux method (described in Medinets et al., 2016, 2021) within a temperature-controlled incubator. Soil chambers were sealed to a Perspex chamber lid (20 cm height) via and neoprene sealing and metal clips. The lids were equipped with a fan to enhance air mixing, temperature and relative humidity probes, and an air inlet and outlet supplied via PTFE tubing. As four chambers could be incubated at a time, each experiment run consisted of measurements from a blank chamber and three sample chambers: either two control and one ERW or two ERW and one control soil chambers, for a given site. Air was supplied to the chambers from a zero-air generator (LNI Swissgas Srl, Italy) with inlet and outlet flow rates regulated by mass flow controllers (Mass-Stream, Bronkhorst GmbH, Germany). The measurement cycle was 60 min, consisting of a 10 min sampling sequence of a blank chamber followed by a sample chamber. The outflowing air was split between two instruments: a proton transfer reaction time-of-flight mass spectrometer with quadrupole ion guide able to measure multiple VOC concentrations simultaneously at 1 Hz (PTR-Qi-ToF-MS; Ionicon, Austria) and a multi-gas analyser able to measure N_2O, NO, NH_3, CO and H_2O at 1 Hz (MIRO MGA10-GP; MIRO, Switzerland) (hereafter referred to as MIRO).

Two sets of measurements were conducted using the dynamic air-through chamber system. The first maintained a constant chamber temperature of 20 °C over a 3 h period. The second experiment was a ramping temperature experiment, in which the chamber temperature was reduced to 5 °C and then increased by 5 °C after 1 h of stable temperature, up to 25 °C This allowed for one period of gas flux measurements per chamber per temperature (5, 10, 15, 20 and 25 °C). For flux calculations using the dynamic chamber technique, the gas concentrations in the last 90 s of the 10 min chamber measurement period were used to ensure that gas concentrations had stabilised. The mean soil chamber gas concentration in the chosen time period was calculated (C, ppm), alongside the previous blank chamber gas concentration (C_0, ppm). The limit of detection was defined as 2 standard deviations of C_0 and thus if C was within this range, $C - C_0$ was considered to have a value of 0. Flux was calculated as:

$$F = (C - C_0)QM_r \times \frac{p}{RTm} \times 3600, \quad (1)$$

where F is flux (μg g^{-1} h^{-1}), Q (approx. 4 m^3 s^{-1}) is the flow rate from the chamber to analyser, M_r (g mol^{-1}) is the gas molecular mass, p is the gas pressure (assumed to be 101325 Pa), R is the molar gas constant (8.315 m^2 kg s^{-2} K^{-1} mol^{-1}), T is the chamber headspace temperature (K) and m (g) is the mass of soil in the chamber. Positive fluxes are considered to be emissions from soils whereas negative fluxes are considered as uptake by the soils. For the 3 h experiment, the mean flux of the three measurement periods was then calculated.

VOCs detected at mass-to-charge ratio (*m/z*) 350 were included in the analyses (covering the most common naturally occurring species). The *m/z* values corresponding to ion source contaminants (e.g. N_2^+, O_2^+, NO_2^+), hydrate clusters and calibration ions

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were excluded from the analysis. The molecular formula of the detected compounds was assigned using the GLOVOCS assignment guide (Yáñez-Serrano et al., 2021), where matches of ion *m/z* values to 4 decimal places (dp) were considered to be an exact match, matches to 3dp a high confidence match, 2dp a medium confidence match and 1dp a low confidence match. In cases where a compound was assigned to more than one peak, the peak with the smallest difference in *m/z* was selected. Similarly, if a peak had more than one compound assigned to it, the compound with the closest *m/z* was selected. A set of target VOCs were also analysed in detail (Table S1). These VOCs were selected based on compounds commonly reported in previous studies of soil VOCs (Abis et al., 2018; Asensio et al., 2007a, b; Gray et al., 2014; Haider et al., 2024; Hellén et al., 2006; Jiao et al., 2023; Legros et al., 2025; Li et al., 2023; Liu et al., 2025; Meischner et al., 2022; Mu et al., 2022; Rocco et al., 2025; Trowbridge et al., 2020; Yang et al., 2024).

As N_2O concentrations were typically close to the limit of detection (i.e. very low), a pressure variation from the zero-air generator caused a sinusoidal pattern in the concentrations (~ 2 ppb) with an approximately 5 min 10 s period (Figure S1). To avoid bias from the positions of crests and troughs in the waves, concentrations from the whole 10 min were used in flux calculations.. NO_2 and O_3 were also measured by the MIRO instrument, but sample fluxes were consistently below the limit of detection, and the fluxes of these gases are not discussed further in this study.

2.4 Closed chamber flux measurements

The fluxes of CO_2 and CH_4 were measured simultaneously using a closed-loop chamber setup, with a LI-COR LI-7810 Trace Gas Analyzer (LI-COR UK Ltd., Cambridge, UK). The soil chamber was fixed to a Perspex lid chamber (20 cm height) with the same construction and sealing mechanism as described above for the dynamic chambers. The analyser was connected to the chamber inlet and outlet via PTFE tubing. Air from the chamber was pumped through the analyser (measurement frequency = 1 Hz) and back into the chamber in a closed-loop system. Measurements were collected for at least 20 min per chamber under room temperature conditions (20 °C). The flux of each gas was calculated as:

$$F = \frac{dC}{dt} \times \frac{pV}{RT} \times \frac{M_r}{m} \times 3600, \quad (2)$$

Where F is flux (μg g^{-1} h^{-1}), $\frac{dC}{dt}$ is the rate of change in gas concentration over time in μmol mol^{-1} s^{-1}, p is the air pressure in Pa (assumed to be 101325 Pa), V is the chamber volume (0.023 m^3), R is the molar gas constant (8.315 m^2 kg s^{-2} K^{-1} mol^{-1}), T is the chamber temperature (assumed to be 293.15 K), M_r is the molar mass of the gas (g mol^{-1}) and m is the mass of soil in the chamber in g.

2.5 Static chamber measurements

The flux of H_2 was measured offline with static chamber sampling, using the method described in Drewer et al. (2026). The soil chamber was fixed to a Perspex lid chamber (20 cm height) with the same sealing mechanism as described above. Sampling was conducted inside an incubator at 20 °C, with tubing (Tygon® E-3603, Cole-Parmer, United Kingdom) to connect the chamber to a three way tap outside of the incubator. After the chamber was sealed, six 100 mL samples were collected at 0, 1,

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2, 3, 5 and 7 min using a syringe. Glass vials (20 mL) were filled with a double-needle system to flush the vials with 5 times their volume. The analysis of H_2 samples and subsequent flux calculations are described in detail in Cowan et al. (2025). In brief, an Agilent 8890 gas chromatograph with a pulsed discharge helium ionisation detector (GC-PDHID; Agilent, Santa Clara, California, USA) was used to measure H_2 concentrations. Fluxes (in μg g^{-1} h^{-1}) were calculated using Eq. (2), where $\frac{dc}{dt}$ was calculated using either a linear or non-linear regression model. The non-linear model used the HMR package for R software (Pedersen et al., 2010), and the most appropriate model was chosen based on the magnitude and uncertainty of the calculated flux relative to the analytical uncertainty.

