



Current rates of CO₂ removal due to rock weathering in the UK

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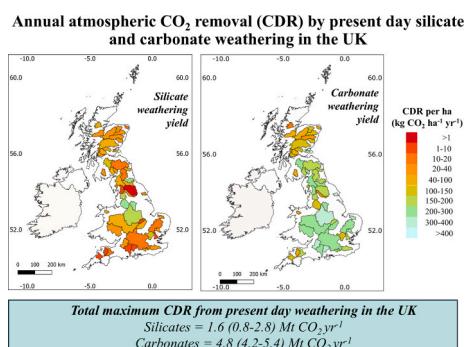
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HIGHLIGHTS

- UK natural weathering could remove 6.4 (4.9–8.1) Mt of atmospheric CO₂ annually.
- 29% of this is derived from silicates and contributes to the longer-term removal of carbon from the atmosphere.
- Sulphuric acid may reduce CO₂ removal from weathering by up to 17% (silicates) and 28% (carbonates).
- Previously proposed additional CDR through enhanced weathering would at least double current UK weathering fluxes.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical weathering of silicate and carbonate rocks via carbonic acid provides a natural sink for carbon dioxide, regulating climate over geological timescales. Although the magnitude of CO₂ removal via weathering has been estimated at a global scale using the geochemistry of the world's largest rivers, it has generally not been quantified at national level. In the United Kingdom, the variable bedrock geology and long-legacy of anthropogenic land use provide challenges to isolating carbonate and silicate mineral weathering, meaning we lack constraint on an important flux in the UK's carbon cycle. Here we use river chemistry data collected over 40 years for 52 catchments across the UK and apply a geochemical inversion model (MEANDIR) to assess the silicate and carbonate contributions to UK river chemistry, and to estimate the CO₂ consumption from natural weathering.

Silicate-derived solutes account for 0–46 % of dissolved river chemistry by mass (median 7 %) and carbonate-derived solutes for 9–82 % (median 49 %), with the remainder attributed to evaporite and cyclic sources. The maximum present-day carbon dioxide removal (CDR) through combined silicate and carbonate weathering is 2.58 MtCO₂ yr⁻¹ for the studied catchments (representing 40 % of total UK area). Extrapolated to the entire UK, the maximum CO₂ consumed by silicate and carbonate weathering is 1.6 (0.8–2.8) MtCO₂ yr⁻¹ and 4.8 (4.2–5.4) MtCO₂ yr⁻¹ respectively. If sulphuric acid replaces carbonic acid in weathering, CDR may be 17 % and 28 % lower for silicate and carbonate weathering respectively. Accounting for sulphuric acid weathering, a conservative estimate suggests a net combined present-day CDR of 4.5 MtCO₂ yr⁻¹ for the UK. This is comparable to the lower-end estimates for potential additional CDR through Enhanced Weathering (EW) in the UK. If EW CDR

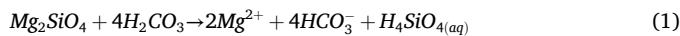
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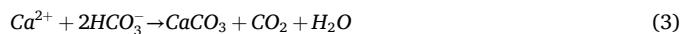
targets are met, EW could more than double the natural weathering flux in rivers, with implications for river chemistry which warrants consideration before national implementation.

1. Introduction

The natural sources and sinks of carbon dioxide are the context in which anthropogenic changes in the carbon cycle are set, and human emissions measured (Friedlingstein et al., 2023). One such sink is the weathering of silicate and carbonate rocks which consumes CO₂ (via Eqs. (1) and (2)) (Berner et al., 1983; Gaillardet et al., 1999). These fluxes can vary spatially (White and Blum, 1995; West et al., 2005; Moon et al., 2014) and temporally (Raymo and Ruddiman, 1992; Tipper et al., 2006), and the environmental drivers of weathering may respond to ongoing future climate and land use change (Regnier et al., 2013; Raymond and Hamilton, 2018; Zeng et al., 2019; Hilton and West, 2020). Identifying the potential variability of these weathering fluxes is crucial to accurately assess the natural carbon cycle. In addition, proposals to enhance mineral weathering (Renforth, 2012; Hartmann et al., 2013; Beerling et al., 2020; Kantz et al., 2022) benefit from knowledge of the baseline natural weathering reactions, as these govern the natural water chemistry and potential for streams and rivers to carry excess solution and carbon species (i.e. Knapp and Tipper, 2022; Zhang et al., 2022; Harrington et al., 2023).



Silicate and carbonate weathering both lead to conversion of soil CO₂ to dissolved inorganic carbon (DIC) to rivers. However, while the DIC from silicate weathering is entirely sourced from CO₂ (Eq. (1)), the DIC from carbonates partially originates from the rock itself (Eq. (2)). Therefore, the total carbon dioxide removed (CDR) due to natural weathering is not equal to the total flux of DIC in rivers. Additionally, due to the eventual re-precipitation of carbonates in the ocean (via Eq. (3)), carbonate weathering does not lead to the long-term removal of CO₂. Therefore, correctly apportioning the DIC between the silicate and carbonate sources is critical when studying the role chemical weathering plays in the natural long-term carbon cycle.



Silicate and carbonate contributions to DIC can be determined from attributing riverine dissolved chemistry to different source endmembers of a known composition or compositional range (Gaillardet et al., 1999; Moon et al., 2014; Tipper et al., 2006). Previous global assessments have demonstrated that natural annual carbon dioxide removal (CDR) due to silicate weathering may range between 330 and 510 Mt CO₂ yr⁻¹ (Gaillardet et al., 1999; Moon et al., 2014), and for carbonates, between 730 and 2570 Mt CO₂ yr⁻¹ (Gaillardet et al., 1999; Zeng et al., 2019). This CO₂ consumption is not evenly distributed globally, due to spatial variations in environmental drivers which are known to influence weathering reactions, such as geological heterogeneity and mineral composition; variability in permeability (Maher, 2011), water availability (Buckingham et al., 2022; Brantley et al., 2023) and the residence time of water within the catchment (Maher, 2011; Maher and Chamberlain, 2014); amount of erosion supplying fresh minerals (Maher and Chamberlain, 2014); temperature; presence of sulphide minerals (Torres et al., 2014; Burke et al., 2018; Hilton and West, 2020; Bufo et al., 2021); and arable land (Perrin et al., 2008; Barnes and Raymond, 2009; Raymond and Hamilton, 2018). As a result, the annual silicate weathering CDR yield of global catchments ranges from 1.2 to 450 kg CO₂ ha⁻¹ (Moon et al., 2014), while carbonate annual CDR yield spans 2 to 1700 kg CO₂ ha⁻¹ yr⁻¹ (Zeng et al., 2019). The UK is typical of many nations, with large spatial variability in catchment characteristics. As such, CDR from weathering may be heterogeneous across the UK, making scaling

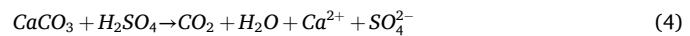
based on global relationships inappropriate to constrain weathering CDR.

The UK's annual riverine DIC flux, and the variation observed between catchments, has been established by two key studies. Jarvie et al. (2017) utilized an extensive geochemical dataset of river chemistry within a carbonate speciation model (THINCARB) to derive DIC flux estimates across all major UK catchments. The study found that average DIC concentrations increased from northwest to southeast, and attribute this to increases in carbonate content within the underlying lithology. Recently, to estimate DIC fluxes and investigate potential environmental drivers of this flux, Tye et al. (2022) performed an extensive year-long sampling campaign across 43 UK catchments, representing 36 % of the UK landmass (8.40 Mha). They report the annual DIC flux to be 647 kt C as DIC yr⁻¹ (equivalent to 2.4 Mt CO₂ yr⁻¹) across the catchments within their study. They also conclude that variability in DIC concentrations is primarily controlled by lithology, while total annual yields are also influenced by water availability.

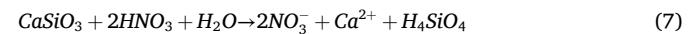
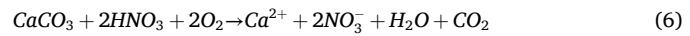
These two studies add to our understanding of the DIC flux and variation in UK rivers. However, the magnitude of CO₂ consumption nationally via the natural chemical weathering of silicate and carbonate minerals is yet to be quantified. This is because the DIC pool represents a mixture of carbonate and silicate weathering inputs but is also potentially influenced by CO₂ evasion from river surfaces, CO₂ inputs from soils and within-stream respiration (Raymond et al., 2013; Ward et al., 2017; Duvert et al., 2018; Dasari et al., 2024). Here, we seek to quantify silicate and carbonate weathering rates across the UK, using dissolved ions that can act as conservative tracers of weathering. We use river geochemical data from catchments representing a broad range in weathering environments. The aims of this work are to (i) provide a value for the annual flux of CO₂ removed due to weathering processes in the UK, and (ii) quantify the spatial and temporal variability of these fluxes across catchments.

An understudied process is the role of strong acids in weathering. Rather than dissolution by carbonic acid, which acts as a sink, these strong acids can lead to CO₂ release. For example, for carbonate dissolution, via Eqs. (4) and (6):

Sulphuric acid



Nitric acid



Sulphuric acid forms from the oxidative weathering of sulphide minerals, common in UK bedrock (e.g. Spears et al., 1999; Spears, 2015; BGS, 2023a, 2023b). However, the distribution of sulphide-rich lithologies is not uniform (Supplementary Information, Fig. 1a) and consequently, it is expected that the underlying geology of a catchment will dictate the extent of sulphuric acid weathering, and therefore the total CO₂ removal due to weathering. Sulphuric acid weathering may be significant: a global study utilising δ³⁴S and river cation concentrations within a geochemical inversion model suggested that 28 % of the total sulphate transported by rivers was derived from the oxidative weathering of pyrite (1.3 ± 0.2 Tmol yr⁻¹) (Burke et al., 2018). A significant source of nitric acid to the weathering zone is fertiliser N, typically ammonium nitrate or urea ammonium nitrate in the UK (National Statistics, 2023). In heavily modified landscapes such as the UK, where 21 % and 52 % of the total land area is arable land and grassland

respectively (Marston et al., 2022), and approximately 87 kg of fertiliser N is applied per hectare per year (DEFRA, 2022a), nitric acid could play a significant role in weathering reactions.

Through the evaluation of the UK's baseline weathering annual CDR fluxes, the objective of this investigation has been to inform future modelling studies, including those of enhanced weathering, and contribute to the current understanding of the United Kingdom's natural

carbon cycling processes.

