



Invited Review

Tracing anthropogenic climate and environmental change using stable isotopes

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ABSTRACT

Human impact on the climate and environment are one of our greatest challenges. Increasing atmospheric greenhouse gas concentrations, rising temperatures and distinct alterations in the global water cycle are problems which impact all environments and human populations. Consequences of anthropogenic activity can be, however, expressed at the regional and local scales, such as the effects of water pollution, reduction in soil quality, and the loss of biodiversity related to resource use and land management strategies in a specific area. Here, we consider how stable isotopes can be used to trace the influence of human impact, drawing from terrestrial records. We review the utility of stable isotopes in palaeoenvironmental archives, and show how these can help to identify the timing and magnitude of past change related to anthropogenic pressures on the environment. We also review how isotopes can be applied to modern monitoring of the environment, to identify changing sources of pollution and the processing of key pollutants once they enter the environment. In combination, isotope data from palaeoenvironmental archives and detailed modern monitoring enable the development of a more holistic temporal understanding of regional-local environmental change and to identify its driving mechanisms. These data are able to provide a key basis for initiating an evidence-based approach toward mitigation and environmental remediation.

1. Introduction

Anthropogenic pressures on the climate and environment are impactful globally, influencing Earth systems over a range of temporal and spatial scales. To better assess and understand the effects of human activity on the environment a wide range of approaches are required to ascertain the nature, timing, and magnitude of these impacts. The scale of impact is also important. Whilst global greenhouse gas emissions and rising temperature may be key threats and targets for mitigation, immediate concerns of local communities are most likely centred on the quality and preservation of natural resources, such as for water and food supply. One of the foremost geochemical techniques employed to understand anthropogenic change are stable isotopes (Galuszka et al., 2017). This paper will build on previous reviews, which, for example, have focussed on the use of isotopes in addressing the question of the Anthropocene (Dean et al., 2014), to show how isotope systems can be used to identify human-induced environmental change on a range of temporal and spatial scales. Initially it focusses on anthropogenic impacts on the atmosphere, considering specifically archives of past

atmospheric change and also recent monitoring of methane emissions. It will then move on to highlight the use of lake sedimentary isotope records for palaeoenvironmental reconstruction (Leng and Marshall, 2004) and how modern monitoring of nitrate ($\delta^{15}\text{N-NO}_3$) and phosphate oxygen ($\delta^{18}\text{O-PO}_4$) isotopes can be used to elucidate the current impacts of anthropogenic pollution through the release of key nutrients to the environment (Talbot, 2001). The review focuses on commonly employed isotope techniques to contextualise the timing of human impact and impactful modern tracer methods.

Human induced changes in the Earth System have often been best demonstrated through globally distributed greenhouse gases within the atmosphere. Since pre-industrial times, large increases in carbon dioxide (CO_2), methane (CH_4) and NO_x concentrations have been seen in the atmosphere (Filonchik et al., 2024). Such rapid rises in global greenhouse gas emissions have had knock-on effects, specifically with regard to increasing global temperatures, unprecedented polar ice melting, sea level rise, ocean acidification, and increases in extreme weather events (Filonchik et al., 2024). The analysis of greenhouse gas stable isotope signatures from palaeo-archives and on-ground collections has had a

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prominent role to play in the identification of gas sources, decoupling natural emissions from those associated with human activities (Graven et al., 2020; IPCC, 2021; Rubino et al., 2013; Schwietzke et al., 2016), for example fossil fuel burning (Sherwood et al., 2017), industrial waste sources (Bakkaloglu et al., 2022), or agricultural intensification (Ruddiman et al., 2011).

There has always been debate as to when human activities first started to impact the planet on a global scale. Some authors (Ruddiman et al., 2011, 2020) suggest that the first signs of global anthropogenic perturbations can be identified within ice cores as far back as the Middle Holocene. Ruddiman et al. (2020) argue that human populations altered their regional environment so significantly at this time, through early deforestation ~7000 years ago and the introduction of wetlands to grow rice ~5000 years ago, that a shift in CO₂ and CH₄ concentrations can be identified in carbon isotope signatures captured in ice cores that act as an archive of global greenhouse gas concentrations. In cases such as this, where early but regional scale environmental management caused an impact in the global record, it is fair to assume that environmental change on the local and regional scale was even more pronounced (Ruddiman et al., 2020). Studies such as this highlight the extensive and long-term environmental degradation some regions of the globe have faced due to human population increases, land management, and pollution (Canfield et al., 2010; Dror et al., 2022). Therefore the isotope records stored in terrestrial located palaeoarchives adjacent to these human activities can offer a valuable tool to identify shifts from natural variation to those driven by anthropogenic activities (Alp and Cucherousset, 2022).