2.6 Data analysis

Flux calculations for CH_4, CO_2 and H_2 as well as the processing of the PTR-Qi-TOF-MS and MIRO data were performed using R software (R Core Team, 2024). All other data processing, analyses and visualisation were performed using Python. Differences in gas fluxes from control and ERW soils were tested with two-sample Welch t-tests, using a significance threshold of $P < 0.05$. As hundreds of VOCs were tested, a false discovery rate correction was applied using the Benjamini-Hochberg procedure (Benjamini and Hochberg, 1995). Averaged data are reported as means with their corresponding standard error. The fluxes in this study are expressed per soil mass rather than soil area as the fluxes from these repacked cores are unlikely to be truly representative of field fluxes. This is common practice in the literature (e.g. Drewer et al., 2026; Toteva et al., 2025).
The diversity of VOCs detected with PTR-Qi-TOF-MS was measured using the Shannon index of diversity, H, which is calculated as:

$$H = -\sum_{VOC} E_{VOC} \ln(E_{VOC}), \quad (3)$$

where E_{VOC} is the flux at 20 °C for each VOC identified, normalised for the total VOC fluxes. H was calculated separately for the sum of all positive fluxes (soil emissions) and the sum of all negative fluxes (soil uptake).

3 Results

3.1 Greenhouse gases and non-VOC trace gases

At 20 °C, arable and grassland soils emitted both CO_2 and CH_4, while the forest soils emitted CO_2 and consumed CH_4 (Fig. 1A,B). ERW had little effect on greenhouse gas fluxes in arable and grassland soils. In arable soil, mean CO_2 emissions were 37 % higher in ERW-treated samples than controls (6.76 ± 1.28 vs. 4.95 ± 0.71 μg g^{-1} h^{-1}) although this was not statistically significant, while CH_4 emissions were more than threefold higher in ERW samples (0.093 ± 0.025 vs. 0.029 ± 0.005 ng g^{-1} h^{-1}) which was marginally significant ($p = 0.05$). Similarly, grassland soils showed no significant treatment effects, with CO_2 emissions of 14.6 ± 3.5 and 19.8 ± 2.4 μg g^{-1} h^{-1} and CH_4 emissions of 0.044 ± 0.011 and 0.442 ± 0.159 ng g^{-1} h^{-1} in ERW and control samples, respectively. N_2O fluxes in arable and forest soils were generally below the limit of detection below 20 °C (Fig. 2A). At 20–25 °C arable and forest soils showed net N_2O uptake, whereas grassland soils were a net source of N_2O with

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highly variable emissions (72.4 ± 31.5 and 59.7 ± 21.5 ng g^{-1} h^{-1} in control and ERW soils, respectively). ERW significantly increased N_2O uptake in arable soil at 20 °C, from –0.35 ± 0.19 to −1.03 ± 0.20 ng g^{-1} h^{-1} ($p < 0.05$), but no significant treatment effects were observed at other temperatures or in other land uses. The strongest ERW responses occurred in forest soils. CO_2 emissions were reduced from 10.1 ± 0.7 to 6.60 ± 0.47 µg g^{-1} h^{-1} in broadleaf forest soil (35 % reduction; $p < 0.01$) and from 16.6 ± 1.0 to 9.57 ± 0.86 µg g^{-1} h^{-1} in conifer soil (42 % reduction; $p < 0.01$). In broadleaf forest soil, CH_4 uptake approximately doubled under ERW (−0.922 ± 0.097 vs. −0.457 ± 0.021 ng g^{-1} h^{-1}; $p < 0.01$), whereas no significant effect was observed in conifer soil. N_2O uptake was similar between treatments in both forest soils.

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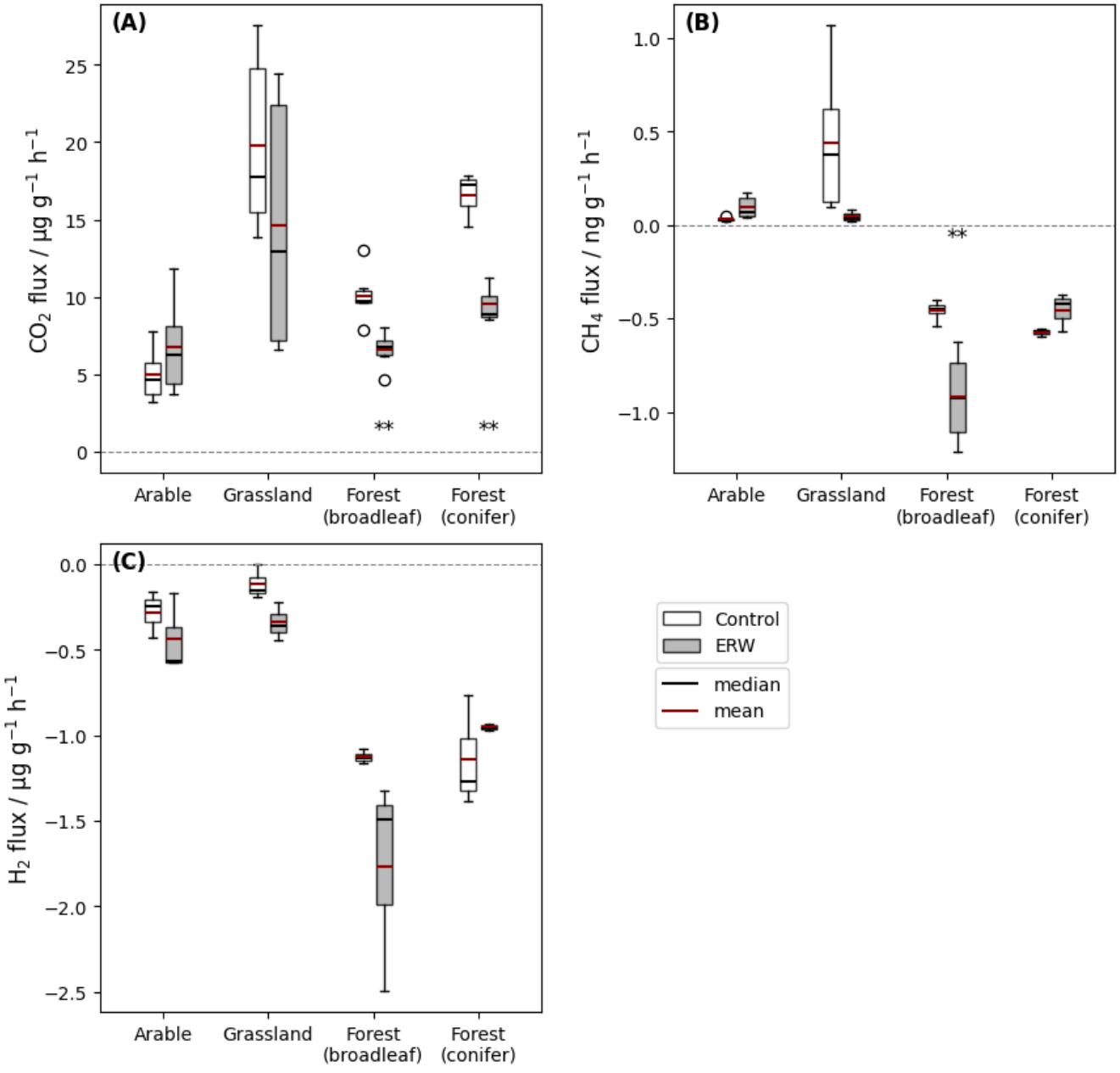