2. Summary of the approach

The main objective of this study was to assess the natural CDR from weathering in the UK and distinguish the proportion from silicate and carbonate weathering. The following summarizes the approach used:

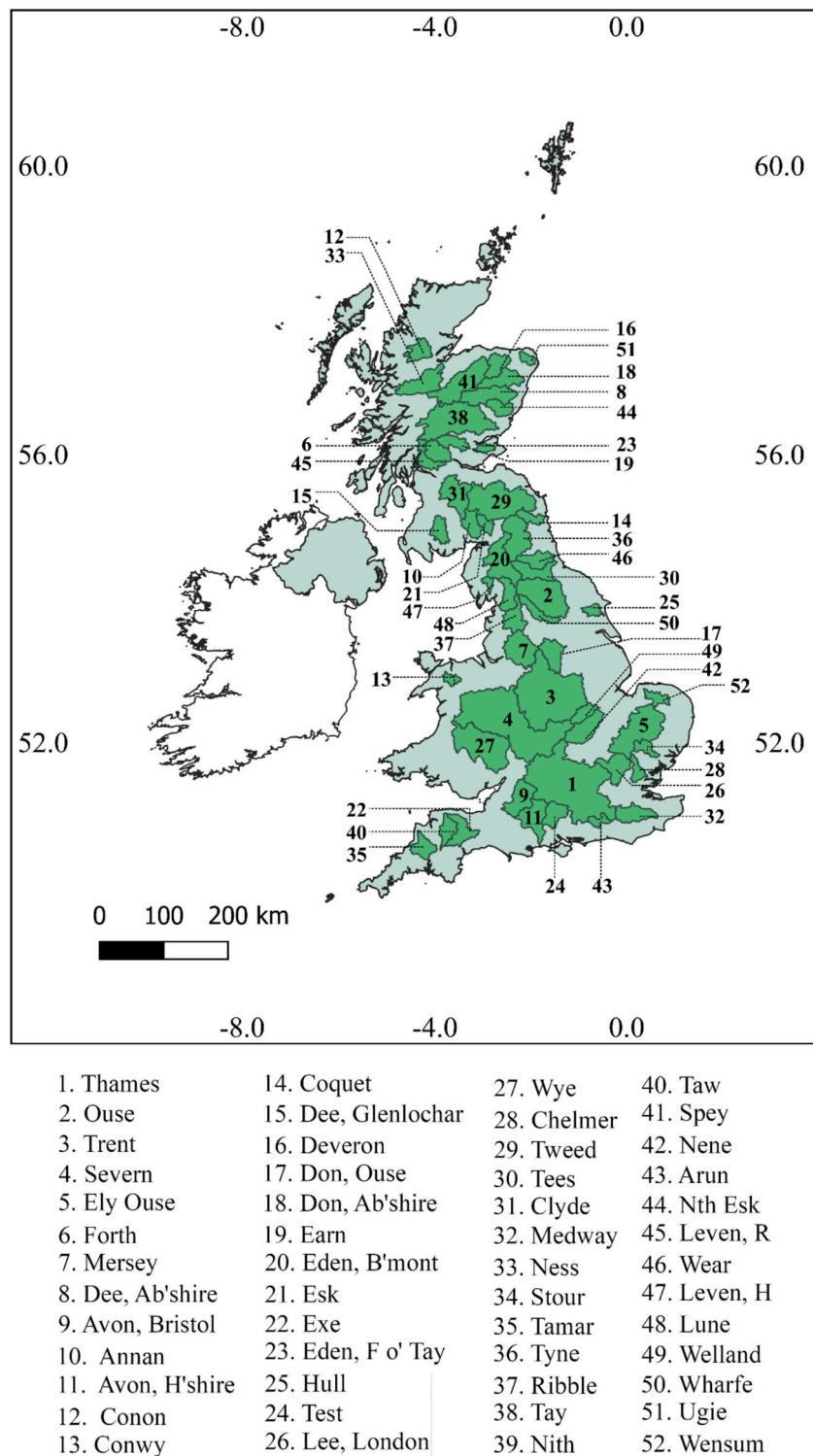


Fig. 1. UK Catchments included in this study. Catchment boundaries were supplied from the National River Flow Archive, by the Centre of Ecology and Hydrology's Integrated Hydrological Digital Terrain Model (IHDTM) (Morris et al., 1990; NRFA, 2023). For specific catchment details see (Supplementary Information Tables A1 and A2 - for area, river flow rate, land use variables and chemistry).

- i) The chemistry of 52 rivers was collated, representing variable UK weathering conditions ([Section 3.1](#)).
- ii) The average DIC concentration was calculated using the natural alkalinity and pH of each river in carbonate speciation equations ([Section 5](#)).
- iii) The portion of DIC from CO₂ (i.e., CDR) was then quantified by assessing the portion of river alkalinity from silicate and carbonates. Under the assumption that: (i) conservative alkalinity is dominated by three main cations (Ca²⁺, Mg²⁺, Na⁺ - see discussion in [Section 4](#)) and (ii) only four endmembers influence their concentrations (silicate, carbonate, evaporite and cyclic sources - see [Section 4](#) for discussion about anthropogenic influences), inversion mixing equations were then used to distribute Ca²⁺, Mg²⁺, Na⁺ between each end-member source. These results are given as fractions ([Section 6.1](#)).
- iv) Fractions of DIC derived from different lithologies were converted to fluxes using river discharge. As the cyclic and evaporite endmembers do not influence CO₂ fluxes, maximum catchment CDR was calculated from the fluxes derived from silicate and carbonate weathering. Here, the term 'maximum' indicates the maximum potential CO₂ consumption from weathering, assuming (i) carbonic acid as the sole weathering reagent, (ii) all products remain dissolved in the water column without secondary mineral precipitation and (iii) before any oceanic processes leading to CO₂ release (i.e. [Section 7.3](#)). Results were collated and upscaled to account for the whole UK land mass. The maximum annual CDR is compared to the total annual DIC to quantify the proportion of DIC from the carbonate rock itself. ([Section 6](#)).
- v) Post inversion, riverine SO₄²⁻ concentrations were then used in simple conservative mixing models to predict the total SO₄²⁻ from sulphides. This value is then used to correct the calculated maximum CDR for strong-acid dissolution ([Section 7.1](#)).

3. UK catchment characteristics

Fifty-two separate UK river catchments were chosen to be included in the study ([Fig. 1](#)) and are assumed to capture the range in weathering styles in the UK due to variations in geology ([Section 3.2](#), Supplementary Information Fig. A1a), topography ([Section 3.2](#), Supplementary Information Fig. A1b), land use ([Section 3.4](#), Supplementary Information, Fig. A2), climate, and water availability ([Section 3.3](#)). The total catchment area of the studied catchments is 9.45 Mha, accounting for 40 % of the total land within the UK (23.35 Mha; [Marston et al., 2022](#)). Variations in catchment parameters are also provided in (Supplementary Information, Table A2).

3.1. River chemistry

UK geochemical data was taken from an extensive dataset from the Harmonised Monitoring Scheme (HMS), Environmental Agency ([DEFRA, 2013](#)), spanning 1970–2013. Rivers from this dataset were only included within the study if the complete suite of geochemical data needed for the inversion and subsequent calculations was available (i.e., Ca²⁺, Mg²⁺, Na⁺, Cl⁻, SO₄²⁻, NO₃⁻, pH, alkalinity, flow rate, temperature). Therefore, for each river, the data was first sorted to exclude any sampling dates without this complete set (provided in datasheets within supporting information). Where data was available, the 20 rivers with the highest flow rate were included ([Marsh et al., 2015](#)). In the event of nationwide implementation of enhanced weathering in the UK, it is anticipated that some application may target catchments with substantial arable land coverage. Consequently, understanding the baseline weathering levels in these catchments is valuable for comparing against the additional contributions resulting from enhanced weathering (such as that calculated in ([Harrington et al., 2023](#))). Accordingly, we prioritised the inclusion of catchments with high arable land content in the study. Only rivers with at least 40 separate measurements (median

number of measurements included in the inversion for each river was 160) were chosen to be included within the study to try to capture the potential seasonal variability in flow and chemistry of each river. [Moon et al. \(2014\)](#) found that the annual silicate weathering rates of global rivers with 40 datapoints was calculated within 40 % uncertainty of those with extensive measurements. However, an exception was made for the Rivers Ouse and Hull (which had only 14 and 21 datapoints with the complete set of geochemical information needed in the inversion respectively) as they are major UK catchments with high arable land content (and therefore potential sites to be used for the application of enhanced silicate weathering, as discussed in [Harrington et al., 2023](#)). There is a need for caution when considering the results of these two catchments.

3.2. Geology and topography

The heterogeneity in bedrock and topography across the UK is likely to influence the chemistry across the catchments within the study. The highlands of NW Scotland are silicate rich and dominated by Precambrian and Cambrian metasediments (Lewisian Gneiss) and meta-igneous intrusions. From the northwest to southeast, lithology gets progressively younger, and the proportion of carbonate lithology increases (Supplementary Information, Fig. A1a). Within the midlands and Wales, carboniferous clays and limestones are also associated with coal measures which are known to have pyrite inclusions ([Spears et al., 1999](#)). High permeability within bedrock can indicate increased weathering within a catchment ([Worthington et al., 2016](#)) due to increased fluid residence times ([Maher, 2011](#)) and therefore an increased flux of weathering sourced solutes to the river. The percentage of high permeability bedrock also increases moving from north to south across the UK. The National River Flow Archive classifies over 70 % of the bedrock in the Ely Ouse, Avon and Stour (Hampshire), Test, Wensum and Hull catchments as highly permeable (these catchments have high proportions of carbonate lithologies). In contrast, 17 catchments in the study have zero bedrock classified as highly permeable (Supplementary Information, Table A2).

Topography in the UK is typically elevated in the northwest of Scotland, North England, and Wales (Supplementary Information, Fig. A1b), however only 8 catchments within the studied regions have maximum elevations >1000 m, and the highest point is ~1300 m (above sea level). Lowland areas are found in the southeast of England, and for 13 catchments the maximum elevation does not exceed 300 m (Supplementary Information, Table A2).

3.3. Hydrology

3.3.1. Rain, evapotranspiration, soil moisture

Chemical weathering rates can be increased by increased water availability and fluid residence time ([Maher, 2010, 2011](#)), and hydrological conditions vary significantly across the UK ([Kay et al., 2013](#); [Buckingham et al., 2022](#)). The average annual UK rainfall is 1175 mm (30-year average, MET office), however this varies across the country due to a rainfall gradient which increases from the southeast to northwest ([Kay et al., 2013](#)). As such, Scotland and Wales have a much higher average annual rainfall than England (1600, 1450, and 875 mm yr⁻¹ respectively), ([NRFA, 2023](#)). In contrast, the potential evaporation (PE) within northern catchments is much lower than the southeast.