Many of our classical terrestrial palaeoarchives not only show points of historical change associated with human impact but that these are also systems with continued and often increasing human pressures. Lake systems especially have been critical to our understanding of past terrestrial environmental change (Leng and Marshall, 2004), but these systems face ever increasing pressures associated with land management, pollution inputs and population growth (Jilbert et al., 2020). At the same time, freshwaters represent one of our most important drinking water resources and their effective management is important for safe and sustainable human development (Jilbert et al., 2020). Modern isotope monitoring plays an important role in understanding the health of these systems, especially in relation to the inputs and cycling of critical nutrients, including carbon (C), nitrogen (N) and phosphorus (P).

The aim of this review is therefore to give an overview of how stable isotope analysis can be used to identify and characterise human impact on the climate and environment, considering both past impacts and how we may trace and contextualise current anthropogenically derived change. This review paper predominantly focuses on terrestrial environmental records, many of which, but not all, are from lakes as these systems offer high temporal resolution archives from spatially diverse settings and preserve both global (through atmospheric deposition) and local (through in wash of pollutants) proxies of environmental change.

2. Stable isotope systematics

To understand the role stable isotopes can play as an environmental tracer we must clearly characterise terminology and highlight the notation and standardisation used across all fields of stable isotope geochemistry. Isotopes are defined as the particular of an element characterised by a specific number of neutrons (Sharp, 2017). As an example, carbon has two stable isotopes, carbon 12, where the atomic nucleus has 6 protons and 6 neutrons and carbon 13, where there are 6 protons and 7 neutrons. This natural disparity in the number of neutrons creates a relative mass difference between the two isotopes, which enables measurement by isotope ratio mass spectrometry. This relative mass difference is reported as a ratio of the heavy to light isotope, e.g. ¹³C/¹²C. As the relative difference in isotope ratios are easier to measure than absolute isotope ratios, it is standard practice to report isotope

ratios using the delta notation (δ). The delta value is given in Equation (1).

$$\delta = \left(\frac{R_x}{R_{std}} \right) \times 1000 \quad \text{Equation 1}$$

Where *R* denotes the ratio of the heavy to light isotopes of a particular element in either a sample (*x*) or standard (*std*) material. Delta values are reported in per mil (parts per thousand; ‰), with a positive δ value meaning the sample has a larger quantity of the heavy to light isotope relative to the standard material, and vice versa for negative δ values (Sharp, 2017). For most environmental studies we are interested in the isotope analysis of elements within a compound, for example the isotope signature of nitrogen and/or oxygen in nitrate (NO₃), or carbon and/or oxygen in carbon dioxide (CO₂).

The utilisation of stable isotope analysis as an environmental tracer relies upon changes in the ratio of heavy to light isotopes within compounds across physical, chemical, and biological reactions, termed fractionation. Isotope fractionation occurs during natural environmental processes or can be forced by anthropogenic processes. Through the accurate measurement of isotope ratios, we can identify process related variations in the stable isotope composition of compounds and relate these to changes in source or cycling within the environment.

3. Identifying human impact on the atmosphere

Stable isotopes are now routinely analysed with the aim of understanding human impact on the atmosphere. When attempting to understand and quantify the main drivers of anthropogenic climate change, we rely on palaeo archives to characterise the scale of natural perturbations and forcing mechanisms within climate and environmental systems (Jongebloed et al., 2023). Where well resolved stable isotope palaeorecords are available that cover the geological to recent past, the magnitude and extent of secondary human induced change can be clearly demonstrated. Where a full review of all stable isotope palaeoclimate records is beyond the scope of this article, the following section gives examples of how palaeorecords can be used to clearly elucidate the impacts of human activity, which have been distributed globally by the atmosphere.