Figure 1. Boxplots of the fluxes of CO_2 (A), CH_4 (B) and H_2 (C) for the control (white) and ERW (grey) soils from different sites at 20 °C. The boxes show quartile 1 to quartile 3 of the data, whiskers show quartile 1 or 3 plus or minus the interquartile range, circles are any points outside of the whiskers' range, red horizontal lines show mean values and black horizontal lines show median values. Note the different scales between plots (CO_2 and H_2 in µg g^{-1} h^{-1}, CH_4 in ng g^{-1} h^{-1}). Asterisks indicate significant difference between control and ERW in Welch two-sample t-test (* P < 0.05, ** P < 0.01, *** P < 0.001).

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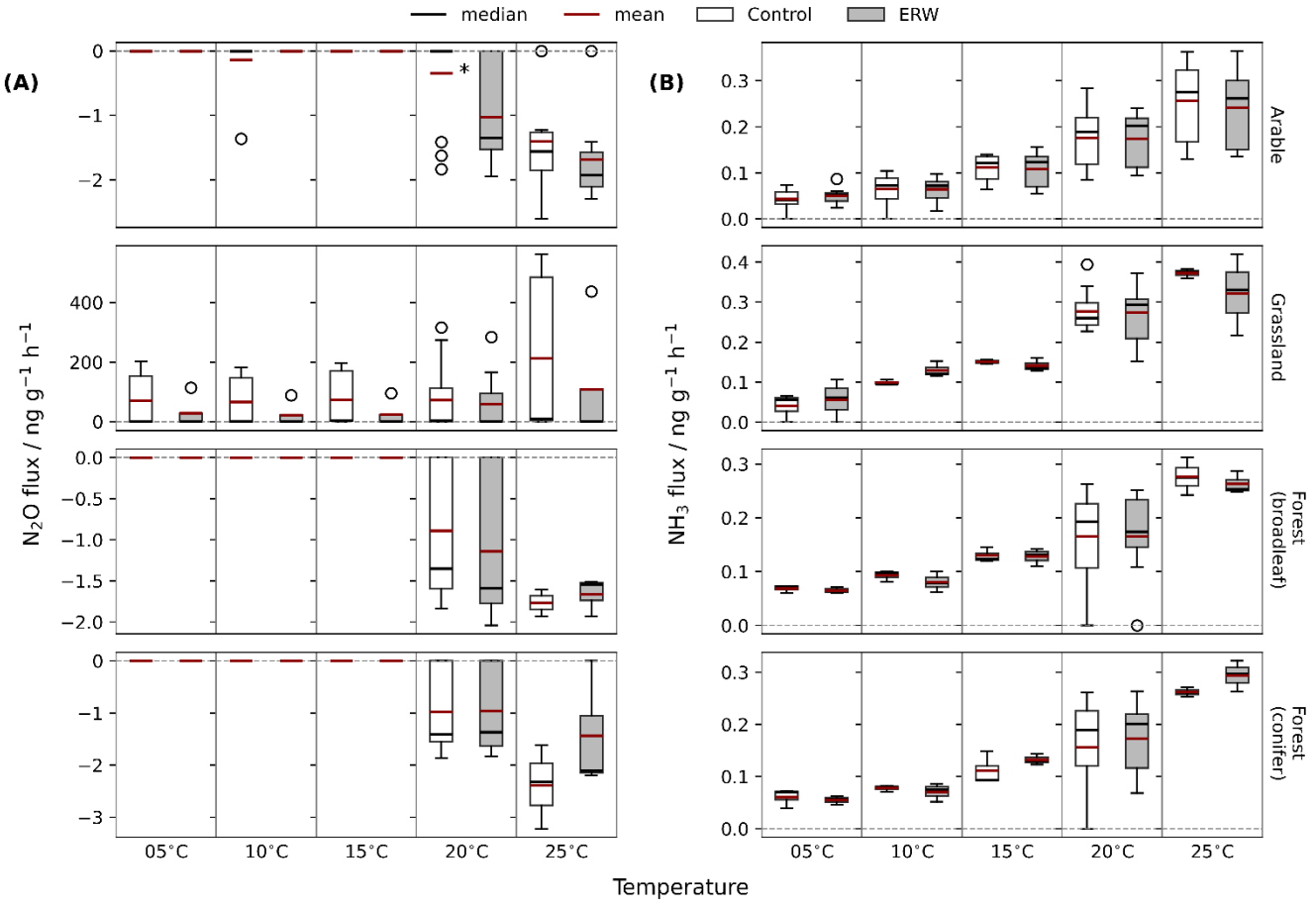

Figure 2. Boxplots of N_2O (A) and NH_3 (B) fluxes measured at different temperatures, reported in ng g^{-1} h^{-1}, for control (white) and ERW (grey) soils from different land uses. The boxes show quartile 1 to quartile 3 of the data, whiskers show quartile 1 or 3 plus or minus the interquartile range, circles are any points outside of the whiskers' range, red horizontal lines show mean values and black horizontal lines show median values. Asterisks indicate significant difference between control and ERW in Welch two-sample t-test (* P < 0.05, ** P < 0.01, *** P < 0.001).

Fluxes of NH_3, NO and CO were measured between 5 and 25 °C, while H_2 fluxes were measured at 20 °C. Across all soils, NH_3 emissions generally increased with temperature but did not differ significantly between control and ERW treatments (Fig. 2B). At 20 °C, NH_3 fluxes ranged from 0.156–0.277 ng g^{-1} h^{-1} across soils, with treatment differences of less than 11 % (Table 3). H_2 uptake was observed in all soils at 20 °C (Fig. 1C). Uptake tended to be greater in ERW-treated arable (−437 ± 136 vs. −281 ± 79 ng g^{-1} h^{-1}), grassland (−341 ± 65 vs. −115 ± 58 ng g^{-1} h^{-1}) and broadleaf forest soils (−1170 ± 365 vs. −1130 ± 25 ng g^{-1} h^{-1}), but none of these differences were considered statistically significant. NO emissions were generally low and increased with temperature (Fig. 3A). At 20 °C, NO fluxes did not differ significantly between treatments in arable, broadleaf or conifer soils, but were approximately sixfold higher in ERW-treated grassland soils (2.56 ± 0.47 vs. 0.42 ± 0.18 pg g^{-1} h^{-1}; $p < 0.001$). In arable soil, a significant increase in NO emission was observed only at 15 °C and was not evident at higher temperatures. In broadleaf forest soil, ERW significantly increased NO emissions at both 15 °C and 25 °C. CO fluxes also

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varied among land uses (Fig. 3B). Arable and grassland soils showed low net emissions (0.23–1.18 ng g^{-1} h^{-1}) with no treatment effects, whereas broadleaf forest soils exhibited significantly lower CO emissions under ERW at 20 °C (0.107 ± 0.067 vs. 0.315 ± 0.054 ng g^{-1} h^{-1}; $p < 0.05$) and 25 °C. Conifer soils showed net CO uptake, which tended to be greater under ERW (−0.708 ± 0.299 vs. 0.007 ± 0.187 ng g^{-1} h^{-1} at 20 °C), although this effect was not significant ($p = 0.060$). Overall, ERW had limited effects on non-VOC trace gas fluxes, with the most consistent responses being increased NO emissions in grassland and broadleaf forest soils and reduced CO emissions in broadleaf forest soil. A summary of non-VOC fluxes is presented in Table 2.