The variation in rainfall and evapotranspiration impacts the amount of moisture found within catchment soils. The average proportion of time that soils within a catchment are defined as 'wet' (PropWET, i.e. see Supplementary Information, Table A2; ([NRFA, 2023](#)) also increases from South to North (The National River Flow Archive define this by the time that soil moisture deficits are <6 mm), with catchments in the South East of England having PropWet < 0.3, while Scottish catchments typically have indexes between 0.5 and 0.8 (Supporting Information, Table A2).

3.3.2. River discharge, BFI and aquifer content

There is a dense network of rivers and streams within the UK. The average riverine discharge varies across the catchments within the study by two orders of magnitude (Supplementary Information, Table A1). Within individual catchments, seasonal variation tends towards a winter maximum flow for most rivers in the UK. The seasonal variation is related to temperature, which increases the potential evaporation of catchments to a maximum during the summer months (April–September). Evaporation increases lead to summer declines in flow rates, the impacts of which is most noted in lowland south-eastern areas.

The groundwater stores in the UK are recharged by approximately $7 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ of water annually (Bloomfield et al., 2013), which accounts for 4.2 % of the total riverine discharge to the ocean (Marsh et al., 2015). The main aquifers (the Chalk, the Permo-Triassic sands, the Jurassic limestones and Lower Greensands) appear in the younger geology of the UK (Supplementary Information, Fig. A1a) and are distributed primarily in the southeast of England and Wales. Scotland has no major aquifers.

The baseflow index (BFI) of catchments, the measure of the proportion of river flow derived from stored sources (i.e. aquifers) varies within the catchments studied, from <0.4 in northern catchments, up to 0.9 in the southeast of England (Supplementary Information, Table A2).

3.4. Land use

UK land is extensively used for agricultural purposes. The total area utilized for arable croplands and grasslands was approximately 17.0 Mha in 2021 (4.9 and 12.2 Mha respectively) (Marston et al., 2022). Croplands are heavily distributed around the lowland southeastern areas (Supplementary Information, Fig. A2). Total agricultural land use has been remained between 17 and 18 Mha for the last two decades (2000–2021) (DEFRA, 2022a). The land use values reported here differ slightly to those used in recent DEFRA publications for the same period (i.e. DEFRA, 2022a, 2022b), due to a slight distinction in the categorization of grassland types. Nevertheless, the overall combined land area for grassland and arable land is comparable for both data sources.

4. Inversion methods

4.1. Inverting chemistry to assess the sources of solutes

We inverted selected river chemistry using the geochemical model MEANDIR (Mixing Elements And Dissolved Isotopes in Rivers). MEANDIR is a set of open-sourced MATLAB scripts developed by (Kemeny and Torres, 2021). These scripts employ a Monte Carlo inversion technique to allocate major riverine solutes (X) to their respective end-member sources (i) via mixing equations such as Eqs. (8) and (9):

$$\frac{X}{Na_{river}} = \sum_i \left(\frac{X}{Na}_i \right)^* \alpha Na_i \quad (8)$$

$$\alpha Na_{silicate} + \alpha Na_{carbonate} + \alpha Na_{evaporite} + \alpha Na_{rain} = 1 \quad (9)$$

X refers to the dissolved ions chosen to be included in the inversion. This study uses $X = Ca^{2+}, Mg^{2+}, Na^+$, and Cl^- ; the latter of which is used to define the rain portion (see relevant section below). K^+ is not included in the inversion due to the increased possibility of contamination from an anthropogenic endmember (i.e., K-rich fertiliser). However, K^+ concentrations in all the UK rivers within this study are consistently an order of magnitude lower than Ca^{2+} , Mg^{2+} , and Na^+ -typically constituting <3 % of the total cation flux in all rivers (Supplementary Information, Table A1). Accordingly, disregarding K^+ is assumed to have minimal impact on the overall weathering derived carbon dioxide removal (CDR) flux calculations performed in our study. Similarly, the concentrations of other trace cations (i.e., $Fe^{3+}/Fe^{2+}, Mn^{2+}, Zn^{2+}$), are two orders of magnitude lower than major ions, and therefore will not influence flux calculations substantially. Consequently, the assumption

that weathering mainly contributes Ca^{2+} , Mg^{2+} , and Na^+ to the riverine cationic load is likely valid here.

X is normalised with respect to a certain element (Eq. (8)), to account for variability in absolute concentrations due to dilution or evaporation. Sodium (Na^+) is commonly used as a normalising ion and here, Na^+ is used following the approach of Burke et al. (2018). αNa_i is the proportion of riverine Na^+ from each endmember i , the sum of which should equal 1 (Eq. (9)).

The endmembers which have contributed to the river chemistry, i , are typically silicate, carbonate, evaporite and rain, although other endmembers, such as anthropogenic sources, could be added. Because of the chemical complexity of the anthropogenic endmember, this endmember is dealt with separately by assessing the impact on each main dissolved species independently (mainly SO_4^{2-}, NO_3^- and Cl^-). For a detailed discussion, see Section 7.1 (SO_4^{2-}), Section 7.2 (NO_3^-) and point i (Cl^-). Therefore, the endmembers considered here are i = silicates, carbonates, evaporites and rain (Table 1). We use the rain endmember to correct the river chemistry prior to the inversion to distinguish between rain and evaporites (point (i) below). We define the silicate endmember using local endmember geology (point (ii) below). For the carbonate and evaporite endmember, this study uses global ranges defined previously by Gaillardet et al. (1999), and used in other river inversion studies i.e., (Moon et al., 2014). A discussion on the selection of the carbonate endmember, including the potential to use UK catchments to define a local endmember, is provided in point (iii) below.

4.1.1. Correcting for rain inputs ($Cl_{critical}$)

Although both rain and evaporites are included within the endmember list, the inversion simulation may not correctly apportion solutes between the two sources due to their similar Cl/Na values (Table 1) (Kemeny and Torres, 2021). Therefore, independently estimating the proportion of riverine Cl^- from rain ($Cl_{critical}$) prior to the inversion can increase the ability of MEANDIR to interpret the river chemistry.

The potential average proportion of riverine Cl^- from rain was determined for each river by deriving the ‘critical’ value of Cl^- ($Cl_{critical}$), and using Eq. (10), i.e.-

$$Cl_{critical} = Cl_{rain} * \text{Annual rainfall} / \text{Annual discharge} \quad (10)$$

Average daily rainfall and flow rate for each catchment was obtained from the National River Flow Archive and converted to annual rainfall and discharge. Precipitation chemistry for the UK was obtained from the Environmental Change Network (ECN, 2015). Because precipitation chemistry was collected from sites not directly linked to the catchments, the data from these sources was collated and the average UK rain Cl^- concentration was used for Cl_{rain} ($116.5 \mu\text{mol L}^{-1}$).

$Cl_{critical}$ values for each river varied between 130 and $2600 \mu\text{mol L}^{-1}$, with an average of $290 \mu\text{mol L}^{-1}$. For any data with a $Cl_{river} > Cl_{critical}$, the remaining Cl^- is assumed to be sourced from either evaporites or anthropogenic sources. Sources of pollutive Cl^- to river water include sewage and wastewater inputs, road salts, and certain agricultural fertilizers (Berner and Berner, 2012). While evaporites and rain exhibit similar Cl/Na ratios (1 and 1.15 respectively), anthropogenic sources typically have much higher ratios (Moon et al., 2014). This implies that if there was a significant input of anthropogenic Cl^- into rivers, the Cl/Na ratio would surpass ($Cl/Na > 1.15$).

To minimise the impact of anthropogenic Cl^- , any datapoints with a $Cl/Na_{river} > 1.2$ were excluded from the study. Therefore, the remaining Cl^- is assumed to be entirely sourced from evaporites, i.e. Eq. (11):

$$Cl_{evaporite} = Cl_{river} - Cl_{critical} \quad (11)$$

Discarded datapoints constituted <7 % of the total data (i.e. Supplementary Information, Fig. A4 - for the Severn and the Thames).

Table 1

Endmember compositions used throughout the study. Molar ratios Ca/Na, Mg/Na and Cl/Na are used in the main inversion, while SO₄/Na is used in post-inversion mixing equations to derive $X_{SO_4\text{excess}}$. Values for carbonates are derived from Gaillardet et al. (1999). Silicates are derived from UK small sub-catchments draining silicates (described in Supplementary Information, Section A8). The evaporite endmember was taken from (Moon et al., 2014).

	Silicate		Carbonate		Cyclic		Evaporite	
	Median	Stdev	Median	Stdev	Median	Stdev	Median	Stdev
Ca/Na	0.669	0.77	60	30	0.023	0.01	0.17	0.09
Mg/Na	0.325	0.27	30	15	0.11	0.01	0.02	0.01
SO_4/Na	0.019	0.005	0.06	0.03	0.060	0.01	0.4	0.2
Cl/Na	0	0	0	0	1.15	0.1	1	0

4.1.2. Silicate endmember

The compositional range in the silicate endmember can vary based on the types of silicate rocks present in the catchment, (e.g., primary rocks of volcanic origin or secondary silicates). Consequently, using the global average (as in Gaillardet et al., 1999) may not accurately represent the geochemistry of UK lithologies. Moreover, silicate minerals typically undergo non-stoichiometric weathering, resulting in discrepancies between river dissolved load chemistry and the actual bedrock lithology (Gaillardet et al., 1999). In an attempt to encompass the diversity of UK silicate lithology and account for the non-stoichiometric weathering behaviour of silicate minerals, this study, following (Gaillardet et al., 1999), estimates the local silicate endmember by analysing the chemical loads of four small UK catchments exclusively draining silicates (River Fal, Fowey, Carnon and Wick). These catchments encompass a variety of silicate rock types (muds, sands and siltstones, felsic intrusions), making them representative of numerous UK rivers draining silicate materials.

To find the chemical range of the silicate endmember using these catchment data, we first corrected the dissolved chemistry from these four catchments for rain inputs (Cl⁻) (See Supplementary Information for extended methodology). Once these inputs are removed, it is assumed that the remaining chemical composition of the river water is entirely sourced from silicate lithologies.

The range in Ca/Na and Mg/Na for the Rivers Fal, Fowey, Carnon, and Wick were collated, and the average and standard deviation was selected as the silicate endmember for this study (Supplementary Information, Fig. A5). The value for Ca/Na , with a median of 0.67 mol/mol, is similar to those reported in Moon et al., 2014 (which ranged between 0.1 and 1 mol/mol). The median Mg/Na value was also similar to the globally assumed values of previous work ($Mg/Na = 0.25 \pm 0.2$, and $Mg/Na = 0.1\text{--}0.6$ from Gaillardet et al., 1999; Moon et al., 2014 respectively).

Identifying rivers that drain silicates or carbonates requires focusing on smaller catchments, for which data is more limited than for larger UK rivers, which typically drain heterogeneous bedrock. The four silicate catchments reported here are the only rivers draining exclusively silicates and likely do not represent all UK silicate lithologies. Gaillardet et al. (1999) and references within, showed that rivers draining basaltic terrains have slightly higher Ca/Na (0.5 ± 0.2) and Mg/Na (0.5 ± 0.2) ratios compared to their silicate endmembers. These higher values fall within our silicate endmember range and are still substantially lower than the carbonate endmember. Thus, the presence of mafic rocks in a catchment would likely not significantly impact the results of the inversion.