3.1. Assessing global impacts of anthropogenic activity using archives of atmospheric change

Human activities are now pervasive across the planet, and it is difficult to find terrestrial palaeo archives that only preserve a record of our impact on the atmosphere, with minimal secondary local alteration. Such records ideally need to be isolated from local pollution sources (for example: agricultural runoff and human population centres), which often act to swamp or complicate the archives of atmospheric deposition. Due to this necessity to isolate from local pollution impacts, the best records of this type are often obtained from uninhabited regions, predominantly preserved in ice cores (Hastings et al., 2009; Jongebloed et al., 2023) and pristine lakes from high or low latitudes (Wolfe et al., 2013), or regions which are largely uninhabited due to their geography (Luo et al., 2023). In this way ice cores and some lakes can uniquely capture the widespread nature of anthropogenic impact on the atmosphere including, but not limited to, changes in atmospheric nitrogen (δ¹⁵N), CO₂ (δ¹³C) and sulfate (δ³⁴S-SO₄) (Fig. 1). These isolated archives are therefore best placed to identify when human impacts have been propagated globally, well away from the point sources of the original pollution.

Anthropogenic sources of nitrogen now account for approximately half of total fixed nitrogen annually on Earth (Canfield et al., 2010), meaning the global nitrogen cycle has been drastically altered within the 20th century. This change has been driven by the invention of the Haber-Bosch process, the burning of fossil fuels, and the application of