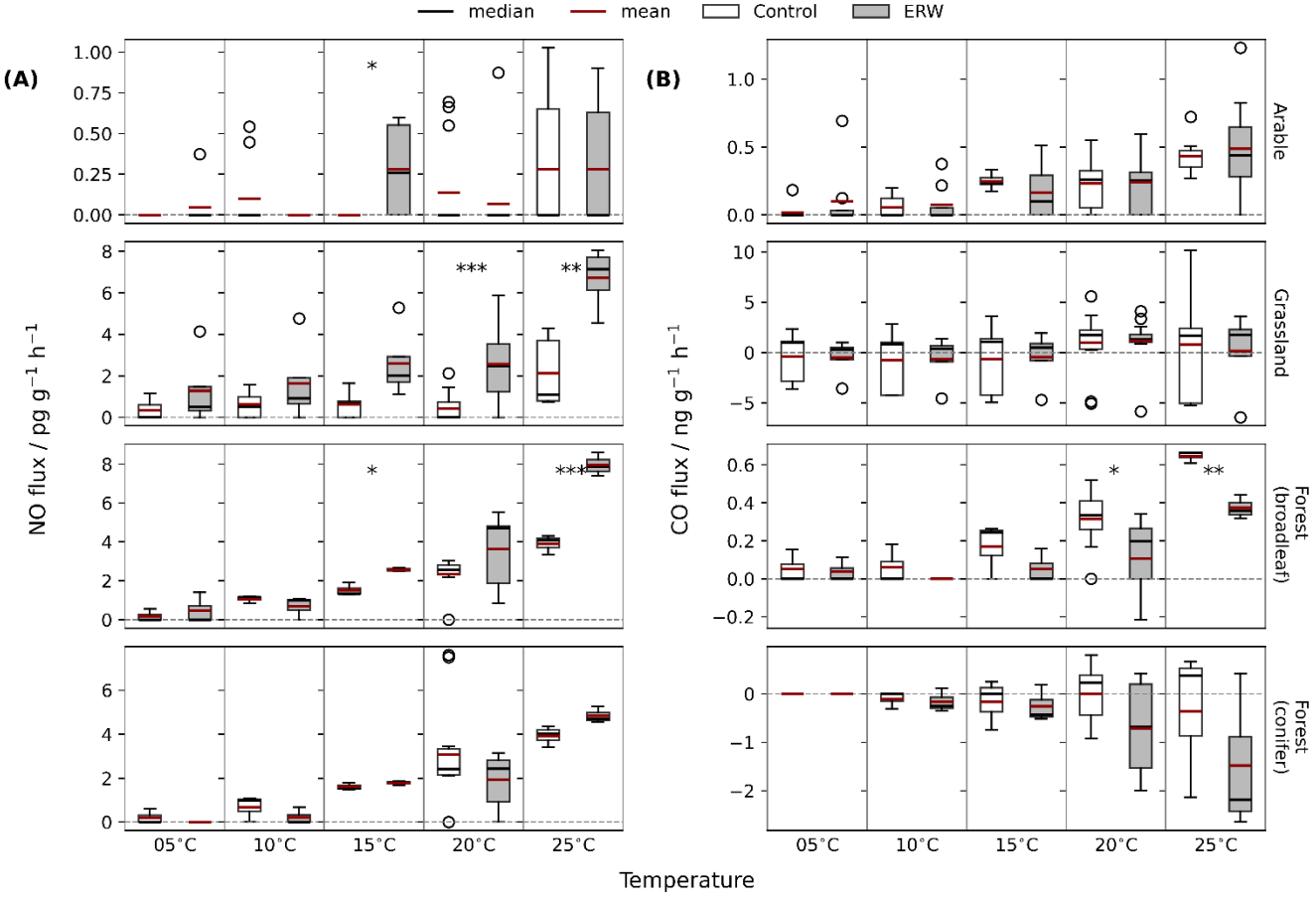

Figure 3. Boxplots of NO (A) and CO (B) fluxes measured at different temperatures, for control (white) and ERW (grey) soils from different land uses. NO is reported in pg g^{-1} h^{-1} and CO is in ng g^{-1} h^{-1}. The boxes show quartile 1 to quartile 3 of the data, whiskers show quartile 1 or 3 plus or minus the interquartile range, circles are any points outside of the whiskers' range, red horizontal lines show mean values and black horizontal lines show median values. Asterisks indicate significant difference between control and ERW in Welch two-sample t-test (* P < 0.05, ** P < 0.01, *** P < 0.001).

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Table 2. Mean soil fluxes of greenhouse gases and other trace gases measured at 20 °C, for control and ERW samples at all sites. The total number of measurements for each flux is n (i.e. the number of flux measurements for each chamber, summed across chambers), and the p-values of the two-sample Welch t-test are provided, with bold values indicating statistically significant differences ($p < 0.05$).

		Arable		Grassland		Forest (broadleaf)		Forest (conifer)	
Trace gas		n	flux ± SE	n	flux ± SE	n	flux ± SE	n	flux ± SE
CO_2	Control	6	5.0 ± 0.7	6	19.8 ± 2.4	6	10.1 ± 0.7	3	16.6 ± 1.0
(μg g^{-1} h^{-1})	ERW	6	6.8 ± 1.3	6	14.6 ± 3.5	6	6.6 ± 0.5	3	9.6 ± 0.9
	p-value		0.253		0.256		**0.003**		**0.007**
CH_4	Control	6	29 ± 5	6	442 ± 159	6	-457 ± 21	3	-576 ± 13
(pg g^{-1} h^{-1})	ERW	6	93 ± 25	6	46 ± 11	6	-922 ± 97	3	-455 ± 59
	p-value		0.050		0.054		**0.004**		0.173
N_2O	Control	14	-0.4 ± 0.2	15	72.4 ± 31.5	9	-0.9 ± 0.3	11	-1.0± 0.2
(ng g^{-1} h^{-1})	ERW	13	-1.0 ± 0.2	15	59.7 ± 21.5	9	-1.1 ± 0.3	10	-1.0 ± 0.3
	p-value		**0.021**		0.742		0.548		0.960
NO	Control	14	0.14 ± 0.07	15	0.42 ± 0.18	9	2.34 ± 0.31	11	3.07 ± 0.75
(pg g^{-1} h^{-1})	ERW	13	0.07 ± 0.07	15	2.56 ± 0.47	9	3.66 ± 0.61	10	1.93 ± 0.36
	p-value		0.493		**< 0.001**		0.079		0.191
NH_3	Control	14	176 ± 17	15	277 ± 16	9	166 ± 28	11	156 ± 27
(pg g^{-1} h^{-1})	ERW	13	174 ± 16	15	274 ± 19	9	165 ± 26	10	173 ± 22
	p-value		0.930		0.895		0.990		0.631
CO	Control	14	0.23 ± 0.05	15	0.99 ± 0.72	9	0.32 ± 0.05	11	0.01 ± 0.19
(ng g^{-1} h^{-1})	ERW	13	0.24 ± 0.06	15	1.18 ± 0.56	9	0.11 ± 0.07	10	-0.71 ± 0.30
	p-value		0.887		0.840		**0.028**		0.060
H_2	Control	3	-281 ± 79	3	-115 ± 58	3	-1130 ± 25	3	-1140 ± 189
(ng g^{-1} h^{-1})	ERW	3	-437 ± 136	3	-341 ± 65	3	-1170 ± 365	3	-952 ± 10
	p-value		0.389		0.061		0.219		0.426