Although it is assumed that the local geology of these catchments is primarily silicate based, the existence of minor carbonate or evaporite inclusions within the lithology cannot be discounted. Although regional geological maps do not suggest the presence of carbonate or evaporite lithologies in these catchments, even small outcrops of these rock types, known for their increased weathering compared to silicates (Lasaga, 1984) can impact river chemistry. However, the resemblance between the silicate endmember in this study and that in (Moon et al., 2014)

suggests that the potential impact from these sources might be insignificant here.

4.1.3. Carbonate endmember

Our aim focused on defining a UK specific endmember, as silicate rocks can show significant chemical variation and weathering rates due to the diversity of mineralogy across various silicates. In comparison, the simplicity of carbonate chemistry- particularly the lack of Na present in carbonate rocks- suggests that is unlikely that the chemistry of a river draining carbonates would deviate substantially across global catchments. Nonetheless, we investigated possible UK catchments which might serve as a carbonate endmember. Of the potential carbonate rich streams, only eight were included in the HMS dataset, four of which were excluded due to the presence of minor silicate bedrock. After correcting for rainwater inputs and compiling the chemical ratios of the remaining four (Test, Wensum, Piddle and Frome), we observed that the median Ca/Na ($Ca/Na_{carb} = 69$) is within the Gaillardet et al. (1999) range; however the median Mg/Na ($Mg/Na_{carb} = 1.3$) is lower than that of Gaillardet et al., 1999 ($Mg/Na_{carb} = 30 \pm 15$). Both Mg/Na_{carb} and Ca/Na_{carb} exhibit high standard deviation (Supplementary Information, Table A8).

The low Mg in these carbonate catchments could support using a lower Mg/Na_{carb} for the UK. However, the large standard deviation suggests a significant additional cation source (likely Na), making the carbonate ratios unreliable for use here. We therefore opted to retain the carbonate endmember from Gaillardet et al. (1999) and Burke et al. (2018).

4.1.4. Sensitivity tests

Sensitivity analyses were conducted to evaluate the impact of varying the (i) silicate endmember range, (ii) rain correction method, and (iii) cost function used in the inversion. These calculations show that the choice of cost function impacts the calculated CDR from weathering by no more than 1.4 %. A rain correction using Cl critical values results in a 7.7 % (Silicates) and 2 % (carbonates) higher calculated CDR than treating rain as a separate endmember. The silicate endmember choice has the greatest impact on CDR. Utilising UK local endmembers yields CDR estimates 38 % higher than global endmembers of Gaillardet et al. (1999), and 14.8 % higher than Moon et al. (2014). See Supplementary Information Section A8 for extended details on sensitivity analysis.

Other parameter choices needed for the inversion model and further discussion is provided within (Supplementary Information Section A8 and Table A10). Input files containing each river's geochemical data were inverted within MEANDIR using the Oxford University Advanced Research Computing Facility (ARC).

For every sample within a catchment's dataset, the MEANDIR inversion uses the river chemistry and endmember compositional range to predict f_x^i : the fraction of the total riverine concentration of element X derived from endmember i (where X = Ca²⁺, Mg²⁺ and Na⁺, and i = silicate, carbonate, evaporite and rain). These fractions were then used to calculate X_i , the concentration of ion X from each endmember (i) ($\mu\text{mol L}^{-1}$) Eq. (12):

$$X_i = f_X^i * X_{\text{river}} \quad (12)$$

where X_{river} is the total concentration of element X in the river. SO_4^{2-} concentrations are not used in the inversion calculations, however $\left(\frac{\text{SO}_4^{2-}}{\text{Na}}\right)_i$ are used in conservative mixing equations after the Monte Carlo simulations to calculate $X_{\text{SO}_4^{2-} \text{ excess}}$, the ‘excess’ portion of SO_4^{2-} not derived from the four end members (discussed in detail within Section 7.1).

Calculations were performed for each chemical datapoint within a catchment’s dataset. Results from the inversion (the median, 25 and 75 percentile fractions of Ca^{2+} , Mg^{2+} and Na^+ from each endmember source (f_X^i) and the fraction of riverine SO_4^{2-} which is excess), were then collated into output files for each river.

4.2. Calculating weathering fluxes and CO_2 removed

The concentration of each major cation (X) from silicate and carbonate rock weathering was then converted into a flow weighted average flux (Q), using the daily average flow rates given in input files (supporting information) i.e., Eq. (13):

$$Q_X^i (\text{mol s}^{-1}) = X_i^* d / 10^6 \quad (13)$$

where i = silicates and carbonates. Cations derived from evaporitic and cyclic sources do not contribute to carbon drawdown and are not important to the following CDR calculations (see below).

The flux of each cation (X) from silicates (Q_X^{sil}) and carbonates (Q_X^{carb}) was then used to calculate the maximum quantity of CO_2 consumed via weathering ($\text{CO}_{2\text{sil}}$ and $\text{CO}_{2\text{carb}}$) using Eqs. (14) and (15), derived from the Steinour equation, (Renforth, 2019). We assume that (i) all cations remain dissolved in the water column and are transported directly to the ocean without secondary carbonate precipitation, and (ii) carbonic acid is the only weathering agent involved in the reactions (the impact of sulphuric and nitric acids to these calculations is considered in Sections 7.1 and 7.2).

$$\text{CO}_{2\text{sil}} (\text{mol s}^{-1}) = \left(Q_{\text{Ca}}^{\text{sil}} + Q_{\text{Mg}}^{\text{sil}} + Q_{\text{Na}}^{\text{sil}} / 2 \right)^* w \quad (14)$$

$$\text{CO}_{2\text{carb}} (\text{mol s}^{-1}) = \left(Q_{\text{Ca}}^{\text{carb}} + Q_{\text{Mg}}^{\text{carb}} \right)^* w \quad (15)$$

w is the molar amount of atmospheric CO_2 needed to balance 1 mol of Ca^{2+} and Mg^{2+} or 2 mol of Na^+ derived from weathering. The value of w depends on the molar ratio of HCO_3^- to CO_3^{2-} in water. In pure water at pH 7, all carbonate species exist as HCO_3^- , so a divalent cation sourced from silicates will be balanced by 2 mol of atmospheric CO_2 as HCO_3^- ($w=2$). A divalent cation from carbonates will be balanced by 1 mol of HCO_3^- from the atmosphere and one from the rock itself (i.e. Eq. (2)), making $w=1$. In seawater, the HCO_3^- to CO_3^{2-} ratio decreases, influenced by temperature, salinity and pCO_2 of the oceanic water column (Renforth and Henderson, 2017). Thus w decreases to 1.4–1.7 for silicates and 0.4–0.7 for carbonates. Here, we first calculate the maximum land-based CO_2 consumption due to weathering processes using $w=2$ for silicates and $w=1$ for carbonates (Section 6.2). We then calculate the potential reduction in the maximum values presented in (Section 6.2) due to the variation in oceanic carbonate speciation in Section 7.3. We use both the upper range of w ($w=1.7$ (for silicates) and $w=0.7$ (for carbonates)), and the lower range (silicates $w=1.4$ and carbonates $w=0.4$) to highlight the possible uncertainty in the extent of CO_2 re-release in the ocean (Section 7.3).

The fluxes were aggregated and upscaled to annual values using linear interpolation for days without measurement. This upscaling approach may miss flow variations like high flow events or dry periods. To minimise bias, we focused on rivers with extensive datasets (with a median of 146 datapoints per river). To assess how well our data represents flow conditions, we compiled key flow metrics from the NRFA

(NRFA, 2023) for each river (mean, median, standard deviation and the 10th and 90th percentile). These metrics were calculated for both the full NRFA record, and the specific study period (Supplementary Information 2, Flow data). The mean flow rates were 9 % lower than the total NRFA data ($1676 \text{ m}^3/\text{s}$ vs $1761 \text{ m}^3/\text{s}$), indicating that our flux estimates are conservative, and actual fluxes may be 9 % higher.

MATLAB calculated results are given in the supporting information files.

5. Dissolved inorganic carbon (DIC) in UK rivers

Given the average alkalinity and pH of each river (Supplementary Information, Table A1), the average total dissolved inorganic carbon (DIC) concentration is calculated for each catchment using carbonate speciation equations in PHREEQC (version 3) (Parkhurst and Appelo, 2013) and a temperature of 10 °C, the approximate annual average temperature of UK rivers (Jonkers and Sharkey, 2016; Worrall et al., 2022) (Supplementary Information, Fig. A6). Concentrations were then converted to a flow weighted annual flux ($\text{mol CO}_2 \text{ yr}^{-1}$), and flow weighted annual yields ($\text{kg CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$). Combined, this indicates that $\approx 3.4 \text{ Mt CO}_2 \text{ yr}^{-1}$ of DIC is annually transported by the catchments within our study, or $8.4 \text{ Mt CO}_2 \text{ yr}^{-1}$ when upscaling to account for the whole UK land area (23.35 Mha; Marston et al., 2022). Six of the catchments (Tweed, Ouse, Wye, Thames, Severn and Trent) transport 45 % of this flux (Supplementary Information, Table A3).

The total UK annual DIC flux reported in this study is slightly higher than given in Tye et al., 2022. They report an annual DIC flux of $647 \text{ kt C DIC yr}^{-1}$ for 2017 (or $2.37 \text{ Mt CO}_2 \text{ yr}^{-1}$) for the catchments that they studied, which represented 36 % of the total land area in the UK. Extrapolating their reported value by UK land mass results in a value of $6.6 \text{ Mt CO}_2 \text{ yr}^{-1}$. Jarvie et al. (2017) did not report a total annual DIC flux for their study catchments, making direct comparison with this study and Tye et al. (2022) challenging. However, Jarvie et al. (2017) did calculate 2007 annual fluxes for seven major British rivers (Trent, Severn, Thames, Tay, Ely Ouse, and Ouse), which are slightly higher than those calculated in our study (Supplementary Information, Table A3). Differences between DIC concentrations between this study, Jarvie et al. (2017) and Tye et al. (2022) likely stem from the inclusion of different catchments and variations in the sampling period. Bell et al. (2021) suggest an inter-annual variability in the UK DIC flux, ranging between 2000 and 3000 kT C yr^{-1} ($7.3\text{--}11.0 \text{ Mt CO}_2 \text{ yr}^{-1}$), likely due to annual variations in flow rates, as well as weathering conditions affecting riverine chemistry and DIC fluxes.