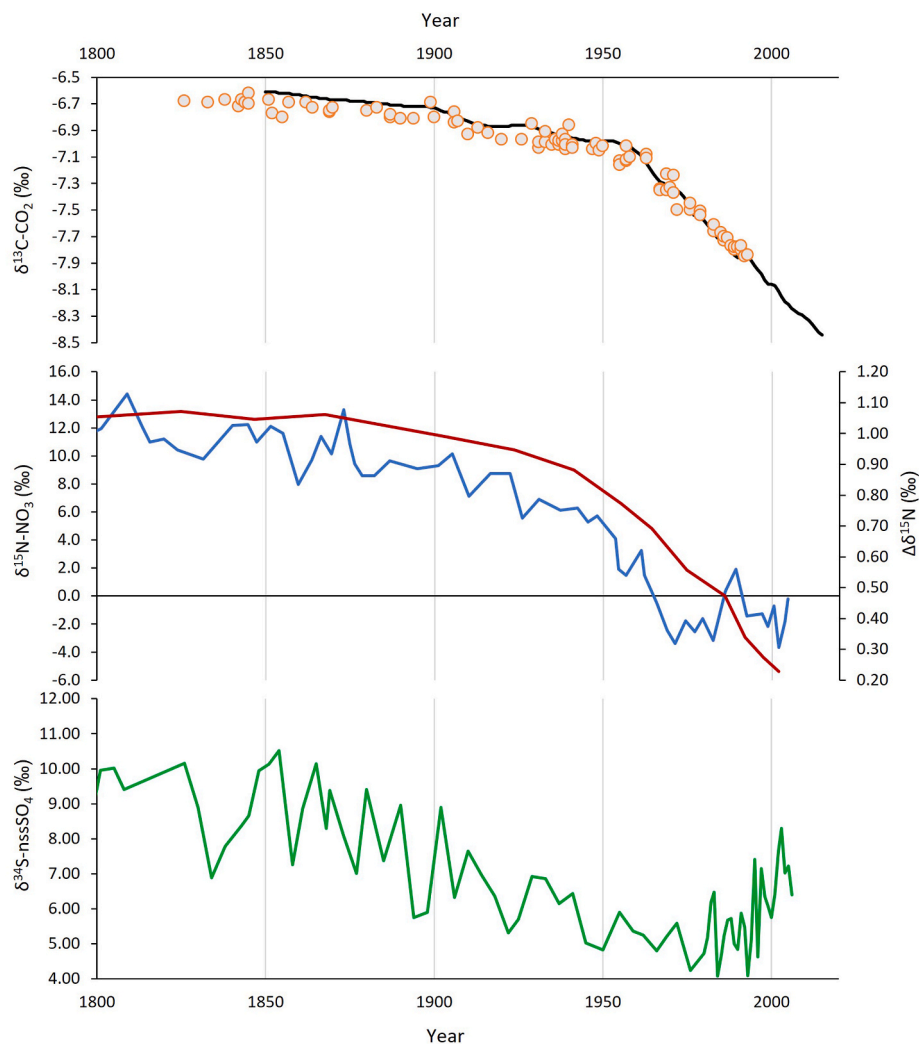


Fig. 1. Compiled stable isotope data from ice core and lake sediments showing gradual decreases in nitrogen, carbon and sulfur isotope values from preindustrial times to modern day, with a clear acceleration in the mid-20th century. **Top** - compilation of global $\delta^{13}\text{C-CO}_2$ values (black line) (Graven et al., 2017) alongside high-resolution ice core and firn $\delta^{13}\text{C-CO}_2$ measurements (grey and orange circles) from Law Dome (Rubino et al., 2013). **Middle** - Ice core $\delta^{15}\text{N-NO}_3$ from Greenland Summit (blue line), alongside data from 13 Rocky Mountain lake $\Delta\delta^{15}\text{N-N}$ (relative departures from mean pre-AD, 1900 $\delta^{15}\text{N}$ values) records (Wolfe et al., 2013). **Bottom** - Greenland summit ice core $\delta^{34}\text{S}$ (nss SO_4) (green line) (Jongeblod et al., 2023), slight increases in isotope signature can be seen from the 1970's.

nitrogen fertilisers around the world (Denk et al., 2017). Rapid changes in atmospheric nitrogen loading and nitrogen isotope composition ($\delta^{15}\text{N}$) have followed (Fig. 1), as demonstrated in palaeorecords from remote regions (Wolfe et al., 2013), including ice cores (Hastings et al., 2009) and lake sediments (Holmgren et al., 2010; Luo et al., 2023; Wolfe et al., 2013). Whilst these records are globally disparate from one another, they frequently preserve a commensurate shift to lower $\delta^{15}\text{N}$ values (Fig. 1) (Holtgrieve et al., 2011). The rapid reduction seen in the $\delta^{15}\text{N}$ value of these records is driven by anthropogenic sources of nitrogen, which typically have lower isotope values (Dean et al., 2014 and refs therein); including increases in nitrogen oxide (NO_x) emissions from fossil fuel combustion, power plants, and the volatilisation of nitrogen fertilisers (Hastings et al., 2013; Luo et al., 2023). Initial changes are first observed in the 1850's with a marked acceleration after ca. 1950 (Fig. 1) (Holtgrieve et al., 2011; Wolfe et al., 2001). Other records only see a change in $\delta^{15}\text{N}$ later in the 20th century (Luo et al., 2023) or not at all (Kang et al., 2019), either due to local effects buffering the anthropogenic nitrogen deposition signal (Kang et al., 2019; Wolfe et al., 2013), or because of the timing of anthropogenic emissions and prevailing weather systems (Kang et al., 2019; Luo et al., 2023).

In a similar manner to atmospheric nitrogen deposition, SO_4 aerosols are well preserved in remote palaeorecords and their sulfur isotope

composition ($\delta^{34}\text{S-SO}_4$) can be used to differentiate between natural and anthropogenic sources (Jongeblod et al., 2023). This source distinction is critically important as SO_4 has a net cooling effect on the climate system (IPCC, 2021). In Greenland ice cores the first indication of anthropogenic SO_4 sources occur as early as 1870 (Patris et al., 2002). Preindustrial sources of SO_4 include sea-salt aerosols, volcanic sulfur emissions, and marine phytoplankton emissions (Jongeblod et al., 2023), whilst anthropogenic emissions are mainly from fossil fuels, soil emissions, and industry, with average $\delta^{34}\text{S-SO}_4$ ranging between 0‰ and 7‰ (Patris et al., 2002). Strong stable isotope evidence shows that an anthropogenically driven reduction in $\delta^{34}\text{S-SO}_4$ between 1870 and the 1970s, after which the introduction of international clean air acts drastically reduced sulfur emissions. This led to a synchronized increase in ice core $\delta^{34}\text{S-SO}_4$ from the 1970's to early 2000's (Fig. 1) (Jongeblod et al., 2023). These sulfur isotopic changes track and help to elucidate the anthropogenic drivers of variations in SO_4 concentrations in the atmosphere.

Arguably the most important anthropogenically forced greenhouse gas is CO_2 . The carbon cycle has, as with sulfur and nitrogen, been influenced by human activities since the industrial revolution. Fossil fuel burning has led to global reductions in the carbon isotope composition ($\delta^{13}\text{C-CO}_2$) of the atmosphere, as ancient carbon released during