3.2 VOCs

PTR-Qi-ToF-MS measurements detected between 595 and 1036 peaks across the four soil types, of which 444–783 were classified as VOCs (Table 3). VOC diversity at 20 °C did not differ significantly between control and ERW treatments within each land use (Table S2), whereas VOC fluxes differed strongly among the soils representing different land uses (Fig. 4).

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Arable and grassland soils were net sources of VOCs at 20 °C, whereas both forest soils were net sinks. Grassland exhibited by far the largest total VOC emissions (41.9 ± 12.7 and 37.9 ± 19.1 ng g^{-1} h^{-1} in control and ERW soils, respectively), while fluxes from arable soil were much smaller (0.278 ± 0.146 and 0.250 ± 0.144 ng g^{-1} h^{-1}). In all soils, increasing the temperature amplified the magnitude of the existing VOC exchange patterns, with either larger VOC uptake or larger emission. However, ERW had little effect on total VOC fluxes. The only significant responses occurred in forest soils, where VOC emissions were higher in control than ERW samples at 25 °C in broadleaf forest ($p < 0.05$) and at 15 °C in conifer forest ($p < 0.05$), resulting in greater net VOC uptake by ERW-treated broadleaf soil at 25 °C ($p < 0.05$).

Table 3. Numbers of peaks detected with PTR-Qi-ToF-MS across both the constant temperature and ramping temperature experiments, and the number of these peaks that were assigned using the GLOVOCS guide at each level of confidence, as well as the total number of peaks that correspond to VOCs.

	Total peaks detected	No compound match	Exact matches	High conf. matches	Medium conf. matches	Low conf. matches	Total matches	VOCs
Arable								
Control	694	151	168	320	15	40	543	532
ERW	698	168	154	325	13	38	530	517
Grassland								
Control	1002	207	255	456	17	67	795	783
ERW	1036	246	247	456	20	67	790	776
Forest (broadleaf)								
Control	630	150	159	282	12	27	480	471
ERW	595	141	152	267	11	24	454	444
Forest (conifer)								
Control	712	165	157	336	16	38	547	538
ERW	633	141	146	303	12	31	492	484

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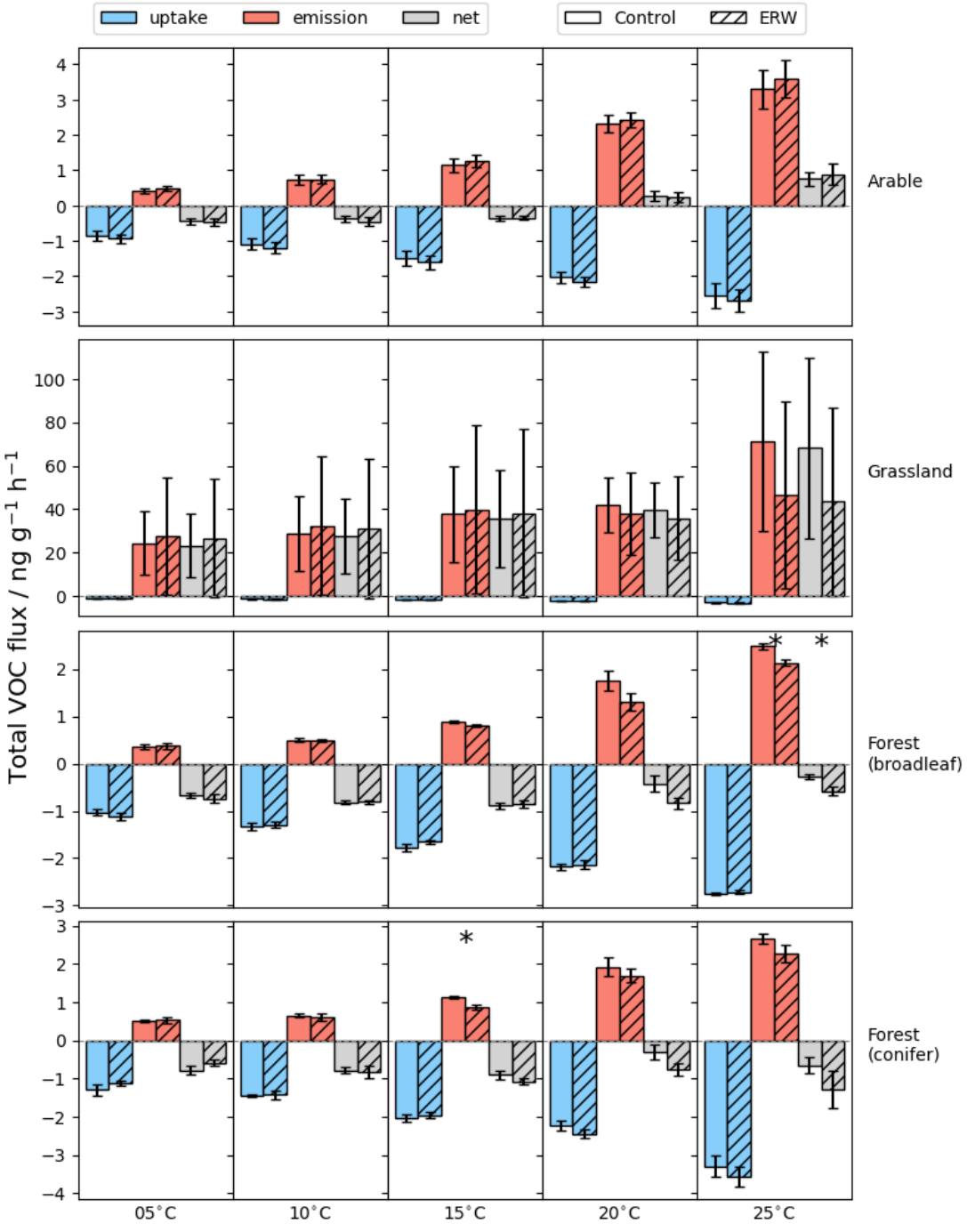

Figure 4. Mean uptake, emission and net flux of total VOCs (ng g^{-1} h^{-1}) measured at varying temperatures for control (empty bars) and ERW (hashed bars) soils from different land uses. Blue represents negative fluxes (uptake), red represents positive fluxes (emissions) and grey represents net flux (sum of uptake and emissions). Error bars represent the standard error. Asterisks indicate significant difference between control and ERW in Welch two-sample t-test (* P < 0.05, ** P < 0.01, *** P < 0.001).