Observing the variation in DIC concentrations across the UK suggests that much of this DIC may be sourced from the weathering of carbonate lithologies, a link which was also made previously by (Jarvie et al., 2017; Tye et al., 2022). There is a significant increase in DIC from the northwest of Scotland to the southeast of England (ranging $200\text{--}5100 \mu\text{mol L}^{-1}$, see Fig. A6, Supplementary Information), corresponding with the increase in carbonate lithological units. This link is also supported by a broad correlation between Ca^{2+} and DIC concentrations and the average DIC yield per hectare (Supplementary Information, Fig. A3a, b).

Increased riverine molar ratios Ca/Na and HCO_3/Na can also be used to infer an increased contribution from carbonates, given the large variation in the end-member chemical ratios of silicate and carbonate lithologies (Table 1) (Gaillardet et al., 1999). There is a large range in Ca/Na and HCO_3/Na within the UK rivers (Supplementary Information, Fig. A3.b). Values typically increase from the northwest to southeast, with the lowest in River Conon ($\text{Ca}/\text{Na}=0.2$) and the highest in the River Test, Hampshire ($\text{Ca}/\text{Na}=5.4$).

The variation in DIC concentrations and chemical ratios initially suggest that (i) lithology plays a dominant role in determining the chemistry of UK rivers, (ii) carbonate weathering dominates the DIC load, and (iii) southeastern catchments may be the most productive exporters of DIC to the ocean. However, the NW-SE trend in DIC

concentration (Supplementary Information, Fig. A6a) also mirrors the NW-SE hydrological gradients discussed in (Section 3.3), and when converting from concentration into flux weighted annual yields, it is catchments within the middle of the UK (Wales, Midlands) which are the most productive annual exporters of DIC (Supplementary Information, Fig. A6b). This suggests that high riverine DIC concentrations do not necessarily imply high export of DIC in UK rivers, and that this export is not only influenced by lithology, but by other catchment parameters, such as hydrology, topography, and land use (discussed in Section 6.2).

6. Silicate and carbonate contributions to DIC

6.1. Sources of solutes

The inversion results suggest that the total fraction of dissolved cations derived from combined silicate and carbonate rock weathering in UK rivers ($f_{total}^{weathering}$, i.e. $f_{Ca}^{sil+carb} + f_{Mg}^{sil+carb} + f_{Na}^{sil+carb}$) averages 60 %; ranging from 23 % (River Conon, Scotland) to 84 % (River Test, Hampshire). These overall contributions by silicate and carbonate weathering reactions align with the global values given in (Gaillardet et al., 1999). Of the total, the average percentage of solutes sourced from silicates is 7 % (0.3 %–46 %), and 49 % from carbonates (9 %–82 %) (Fig. 2).

The remaining dissolved ion load derives from, in part, evaporite weathering and cyclic (rain) sources. Rivers draining Scotland, with high discharges and relatively low cation concentrations (Supplementary Information, Table A1), typically have higher percentages of solutes sourced from rain (i.e. Fig. 2). The high dissolution kinetics of evaporitic rocks means that even the presence of small outcrops within a catchment can influence catchment chemistry by contributing a substantial amount of Na^+ , Cl^- , and, depending on evaporite composition, SO_4^{2-} , to rivers (Berner and Berner, 2012). For instance, the Trent and Don catchments have Na^+ , Cl^- and SO_4^{2-} concentrations 3–4 times higher than the average across the catchments within the study (Supplementary Information, Table A.1). This is consistent with the British Geological Survey's report of evaporite deposits within the Mercia mudstone

formation, (BGS, 2023b) which outcrops throughout these catchments. These observations support the inversion results, which indicate high evaporite contributions within these catchments (i.e. Fig. 2).

6.2. Annual land-based CDR from natural weathering in the UK (maximum)

The inversion calculations suggest that the maximum total annual CO_2 consumed due to silicate weathering for the catchments within the study is 0.63 (0.31–1.12) Mt $\text{CO}_2 \text{ yr}^{-1}$, (Table 2). Under the simple assumption that these 52 catchments capture the range in weathering conditions in the UK (i.e., from differences in geology, topography, temperature, land use and water flux, discussed in Section 2), upscaling these values to account for the whole UK landmass (23.35 Mha) (Marston et al., 2022) leads to a national maximum silicate CO_2 consumption rate of 1.6 Mt $\text{CO}_2 \text{ yr}^{-1}$.

In comparison, the maximum annual quantity of CO_2 consumed due to carbonate weathering for the catchments combined is 1.95 (1.7–2.2) Mt $\text{CO}_2 \text{ yr}^{-1}$. Upscaling this in the same way to account for the whole UK landmass increases this value to 4.8 Mt $\text{CO}_2 \text{ yr}^{-1}$ (Table 2). This leads to a combined maximum for present-day CDR for UK land of 6.4 Mt CO_2

Table 2

Maximum consumed annual CO_2 due to silicate and carbonate weathering in the catchments studied, and upscaled to include the whole UK landmass. Silicate and carbonate CDR fluxes do not equal the riverine DIC flux because some riverine DIC is sourced from the carbonate rock rather than from the atmosphere. Maximum values are based on the assumption that all weathering occurs via carbonic acid, and are prior to correction to account for oceanic processes.

	DIC flux Mt $\text{CO}_2 \text{ yr}^{-1}$ (this study)	CDR silicates Mt $\text{CO}_2 \text{ yr}^{-1}$ (w = 2)	CDR carbonates Mt $\text{CO}_2 \text{ yr}^{-1}$ (w = 1)	CDR total Mt $\text{CO}_2 \text{ yr}^{-1}$
Studied rivers	3.4	0.63 (0.3–1.1)	1.95 (1.7–2.2)	2.58 (2.0–3.3)
UK total	8.5	1.6 (0.8–2.8)	4.8 (4.2–5.4)	6.4 (4.9–8.1)

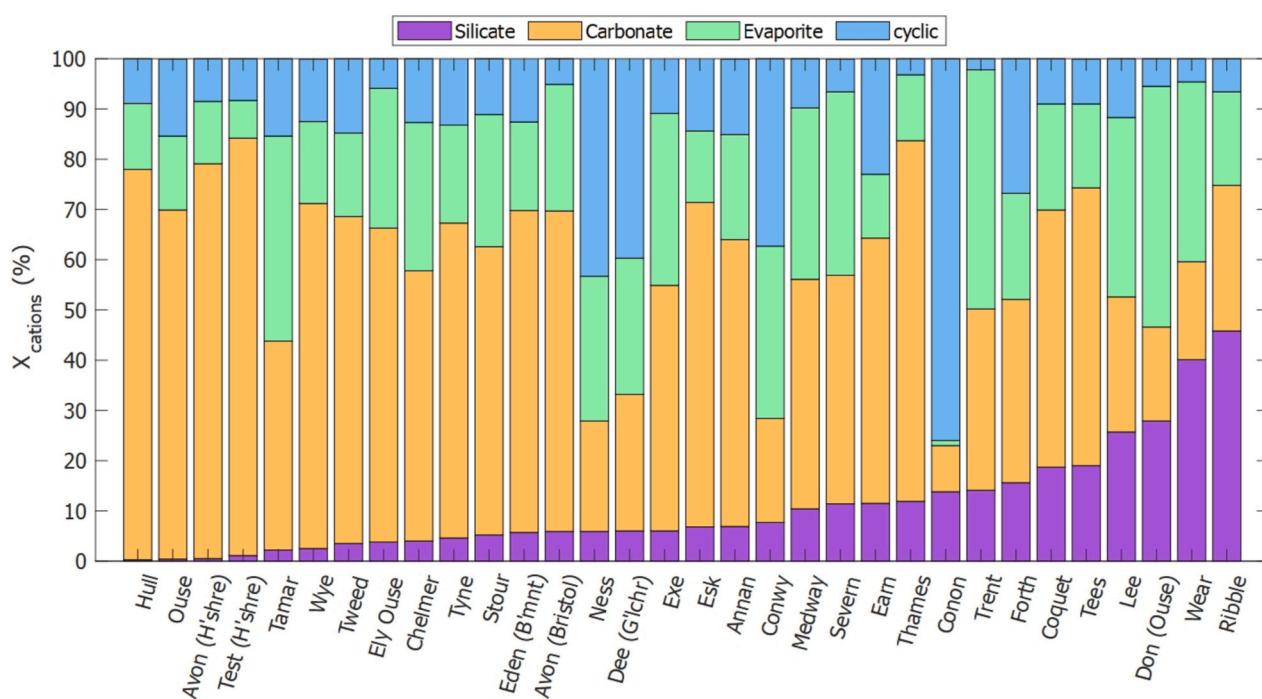


Fig. 2. Results of the inversion showing the fraction of total major cations (Ca^{2+} , Mg^{2+} , and Na^+) from each source endmember i (where i = silicate, carbonate, evaporite and rain) in UK rivers, following (Gaillardet et al., 1999). Rivers are ranked in ascending order of silicate %. H'shre = Hampshire, B'mnt = Beaumont, G'lchr = Glenlochar.

yr^{-1} .

The annual CO_2 yield due to carbonate weathering increased from north to south (Fig. 3b). High annual yields were typically observed in catchments with increased carbonate lithologies, i.e. those that drain the chalk aquifers (i.e., Thames, Hull, Stour, Avon (Hampshire), Test), or

Jurassic Ooidal limestone (i.e., Severn, Avon (Bristol), Trent) (Geology: Supporting Information, Fig. 1A and yield: Fig. 3b). High carbonate yields were also seen in catchments within the north of England and the south of Scotland (Clyde, Tees, Esk, Eden), likely due to the presence of localised limestone bedrock. Carbonate rich lithology that may have