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VOC composition was broadly similar between treatments but differed among land uses (Fig. 5). Oxygenated compounds dominated emissions from arable and grassland soils, contributing approximately 60 % and 75 % of total VOC emissions, respectively. In contrast, forest soils were characterised by uptake of hydrocarbons and halogenated compounds and emission of sulfur-containing compounds. Most compound classes showed no treatment effects (Tables S3, S4). The principal exception was in forest soils, where hydrocarbon uptake was greater under ERW, particularly in conifer soils ($p < 0.05$), while hydrocarbon emissions were significantly higher in broadleaf control soils ($p < 0.05$). Classification of hydrocarbons by degree of unsaturation (double bond equivalent (DBE); Fig. S2) revealed similar patterns across soils. Alkanes were absent or negligible, compounds with DBE = 2 generally showed net emission, and more unsaturated compounds (DBE ≥ 3) showed net uptake. Significant treatment effects were confined to forest soils, where aromatic compounds (DBE ≥ 4) exhibited higher emissions and lower net uptake in control than ERW samples ($p < 0.05$ in broadleaf and conifer emissions and net fluxes). This effect was largely attributable to a compound assigned as naphthalene (*m/z* 129.070), which was consistently more abundant in control soils.

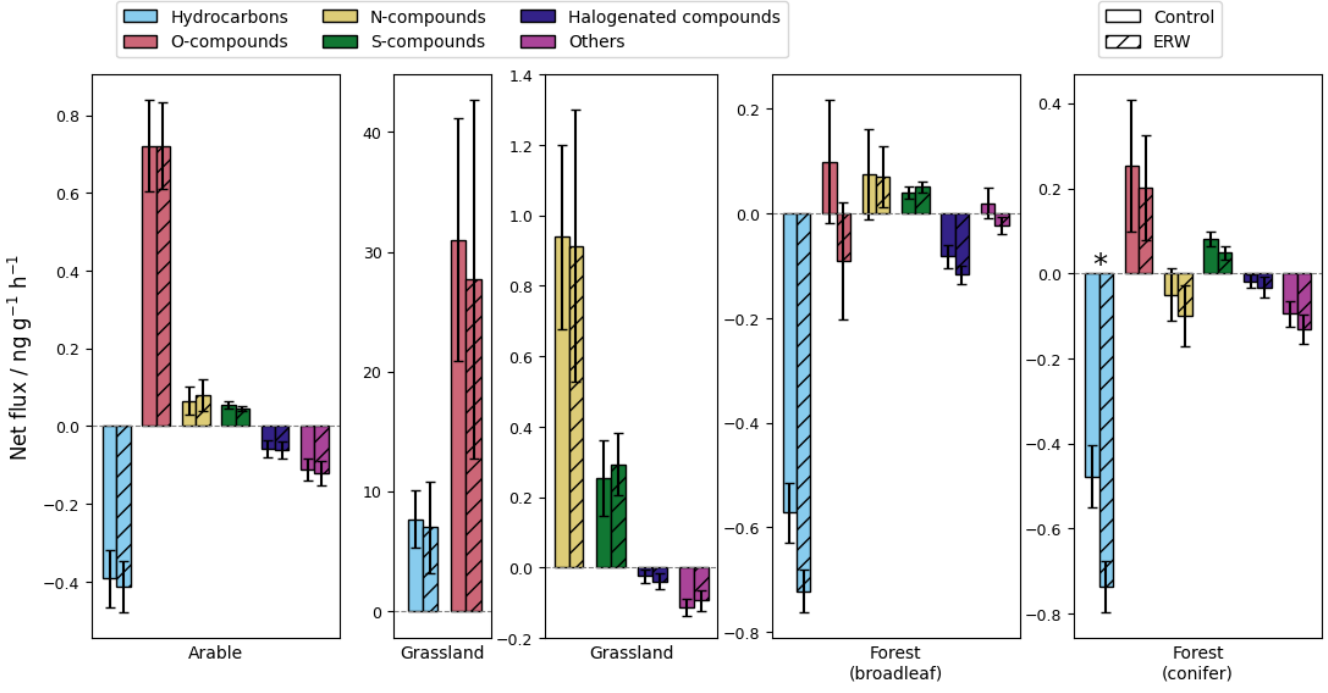

Figure 5. Net fluxes (ng g^{-1} h^{-1}) of different VOC compound types for control (clear bars) and ERW (hashed bars) soils from different land uses, measured at 20 °C The error bars represent standard error. Note that grassland fluxes are represented on two separate axes due to the different scales of fluxes between hydrocarbons and O-compounds versus the other compound types. Asterisks indicate significant difference between control and ERW in Welch two-sample t-test (* P < 0.05, ** P < 0.01, *** P < 0.001).

Analysis of the most abundant individual VOCs (Tables S5–S7; Figs. S3–S5) showed that oxygenated compounds dominated emissions across all land uses. Methyl ethyl ketone (MEK; C_4H_8O, *m/z* 73.065) was the largest emitter in arable and forest

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soils, contributing 20–30 % of total VOC emissions, while acetone (*m/z* 59.049) dominated grassland emissions, contributing 31–37 %. The most strongly absorbed compound in both arable and grassland soils was *m/z* 53.039 (C_4H_4). Fluxes of the dominant emitted and absorbed VOCs were generally similar between control and ERW treatments. Despite the large number of VOCs detected, relatively few individual compounds differed significantly between treatments at 20 °C. Four compounds in arable soil, four in grassland soil, five in broadleaf forest soil and eight in conifer forest soil showed nominally significant differences. Most contributed less than 0.5 % of total VOC fluxes, although naphthalene and related aromatic compounds contributed substantially to the reduced hydrocarbon emissions observed under ERW in forest soils. However, none of the individual VOCs remained significant after correction for multiple testing using the false discovery rate procedure.

4 Discussion

This study trace presents gas fluxes at snapshot in time for four soil land uses from three ERW field trials. Because soil trace gas fluxes vary seasonally and respond to environmental conditions, fertiliser inputs and crop type (Barton et al., 2013; Cowan et al., 2018), the results should be viewed as an initial assessment of ERW effects rather than a complete evaluation. Moreover, the impacts of ERW may evolve over time as feedstocks continue to weather and are reapplied. Comparisons among land uses should also be treated cautiously as the sites differed in ERW application rates and trial durations. However, each site comprised paired control and ERW plots, and the consistent increase in soil pH in ERW-treated plots (Table 1) provides a useful framework for interpreting treatment effects.