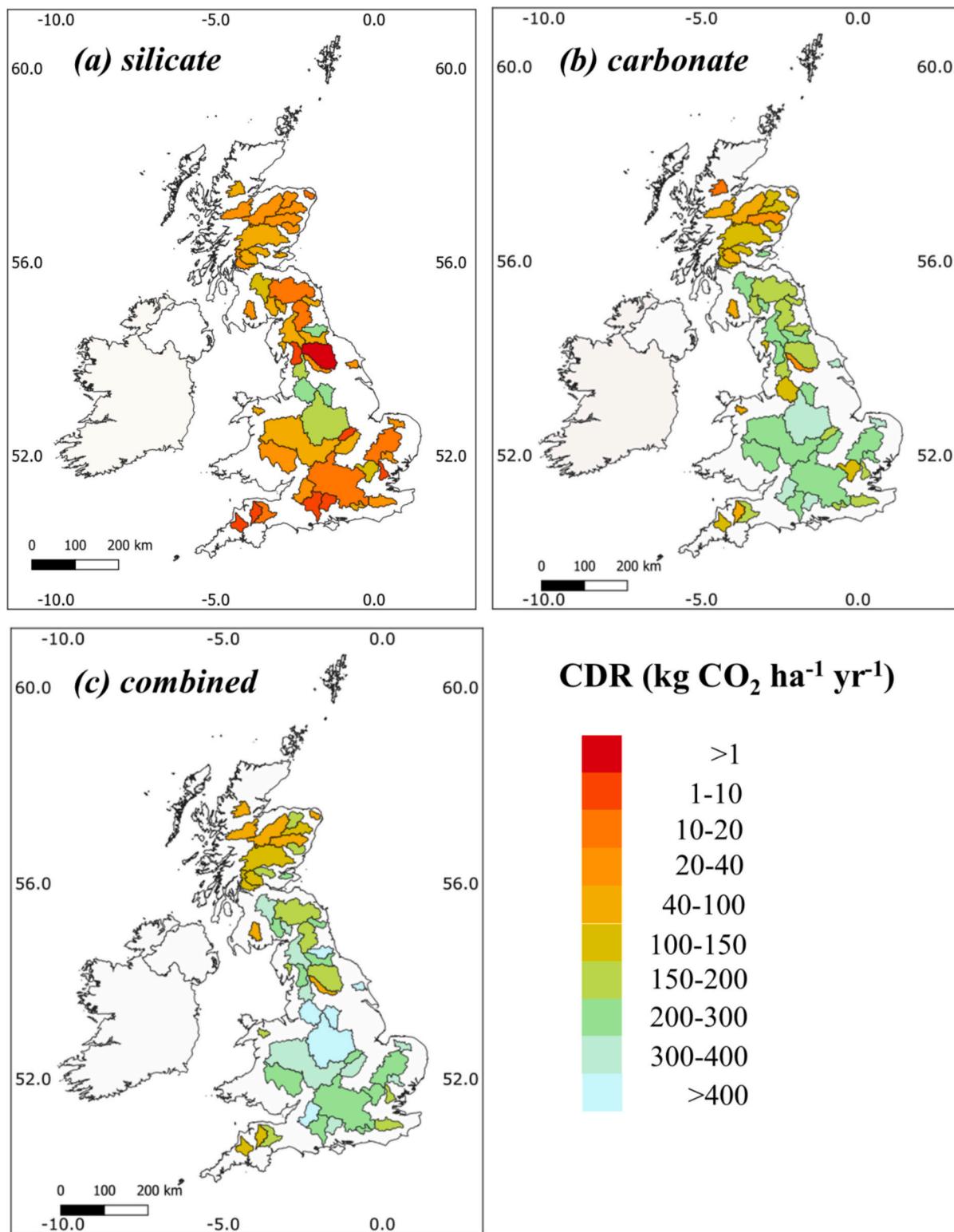


Fig. 3. The potential maximum annual CDR yield due to present day (a) silicate and (b) carbonate weathering in the catchments within the study. (c) is the total combined annual CDR for present day weathering. Annual yields are calculated from the median fraction of ions from silicate and carbonate sources as predicted by the inversion results (See supporting information for extended tabulated results).

contributed to the high yields within these catchments include the Clackmannan group, part of the limestone coal formation (Clyde, Eden) (Vincent et al., 2010), the Edlington, Seaham and Roxby formations (Tees) (Tucker, 1991), and the Yoredale group (Esk) (BGS, 2023c). The annual CO₂ yield due to silicate weathering varied significantly across the UK (Fig. 3a). There are typically higher CO₂ yields from silicate weathering in silicate rich, Scottish catchments, and lower yields are seen in catchments which drain the chalk (Fig. 3a).

Regressions did not reveal any relationship between environmental parameters and silicate weathering annual yields (Supplementary Information, Figs. A7 and A8) at national scale, although there were initial indications of lithology imparting some control over yield when comparing sites of high yields (Fig. 3) with UK geology (Supplementary Information, Fig. A1). This aligns with previous global findings, which suggest that determining the main control over silicate weathering rates can be challenging because yields can be governed by multiple catchment parameters simultaneously (West et al., 2005). Conversely, the regressions revealed clear relationships between annual carbonate yield and various climatic, geomorphic and land use characteristics of the catchment areas (i.e., percentage arable land, runoff, elevation, permeability, (Supporting Information, Figs. A7 and A8)) at national scale. However, these patterns co-vary with the NW-SE pattern in lithology seen across the UK. Consequently, it is challenging to isolate the key environmental drivers of carbonate weathering, because the presence (or absence) of carbonate lithologies is likely to be a primary factor driving variations in annual carbonate yield.

This maximum CDR describes only the contribution of weathering products transferred by rivers. Groundwater aquifers also play a significant role in weathering due to prolonged water-rock interactions. The calculated CDR value includes groundwater that recharges into rivers but excludes submarine groundwater that discharges directly to the ocean. Consequently, the actual CDR from silicates and carbonates may be higher than the values given in Table 2. To effectively compare catchments of different sizes, the annual CO₂ flux sequestered during weathering for each catchment was converted to annual yield. The average carbonate weathering annual CDR yield in UK catchments was significantly higher than silicate yield: 196 and 64 kg CO₂ ha⁻¹ yr⁻¹ respectively.

Approximately 2.8 Mt of Agri-lime (CaCO₃) is applied to UK fields annually (DEFRA, 2022c). If some Ca²⁺ from Agrilime enters rivers and balances with DIC (as HCO₃⁻), a portion of the estimated annual DIC flux (8.4 Mt CO₂ yr⁻¹) may originate from the dissolution of added CaCO₃ rather than from weathering of existing soils or bedrock. Given that lime is applied to acidic topsoil where it rapidly dissolves, its contribution to riverine DIC may be significant. In a hypothetical maximum scenario where all lime derived Ca²⁺ enters rivers (1.1 Mt Ca yr⁻¹) and is entirely balanced by HCO₃⁻, then a maximum 2.2 Mt DIC yr⁻¹ in rivers may originate from lime, accounting for 26 % of riverine DIC.

Although our method cannot differentiate between the carbonates from natural sources and lime due to their similar chemistry, this distinction is less critical for our discussion here since it does not impact the overall CO₂ consumption from carbonates. Nonetheless, initial evidence suggests that the annual CDR from carbonates is primarily driven by natural weathering rather than lime. Firstly, lime is added to less than 1Mha of UK land (i.e. 6.4 % of all UK tilled crops and grasslands were limed in 2020, (0.7Mha), DEFRA, 2022c), and the observed lithological control on carbonate yield and the positive relationship with arable land means that many of the top carbonate yielding catchments are unlikely to be limed (Fig. 3, and see Supplementary Information, Fig. A2 (UK geology) and Fig. A8 (correlations between yield and catchment parameters)). Additionally, there was a significant decline in lime production and application to UK soils in the UK from 1995, which did not lead to corresponding decreases to the calculated flux of riverine Ca from carbonates in any of the top yielding catchments (Fig. A11). Diverse lithologies exist in the catchments within Fig. A11, with varying carbonate content and potential for liming. Despite this, no

corresponding decrease occurred, indicating that broadly river chemistry may not have been significant modified following the decline in liming in 1995.

7. Factors that may make the maximum annual CDR value an over-estimate

7.1. Sulphuric acid mediated weathering

When sulphuric acid (H₂SO₄) replaces carbonic acid (H₂CO₃) as the reagent in weathering reactions, no CO₂ is consumed via silicate weathering, while CO₂ is released in carbonate weathering (Burke et al., 2018; Hilton and West, 2020). As sulphate ions (SO₄²⁻) are released from sulphuric acid weathering (via Eqs. (4) and (5)), variations in riverine SO₄²⁻ can be used to estimate the extent of sulphuric acid weathering within a catchment. However, there are multiple potential sources of SO₄²⁻ to rivers: sulphides, evaporites, non-sulphide silicates, volcanic deposition, biogenic emissions, and agricultural fertilizers. The goal of this section is to extract the sulphide portion of riverine SO₄²⁻ and use this to correct the calculated maximum values for CDR caused by the presence of some sulphide weathering (Net CDR_{sil} and Net CDR_{carb}).

7.1.1. Variations in riverine SO₄²⁻

Sulphate concentrations increase significantly from the northwest to the southeast. Rivers within Scottish catchments have SO₄²⁻ concentrations typically below <200 μmol L⁻¹, while south-eastern catchments have concentrations of up to 2000 μmol L⁻¹ (i.e., Supplementary Information, Table A1). There are at least 4 possible explanations for this NW-SE increasing trend:

- i. Higher water availability in the northern catchments (due to increased rainfall caused by the NW-SE rain gradient discussed in Section 3.3); typically leading to dilution in Scottish catchments, and higher evapotranspiration and lower flows concentrating sulphate within south-eastern catchments (Kay et al., 2013)
- ii. An increase in evaporite deposits moving south from NW Scotland, predominately associated with Permian-Triassic sediments in Yorkshire and the Midlands (Howard et al., 2008; Newell, 2018)
- iii. An increased contribution from sulphides from Carboniferous coal deposits and late-Triassic/Jurassic sediments (i.e., Supplementary Information, Fig. A1a)
- iv. An increased contribution from sulphate derived from agricultural fertilizers, as arable land content increases towards the southeast (Supplementary Information, Fig. A2).

Sulphate concentrations are converted into annual flux-weighted yields to investigate the impact of water availability, i.e., point (i). This reveals that although southeastern catchments have higher sulphate concentrations, it is the Midlands catchments which have the highest overall sulphate yields per hectare (Fig. 4a). These high yields could equally result from an increased contribution of sulphides or evaporites: given the presence of both Carboniferous coal deposits and evaporitic deposits (i.e. the Mercia Mudstones) (Newell, 2018) in the region. To disentangle (and remove) the evaporite contribution to better predict the amount of sulphate from sulphides, this study follows the methodology of (Burke et al., 2018) to calculate X_{excess SO₄²⁻}, the proportion of riverine sulphate which is not derived from evaporites and non-sulphide silicates.