4.1 ERW impact on greenhouse gas fluxes

The measured CO_2 fluxes are assumed to primarily reflect microbial respiration because soil preparation removed most living roots. ERW effects on CO_2 emissions varied among the soils representing different land uses, with slightly higher emissions in arable soils but lower emissions in grassland and forest soils, the latter being significant. Previous studies have reported contrasting responses to ERW, including increased CO_2 emissions in agricultural soils (Anthony et al., 2025; Kantola et al., 2023; Li et al., 2025), positive relationships between CO_2 fluxes and ERW-induced increases in soil pH and nutrient availability (Dietzen et al., 2018; Yan et al., 2023), and reduced emissions following ERW application in mesocosm and field studies (Chen et al., 2025; Vienne et al., 2024). Continuous field measurements by Milliken et al. (2025) further showed that differences between ERW and control soils can vary substantially over time, highlighting the importance of seasonal controls such as soil moisture.

The land use-dependent responses observed here are consistent with those reported by Yan et al. (2023). In particular, the lower CO_2 emissions measured in forest soils agree with observations by Chen et al. (2025), Milliken et al. (2025) and Vienne et al. (2024). Although total organic carbon did not differ greatly between treatments, ERW may have altered carbon availability or microbial decomposition processes. Overall, the highly variable responses reported across studies indicate that

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ERW effects on soil CO_2 fluxes are strongly context-dependent and that further research is needed to understand the microbial and biogeochemical mechanisms controlling carbon cycling under ERW.

Arable and forest soils showed a slight net uptake of N_2O, whereas grassland soils were a net source. The high variability observed in grassland N_2O fluxes likely reflects a rewetting effect, as the largest emissions occurred early in the measurement period. Transient increases in N_2O emissions following rapid increases in soil moisture are well documented (Barrat et al., 2021; Medinets et al., 2021). Increased soil pH is generally expected to reduce N_2O emissions by promoting the assembly and activity of N_2O reductase, which catalyses the reduction of N_2O to N_2 (Bakken et al., 2012; Bergaust et al., 2010; Liu et al., 2010). Consistent with this mechanism, a global meta-analysis found that N_2O emission factors increase with decreasing soil pH (Wang et al., 2018).

Previous ERW studies have reported mixed effects on N_2O fluxes. Reductions in N_2O emissions following basalt application have been observed in arable mesocosms (Chiaravalloti et al., 2023a) and grazed grasslands (Anthony et al., 2025), whereas increased emissions following wollastonite addition have been reported in a tropical rubber plantation, potentially due to stimulation of microbial N-cycling pathways (Chen et al., 2025). In contrast, Taylor et al. (2021) found no effect of wollastonite treatment on forest N_2O fluxes over 15 years. In the present study, ERW generally reduced N_2O emissions or increased N_2O uptake relative to controls, but this effect was only significant in arable soil at 20 °C. However, it should be noted that there was added uncertainty in the flux measurements of grassland and forest soils due to concentrations being close to the instrument limit of detection, as well as uncertainty from the aforementioned suspected rewetting emissions spike in the grassland soils, which hinders the comparison of control and ERW soils. Nevertheless, the contrasting responses among studies suggest that ERW impacts on N_2O are strongly context-dependent and may be mediated by changes in microbial nitrification and denitrification processes, warranting further investigation using metagenomic approaches.

Soil CH_4 fluxes reflect the balance between microbial CH_4 production and oxidation. Arable and grassland soils were net sources of CH_4, whereas forest soils were net sinks, likely reflecting differences in drainage and oxygen availability that favour methanogenesis in the former and CH_4 oxidation in the latter. The relationship between CH_4 fluxes and soil pH is complex: increasing pH can stimulate both methanogenesis (Kusin et al., 2025; Wang et al., 1993; Ye et al., 2012) and CH_4 oxidation (Gatica et al., 2020; Hütsch et al., 1994; Levy et al., 2012; Weslien et al., 2009), although CH_4 uptake may plateau above an optimum pH (Abalos et al., 2020; Reddy et al., 2020).

Previous ERW studies have also produced contrasting results. Enhanced CH_4 uptake has been reported in ERW-treated grassland and forest ecosystems (Anthony et al., 2025; Taylor et al., 2021), whereas Chen et al. (2025) observed no effect in a tropical rubber plantation. In addition, Zhang et al. (2024) showed that basalt can stimulate CH_4 production in a methanogen culture. In the present study, CH_4 fluxes were lower in ERW-treated grassland and broadleaf forest soils, although the effect was only significant in the broadleaf forest, while arable and conifer soils showed no significant treatment response. These contrasting findings suggest that ERW effects on CH_4 cycling are highly dependent on site conditions and the relative responses of methanotrophic and methanogenic communities, which warrant further investigation.

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4. 2 ERW impact on NO, NH_3, CO and H_2 fluxes

All soils were net sources of NO, with lower emissions from arable soils than from grassland and forest soils. As with N_2O, NO fluxes are largely controlled by nitrification, denitrification and chemodenitrification processes (Medinets et al., 2015; Pilegaard, 2013). However, the relationship between soil pH and NO emissions is inconsistent across studies, with both increases and decreases in NO reported following liming, depending on soil type and pH range (Gasche and Papen, 1999; Homyak et al., 2017; Nägele and Conrad, 1990; Yamulki et al., 1997). Although modelling studies have predicted reduced NO emissions under ERW due to its expected effects on nitrogen cycling (Beerling et al., 2025; Val Martin et al., 2023), NO emissions were generally higher in ERW-treated grassland and broadleaf forest soils in this study, while little effect was observed in arable and conifer soils. These observations indicate that NO responses to ERW may differ among soils and are not fully captured by current expectations based on pH effects alone. Measurements of nitrification, denitrification and other N-cycling processes are needed to identify the underlying mechanisms and evaluate model predictions.

NH_3 emissions did not differ between control and ERW soils across any land use. These measurements should, however, be interpreted with caution as NH_3 concentrations did not stabilise within the chambers during the 10 min sampling period. The 'stickiness' problem of NH_3 is a well-known limitation of chamber-based NH_3 measurements (Kim et al., 2021a): the airflow rate (~4 m^3 s^{-1}) used in this study may have been insufficient to desorb any NH_3 molecules adsorbed to surfaces such as the chamber walls. Increased soil pH is generally expected to enhance NH_3 volatilisation by shifting the NH_4^+/NH_3 equilibrium towards NH_3 (Kim et al., 2021b; Krichels et al., 2023; Mkhabela et al., 2006; Zhenghu and Honglang, 2000), leading to predictions of increased NH_3 emissions under ERW (Val Martin et al., 2023). However, our results agree with Chiaravalloti et al. (2023b), who also found no statistically significant effect of ERW on NH_3 emissions. Potential explanations include increased soil cation exchange capacity associated with ERW, which can enhance NH_4^+ retention (Beerling et al., 2024; te Pas et al., 2023; Vienne et al., 2022), and enhanced nitrification at higher pH, which could reduce the NH_4^+ pool available for volatilisation (Ge et al., 2025). Further studies combining measurements of soil chemical properties and N-cycling processes are needed, ideally using field-based techniques better suited to NH_3 measurements (Vettikkat et al., 2026).

CO fluxes varied among land uses, with net emissions observed from arable and broadleaf forest soils and net uptake from conifer soils, while grassland soils shifted from uptake at low temperatures to emission at high temperatures. Because measurements were conducted in darkness, CO emissions were likely driven by thermal degradation of organic matter rather than photodegradation (Conrad, 1996; Conrad and Seiler, 1980; van Asperen et al., 2015). Both CO uptake and emission have previously been reported from temperate soils (Cowan et al., 2018; Murphy et al., 2023; van Asperen et al., 2015; Yonemura et al., 2000). While no studies have examined ERW effects on CO fluxes, significantly lower CO emissions from ERW-treated broadleaf forest soils suggest enhanced microbial CO consumption, potentially through changes in soil pH or physical properties affecting gas diffusion.

All soils acted as sinks for atmospheric H_2, with substantially greater uptake in forest soils than in grassland or arable soils. This pattern is consistent with global observations (Ehhalt and Rohrer, 2009) and previous work suggesting that better-aerated

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forest soils favour microbial H_2 oxidation (Cowan et al., 2025). The effect of pH on H_2 uptake remains uncertain, with studies reporting variable or absent pH responses (Fallon, 1982; Popelier et al., 1985; Schuler and Conrad, 1991), and soil pH was not identified as a major driver of H_2 uptake by Drewer et al. (2026). Although ERW-treated soils generally showed slightly greater H_2 uptake, no differences were statistically significant. Given that H_2 uptake is microbially mediated and ERW influenced other microbially controlled trace gases, further investigation of H_2 cycling under ERW is warranted.

4.3 ERW impact on VOC fluxes

Although the effects of soil pH on soil VOC fluxes have not been directly studied, soil pH can affect the various processes that drive VOC fluxes. Soil pH has been found to affect the rate of litter decomposition, although different studies have observed different relationships between pH and decomposition rates (Dawson-Glass et al., 2023; DeForest, 2019; Forey et al., 2015; Fu et al., 2022; McCay et al., 2013; Shen et al., 2021). Soil pH also affects soil bacterial and fungal communities. Studies have generally found that increasing soil pH increases bacterial diversity and biomass, with peak diversity observed around near-neutral soil pH (Bååth and Anderson, 2003; Lauber et al., 2009; Rousk et al., 2010). Similarly, increasing soil pH has been found to increase fungal biomass (Bååth and Anderson, 2003; Carrino-Kyker et al., 2016), as well as affecting the morphology and root colonisation of arbuscular mycorrhizal fungi (Coughlan et al., 2000; Van Aarle et al., 2002). Soil pH has also been found to influence the sorption of VOCs in soils, with the soil composition and VOC chemical structure determining the relationship between soil pH and VOC sorption (Delle Site, 2001; Serrano and Gallego, 2006).

In the arable and grassland soils, ERW treatment had no significant effects on the diversity, total emission, total uptake and net flux of VOCs, nor was there any effect on the fluxes of different compound types and hydrocarbon types. In the forest soils however, there were greater total VOC emissions from control samples (significant at 25 °C in the broadleaf soil and 15 °C in the conifer soil), resulting in greater net uptake by the ERW soils (significant at 25 °C in the broadleaf soil). This was found to result from greater emissions of naphthalene from the control soils of both the conifer and broadleaf forests, also evidenced by the greater emission of total hydrocarbons and aromatic hydrocarbons. The sorption of naphthalene to soil organic matter has been shown to decrease with increasing pH, which is in contrast with the observation in this study of increasing emission of naphthalene with an increased soil pH. However, naphthalene can also be degraded in soils by bacteria and fungi (Park et al., 2001, 1990). Therefore, an explanation for the decreased emissions of naphthalene with ERW treatment could be increased microbial activity from the increased soil pH, resulting in increased biodegradation of naphthalene and therefore reduced emission from the soil. Otherwise, the diversity and fluxes of other VOCs from other compound groups were unaffected by ERW treatment in the forest soils.

ERW treatment altered the fluxes of a few target compounds, although this was land use dependent. The average emission of methanethiol was higher in ERW samples of the grassland soil. This is in line with the findings of a study on agricultural soils, where an increase in methanethiol production was measured with a pH increasing from 4 to 6 (Liu et al., 2017). Methanethiol is produced from the microbial metabolism of sulfur-containing amino acids in soils (Higgins et al., 2006), and so it is possible that these observations result from increased microbial activity in the soil. In the conifer forest soil, the emission of

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monoterpenes from ERW samples was lower than from the control samples. These compounds are likely to arise from needle litter as Sitka spruce trees (the conifer species used in this plantation) emit high levels of monoterpenes (Evans et al., 1985; Furnell et al., 2025; Hayward et al., 2001; Purser et al., 2021). This observation could, therefore, result from a decreased rate of litter decomposition with the increased soil pH leading to decreased volatilisation of the monoterpenes from the needle storage pools. Another possibility is that there is increased microbial activity with the increased soil pH, resulting in increased microbial metabolism of the monoterpenes and therefore lower emissions from the ERW samples.

Overall, despite screening an extensive range of VOCs, ERW treatment altered the fluxes of only a few. Nevertheless, since these changes were enough to alter the net VOC fluxes of the treated forest samples, sustained measurements over time and across multiple field trials are needed to identify whether these responses are consistent and/or land use dependent.

5 Conclusions

This preliminary study examined the effects of ERW treatment on soil trace gas fluxes across arable, grassland and forest ERW field trials in the UK under controlled laboratory conditions. Whilst the soil GHG responses to ERW treatment have previously been reported, the results of this study also include the novel measurements of non-GHG trace gases, such as NO and VOCs, from ERW field trials. ERW altered the fluxes of trace gases in these soils, but the directions of the responses varied between gases and between land uses, with no single consistent pattern. NO emissions were higher in ERW-treated grassland and broadleaf forest soils, contrasting the reductions predicted by current ERW-coupled models. This suggests an incomplete representation of how ERW affects soil N-cycling processes, and marks NO as a priority for reconciling models with observations. Among VOCs, only a few compounds responded to treatment, yet these were sufficient to shift net fluxes in the forest soils. Most notably there were lower naphthalene emission from ERW soils, which runs counter to the reduced sorption expected at higher pH and instead implicates enhanced microbial degradation. This response of a reactive aromatic hydrocarbon to ERW illustrates the need to examine trace gases beyond greenhouse gases in ERW studies.

Whilst this study has examined these changes in the context of the increased soil pH, ERW can simultaneously alter other soil properties (moisture retention, cation availability, microbial community composition) that also regulate trace gas exchange, and their relative contributions cannot be separated here. Resolving them will require trace gas measurements on ERW field trials coupled with in-depth physical, chemical and microbial soil characterisation, sustained over the weathering lifetime of the applied material. For NH_3 in particular, more optimised measurement approaches are also warranted. The understanding of a wider range of trace gas fluxes is necessary to support comprehensive GHG accounting (including direct and indirect climate effects) and to assess potential co-benefits and risks of large-scale ERW implementation.

Code and data availability

Data is being prepared for submission to EIDC.

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Author contributions

JD and KR conceptualised the study. Funding was acquired by MVM. The methodology development and study investigation were conducted by AB, NC, JD, RD, MH, BL, SM and KR. The formal analysis was performed by KR with support from AB, NC, JD and SM. The visualisation and original draft preparation was carried out by KR with supervision from DB, JD and MVM. All coauthors contributed to the review and editing of the manuscript.

Competing interests

At least one of the (co-)authors is a member of the editorial board of Biogeosciences. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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