7.1.2. Predicting the proportion of riverine sulphate from sulphides

The methodology for calculating X_{excess SO₄²⁻} has been introduced previously in (Burke et al., 2018; Kemeny and Torres, 2021). Briefly here, once the Monte Carlo simulation within MEANDIR has best fit the major cations (Ca²⁺, Mg²⁺, Na⁺) to their sources, a conservative mixing

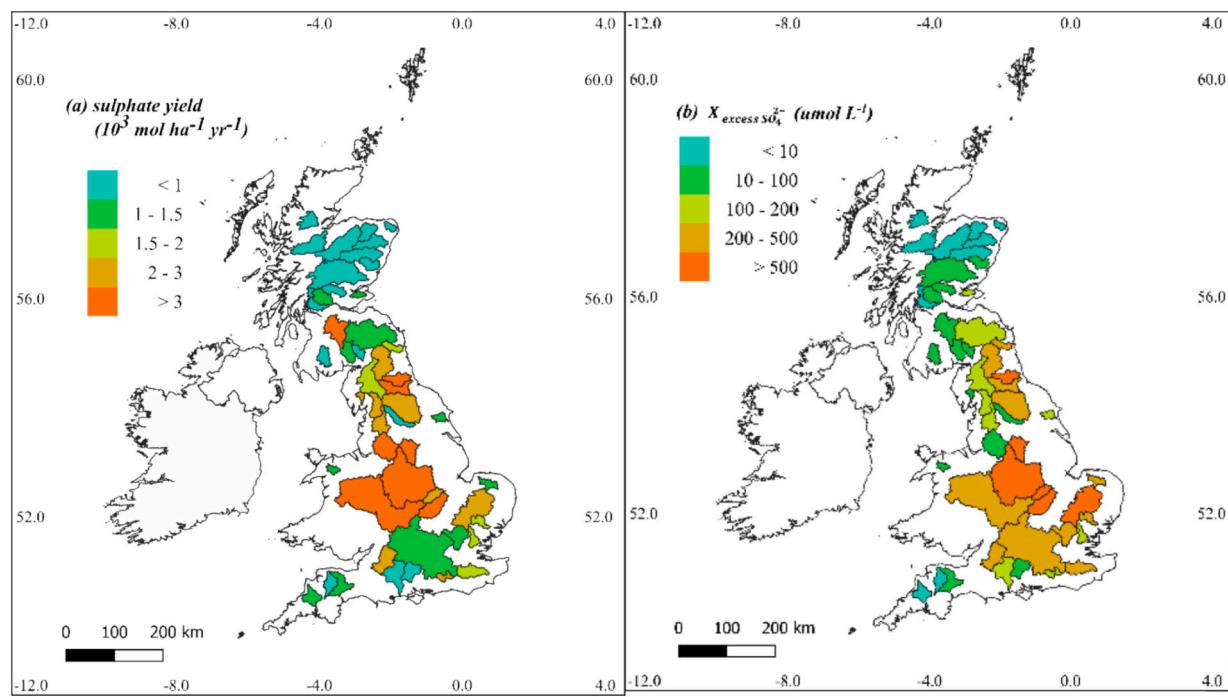


Fig. 4. Presents the contrast in (a) sulphate yields ($\text{mol ha}^{-1} \text{ yr}^{-1}$) and (b) the amount of total sulphate from excess ($\mu\text{mol L}^{-1}$) for the catchments in the study. See main text for details on excess sulphate.

equation will then attribute a portion of riverine SO_4^{2-} to each endmember, given the endmember's $\text{SO}_4^{2-}/\text{Na}$ ratio (Table 2). Any SO_4^{2-} unaccounted for by the four endmembers is the excess sulphate ($X_{\text{excess SO}_4^{2-}}$), i.e., Eq. (16)-

$$X_{\text{excess SO}_4^{2-}} = X_{\text{river SO}_4^{2-}} - \sum [\text{SO}_4^{2-}i]^n \quad (16)$$

where $\sum [\text{SO}_4^{2-}i]^n$ is the sum of contributions of sulphate from each endmember (i), and n is the number of endmembers (i.e., 4). This remaining excess riverine SO_4^{2-} ($X_{\text{excess SO}_4^{2-}}$) will be a combination of SO_4^{2-} sourced from volcanic atmospheric deposition, biogenic emissions, anthropogenic pollution, and the oxidative weathering of pyrite.

Results derived from the conservative mixing equations in MEANDIR suggest that the fraction of $X_{\text{excess SO}_4^{2-}}$ relative to the total riverine SO_4^{2-} , varies considerably amongst UK catchments- from 0 % in some Scottish catchments, to up to 92 % in the River Nene catchment, a range similar to that of global rivers derived in (Burke et al., 2018). Like sulphate concentrations, $X_{\text{excess SO}_4^{2-}}$ in UK rivers increases in a NW-SE direction (Fig. 4b), however, converting to a flux weighted yield suggests that it is again the midlands catchments which transport the most annual $X_{\text{excess SO}_4^{2-}}$ per hectare.

$X_{\text{excess SO}_4^{2-}}$ is corrected for volcanic atmospheric deposition and biogenic emissions, given that these sources account for an average of 7 % and 3 % of global river sulphate concentrations, respectively (Meybeck, 2003). The remaining riverine SO_4^{2-} ($\text{SO}_4^{2-}\text{corrected} = \text{River SO}_4^{2-} - \text{SO}_4^{2-}$ (evaporite + non-sulphide silicate + volcanic + biogenic)) will be from a mixture of two sources: sulphides and agricultural fertiliser. It is difficult to accurately disentangle these two sources without extra data (for instance, through $\delta^{34}\text{S}$ water measurements) (Relph et al., 2021). This study therefore assumes that the remaining $\text{SO}_4^{2-}\text{corrected}$ is completely derived from sulphide oxidation ($\text{SO}_4^{2-}\text{sulphide}$), and values given below are therefore conservative. This $\text{SO}_4^{2-}\text{sulphide}$ is apportioned between the carbonate and silicate endmembers in the ratio of weathering on the catchment to correct the maximum calculated CDR in

Section 6.2 (for details, see Supplementary Information, Section A11).

7.1.3. Corrected annual CDR

The corrected CDR due to sulphuric acid weathering of silicates and carbonates (*Net CDR_{sil}* and *Net CDR_{carb}*) can then be equated by Eqs. (17) and (18), i.e.-

$$\text{Net CDR}_{\text{sil}} (\text{mol s}^{-1}) = \text{Max CDR}_{\text{sil}} * (100 - \% \text{H}_2\text{SO}_4) \quad (17)$$

$$\text{Net CDR}_{\text{carb}} (\text{mol s}^{-1}) = \text{Max CDR}_{\text{carb}} * \underbrace{(100\% - \% \text{H}_2\text{SO}_4)}_{\text{Reduced drawdown}} - \underbrace{\text{Max CDR}_{\text{carb}} * \% \text{H}_2\text{SO}_4}_{\text{Re-released CO}_2} \quad (18)$$

where $\% \text{H}_2\text{SO}_4$ is the percentage of the total acid involved in weathering reactions that was H_2SO_4 . The results suggest that the impact of sulphuric acid weathering on the quantity of CO_2 consumed due to silicate and carbonate weathering is highly variable across catchments (Fig. 5a, b). Scottish catchments, with very low $X_{\text{excess SO}_4^{2-}}$, see very small corrections to natural weathering CDR. In contrast, the annual CDR of weathering in catchments in the middle of the UK must be significantly corrected to account for sulphuric acid weathering. Large catchments such as the Severn, Trent and Ouse, experience 17 % 24 % and 35 % reductions in CO_2 consumed by carbonate weathering when sulphuric acid is considered in the equations (Fig. 5, and see Supporting Information, Document 2). Combined, the calculated maximum CO_2 consumed by silicate weathering in the 52 UK catchments studied is reduced by a maximum of 17 % (11–25 %), lowering annual CO_2 consumed from $0.63 \text{ Mt CO}_2 \text{ yr}^{-1}$ to 0.52 (0.47 – 0.56) $\text{Mt CO}_2 \text{ yr}^{-1}$. In comparison, the calculated maximum annual quantity of CO_2 consumed by carbonate weathering is reduced by 28 % (21–40 %); from $1.95 \text{ Mt CO}_2 \text{ yr}^{-1}$ to 1.31 (1.16 – 1.46) $\text{Mt CO}_2 \text{ yr}^{-1}$.

7.2. Nitric acid weathering

Another important feature in weathering landscapes is the potential for nitric acid to replace carbonic acid in weathering reactions. Nitric acid is produced through the biological fixation of soil ammonium and,

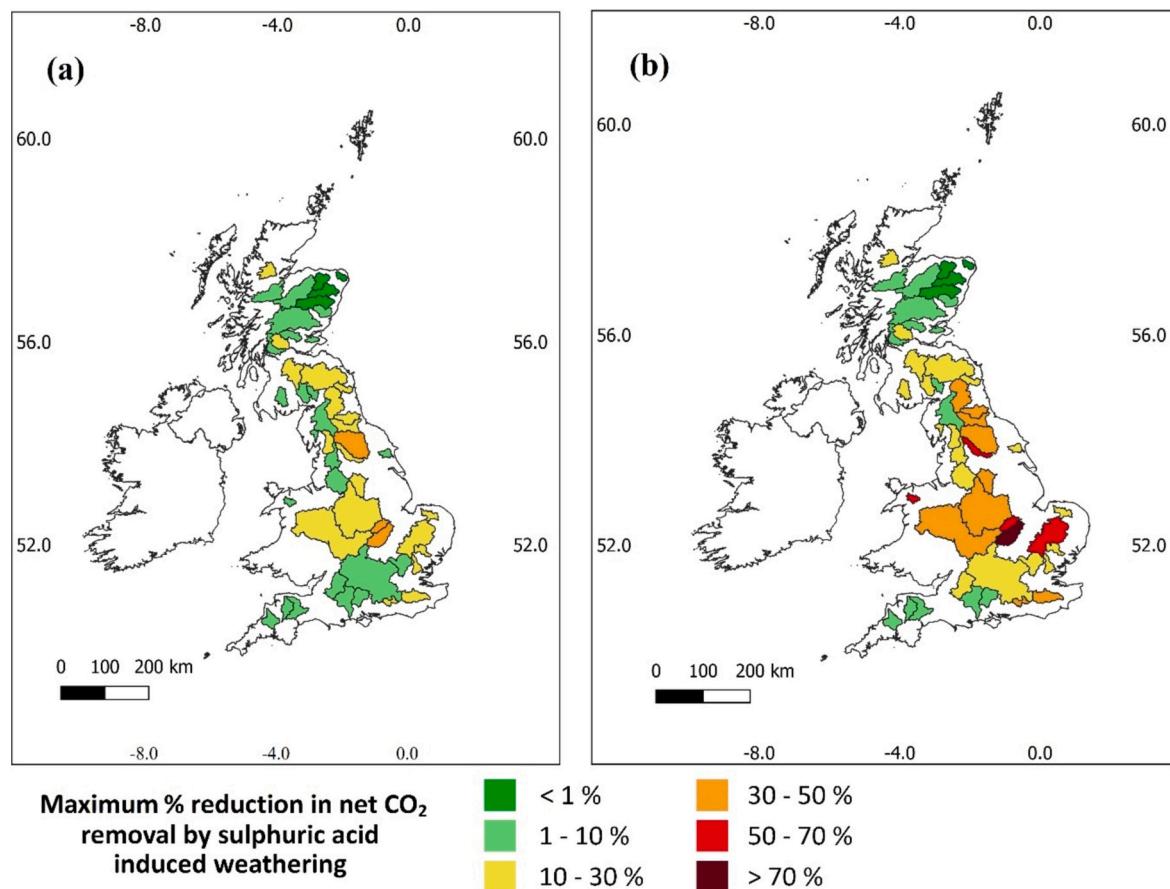


Fig. 5. The potential maximum reduction to the calculated maximum annual quantity of CO₂ consumed due to sulphide produced sulphuric acid weathering of (a) silicates and (b) carbonates in the catchments studied. In percentage reduction from the calculated maximum total CO₂ removed per catchment.

in anthropogenically modified landscapes, the nitrification of ammonium and ammonium nitrate from fertilizers (Eqs. (19) and (20)).

Nitrification of ammonium and ammonium nitrate:



When the protons created in Eqs. (19) and (20) act as the acid source in carbonate weathering, CO₂ is released (Perrin et al., 2008), while there is no impact on carbon for silicate weathering by nitric acid (Barnes and Raymond, 2009), i.e. Eqs. (6) and (7).

In the UK, fertiliser derived N is a significant source of nitric acid to the weathering zone. Annually, approximately 118 kg ha⁻¹ yr⁻¹ of nitrogen rich fertiliser is applied to soils to replenish bioavailable N which is quickly depleted due to the annual harvesting of crops (DEFRA, 2022c). As a result, approximately 70 % of riverine nitrate is sourced from agricultural fertiliser (Environmental Agency, 2021). Consequently, the extent of nitric acid weathering in the UK may be influenced by the degree of land modification within a catchment. To investigate this, and correct the weathering induced CDR estimates given in Section 6 for the effects of nitric acid weathering, we make the following assumptions:

- (i) Riverine NO₃⁻ concentrations can be used to infer nitric acid weathering, assuming that this NO₃⁻ balances cations in solution instead of DIC.
- (ii) NO₃⁻ agricultural will be apportioned to riverine cations derived from silicate and carbonate weathering in the same ratio that they were weathered on the catchment (i.e., the carbonate to silicate weathering ratio, carb/sil, see Section 6.2)

- (iii) Given the stoichiometry of weathering reactions (Eqs. (6)–(7)), 2 mol of NO₃⁻ agricultural are responsible for the release of 1 mol of Ca²⁺ and Mg²⁺ and ½ mol of Na⁺.

Corrections to the calculated CDR to account for nitric acid weathering suggest that nitric acid weathering only reduces the CDR values given in Section 6.2 for silicate weathering in the studied catchments by a very small amount (2.5 %), from 0.63 to 0.62 Mt CO₂ yr⁻¹, and carbonate weathering by 4.5 %, from 1.95 to 1.87 Mt CO₂ yr⁻¹. Only a few major catchments are corrected by >5 % (Supplementary Information, Fig. A10). The UK is heavily modified by agriculture, which should indicate that nitric acid weathering will significantly reduce catchment annual CDR yields. However, this reduction is minimal. If other heavily modified catchments behave in a similar manner, then these results suggest that globally, nitric acid weathering is unlikely to significantly impact weathering yields.

7.3. Variations in how the sequestered CO₂ speciates in solution (*w* value)

The maximum values reported in Section 6.2 use a *w* = 2.0 for silicates and *w* = 1.0 for carbonates: representing the land-based CO₂ consumption due to silicate and carbonate weathering. However, some CO₂ is re-released upon reaching the ocean, reducing the overall CDR due to weathering. As mentioned in Section 4.2, the CDR for silicates could reduce from 2 mol per divalent cation (*w* = 2.0, Eqs. (14) and (15)) to between 1.4 and 1.7 mol (*w* = 1.4–1.7), while the total CO₂ consumed for carbonates could reduce from 1 mol per divalent cation to 0.4–0.7 (*w* = 0.4–0.7). Consequently, using these lower values in calculations reduces the CDR for silicate weathering from 1.6 to 1.1–1.3 Mt CO₂ yr⁻¹, and carbonate weathering from 4.8 to 1.9–3.3 Mt CO₂ yr⁻¹ (whole UK

landmass, [Table 3](#)). The uncertainty caused by the potential variation in w underscores the need to understand spatial and temporal variations in oceanic carbonate speciation.

Additionally, these CDR values assume that the weathering derived solutes remain dissolved in the oceanic water column. When these solutes precipitate as carbonates, 1 mol of CO₂ will be re-released (i.e. Eq. (3)). Consequently, the net CDR due to carbonate weathering is zero, while the net CDR due to silicate weathering effectively is halved.

8. Overall CDR due to present-day weathering in the UK

[Table 3](#) summarizes the various calculations made within Sections 5–6. Notably, it highlights the potential for sulphide weathering to reduce the maximum estimates presented in [Section 5](#). For context, the maximum annual CO₂ removed from natural silicate and carbonate weathering (6.4 Mt CO₂ yr⁻¹) is approximately 1 % of the UK's annual greenhouse gas emissions (417.1 Mt CO_{2eq} in 2022, ([DESNZ, 2023](#))).

8.1. Global comparison

Comparisons with global CO₂ consumption estimates from silicate ([Hilton and West, 2020](#)) and carbonate weathering ([Zeng et al., 2019](#)) suggests that the values reported here correspond to approximately 0.3–0.4 % and 0.2–0.7 % of total global fluxes respectively (Supplementary Information, Table A12).

In assessing the efficacy of weathering in the UK relative to other global catchments, adjusting for catchment area provides a more informative comparison. The weathering yields calculated here ([Fig. 3](#), and Supplementary Information, Table A12) are compared to silicate yields from global catchments ([Moon et al., 2014](#)), and carbonate yields from [Zeng et al. \(2019\)](#). To allow comparison with ([Moon et al., 2014](#)), their annual silicate weathering CO₂ consumption rates from 32 global catchments were converted into yields using published basin areas. It is worth noting that the UK yields are from a relatively small geographical area (9.4 Mha) compared to the median global basin size (40 Mha).

Although considerable variation occurs across UK catchments, both the mean silicate and carbonate weathering yields in the UK are slightly higher than the global catchment averages (Supplementary Information, Table A12) - an unexpected finding. This challenges the conventional view that the UK's environmental conditions, with low temperatures, moderate runoff, and low erosion rates, are suboptimal for weathering.

8.2. Implications for deliberate additional CDR by enhanced weathering in the UK

To achieve the climate targets set by the United Kingdom to reach net zero by 2050 ([Lezaun et al., 2021](#)), various strategies will need to be implemented to both drastically reduce emissions and remove carbon from the atmosphere. Enhanced Weathering (EW) is a strategy aimed to enhance natural weathering processes and drawdown excess atmospheric CO₂ by adding crushed silicates to arable cropland ([Renforth,](#)

[2012; Hartmann et al., 2013; Beerling et al., 2018](#)). Current estimates for the potential for CDR by the application of EW to UK crops suggest annual sequestration from as much as 6–30 Mt CO₂ yr⁻¹ ([Kantzias et al., 2022](#)), to as little as 0.13 (±0.1) Mt CO₂ yr⁻¹ ([Buckingham et al., 2022](#)).

It is useful to compare these estimates with the CDR due to natural weathering in the UK predicted here. The combined maximum annual CDR of natural silicate and carbonate weathering (CDR_{Max} = 6.4 Mt CO₂ yr⁻¹) in the UK lies on the lower end of the range predicted by ([Kantzias et al., 2022](#)). This suggests that the implementation of EW could more than double the production and flux of natural weathering products in the UK. Given the small particle size of applied silicates and acidic cropland this may be achievable ([Beerling et al., 2018](#)), but further work is needed to investigate the viability of this approach and the potential impacts of doubling (or even greater increases) from present-day weathering rates on soils groundwaters chemistry, the health of river ecosystems.

9. Conclusions

This study presents the first assessment of the annual amount of CO₂ consumed due to natural weathering processes in the UK. The analysis presented here demonstrates that on average, 7 % of the major cations within UK rivers are sourced from silicate rock weathering, and 49 % are sourced from carbonates. The annual CDR due to natural present-day weathering in the 52 catchments studied here is 2.6 Mt CO₂ yr⁻¹, assuming an ideal scenario whereby no re-release of CO₂ occurs during transport, and all reactions proceed via carbonic acid weathering (Eqs. (1) and (2)). This scales to 6.4 Mt CO₂ yr⁻¹ when considering the whole area of the UK, of which 1.6 Mt CO₂ yr⁻¹ is from silicates, and 4.8 Mt CO₂ yr⁻¹ is from carbonates.

Strong acids (sulphuric and nitric) will reduce the true value of CDR from the maximum calculated CDR. Nitric acid does not, however, significantly impact weathering CDR, reducing the overall CO₂ consumed by only 2 % for silicates and 3 % for carbonates. The potential reduction in the CO₂ consumption due to sulphuric acid is variable across catchments, with the maximum reduction in CO₂ yield occurring within midlands catchments-linked with shale and carboniferous coal deposits. The presence of sulphides could make the true annual CDR as much as 17 % (silicates) and 28 % (carbonates) lower than the calculated maximum CDR.

By quantifying the natural fluxes of silicate and carbonate weathering, this work expands the current understanding of the UK's carbon cycle. Constraining these baseline natural fluxes is critical to inform climate modelling and delimit the potential of various suggested land-based CDR strategies.

CRediT authorship contribution statement

Kirsty J. Harrington: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gideon M. Henderson:** Writing – review & editing,

Table 3

Maximum potential CDR due to natural weathering in the UK catchments, and upscaled to account for UK landmass. Given in annual flux (Mt CO₂ yr⁻¹). The maximum was calculated assuming complete dissolution by carbonic acid, and prior to correction for oceanic processes. This maximum is then corrected for oceanic speciation, and potential sulphuric and nitric acid weathering.

	Studied catchments			Total UK		
	Combined	Silicate	Carbonate	Combined	Silicate	Carbonate
Maximum CDR (Mt CO ₂ yr ⁻¹)	2.58	0.63	1.95	6.37	1.56	4.82
Maximum CDR range (Mt CO ₂ yr ⁻¹)	2.0–3.3	0.3–1.1	1.7–2.2	4.9–8.1	0.8–2.8	4.2–5.4
Corrected for oceanic speciation ($w = 1.7$) (Mt CO ₂ yr ⁻¹)	1.89	0.54	1.35	4.7	1.3	3.3
- Sulphides	–25 %	–17 %	–28 %	–25 %	–17 %	–28 %
- Nitric acid	–3.9 %	–2.5 %	–4.5 %	–3.9 %	–2.5 %	–4.5 %
Overall reduced Mt CO ₂ yr ⁻¹	1.34	0.43	0.91	3.3	1.07	2.25
Overall reduced CDR range (Mt CO ₂ yr ⁻¹)	1.02–1.75	0.22–0.76	0.79–1.02	2.52–4.32	0.53–1.90	1.95–2.52

Supervision, Methodology, Funding acquisition, Conceptualization. **Robert G. Hilton:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization.

Declaration of competing interest

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.177458>.

Data availability

Data will be made available on request.

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