burning is depleted in the heavier isotope (^{13}C) (Graven et al., 2017; Mackensen and Schmiedl, 2019). This transition to lower $\delta^{13}\text{C}$ is clearly observed within records of atmospheric CO_2 from ice cores, despite the role the global oceans and plants play in moderating carbon fluxes and sequestration (Graven et al., 2020) (Fig. 1). Rubino et al. (2013) present an exemplar 1000-year $\delta^{13}\text{C}$ - CO_2 dataset from Law Dome (East Antarctica), which demonstrates that average preindustrial atmospheric $\delta^{13}\text{C}$ - CO_2 was -6.5‰ and reveals a change to lower values since the 1850's, with $\delta^{13}\text{C}$ - CO_2 of -8.2‰ in the early 2000's. The majority of the change in $\delta^{13}\text{C}$ - CO_2 (1.5‰) occurs post 1950, concurrent with the highest emission period (Graven et al., 2017; Rubino et al., 2013). Plant CO_2 uptake appears to be increasingly discriminating against ^{13}C during photosynthesis due to rising CO_2 concentrations (Keeling et al., 2017), slightly offsetting the anthropogenically forced reduction in atmospheric $\delta^{13}\text{C}$ - CO_2 (Graven et al., 2020). However, a continued switch from the burning of coal ($\delta^{13}\text{C}$ - $\text{CO}_2 \sim -24\text{‰}$) to natural gas ($\delta^{13}\text{C}$ - $\text{CO}_2 \sim -44\text{‰}$) may exacerbate the anthropogenically-forced change to lower $\delta^{13}\text{C}$ - CO_2 in the atmosphere (Graven et al., 2020).

When we consider these atmospheric stable isotope records in a combined way, the effects of human impact have a clear global distribution (Fig. 1). Most records demonstrate atmospheric change since the onset of the industrial revolution, but the most pronounced changes take place after ca. 1950 (Fig. 1). These global changes may originate from a range of anthropogenic sources, primarily fossil fuel burning and agricultural intensification, but they produce a clear line of evidence to support the idea of a great intensification of impact in the middle of the 20th century (Steffen et al., 2007, 2015a). Whilst we can use palaeorecords to highlight this inflection point of change, we must also consider this change as an ongoing process and one which requires us to understand, quantify and if possible mitigate future inputs of greenhouse gases into the atmosphere. The next section looks at how isotopes of methane can be used to trace sources both natural and anthropogenic emissions of this important greenhouse gas.

3.2. Assessing modern methane emission sources using stable isotopes

Carbon emissions, mainly as CO_2 and CH_4 , continue to be of major importance within the global climate system. As shown above rapid increases in greenhouse gases are well preserved within the palaeorecord and continue to increase. Carbon isotope analysis of both CO_2 and CH_4 has shown to be key for the identification of natural and anthropogenic sources of carbon. This is of great current importance due to both enhanced direct anthropogenic emission potentials from industry and agriculture, and indirectly forced emissions deriving from regions of the globe impacted by climate change.

Methane emissions have an important role to play in future global warming and are thought to be accountable for up to half of net temperature rise since the preindustrial era, having a current growth rate in the atmosphere of 10 ppm/year (Nisbet et al., 2020) and a global warming potential 30 times higher than CO_2 (Saunois et al., 2020). However, methane's atmospheric lifespan is much shorter than CO_2 , making it a primary target for greenhouse gas reduction and mitigation policies (Saunois et al., 2020). Since its launch at COP26 (Nov 2021), over 150 countries have signed the Global Methane Pledge (GMP) and more than 50 have established national methane action plans. Rapid ratification of the GMP signifies meaningful momentum for international collaboration to characterise, combat and reduce anthropogenic methane emissions. However, the extent to which emission reduction policies will help to reduce total atmospheric methane is currently unknown and depends upon our ability to 1) accurately identify and characterise anthropogenic emission sources and 2) future variations in natural fluxes under changing climate scenarios.

Major natural sources of CH_4 include shallow wetlands and saturated soils (Fisher et al., 2017; Sancu and Panarello, 2015), digestive systems of ruminants and termites, geological sources (Saunois et al., 2020), and carbon degradation in thawing permafrost regions (Knoblauch et al.,

2018; Schaefer et al., 2014). Anthropogenic emissions include agriculture (including importantly rice farming) (Zazzeri et al., 2017), subsurface natural gas extraction and provision (Cahill et al., 2019), and waste management (Fig. 2). Dual stable isotope analysis of CH_4 ($\delta^{13}\text{C}$ - CH_4 , $\delta^2\text{H}$ - CH_4) can help elucidate the three major sources of CH_4 ; biogenic, thermogenic (or geological) and pyrogenic (mainly biomass burning) due to their distinct isotope ratios (Fig. 2) (Fujita et al., 2020; Smith et al., 2021b). Thermogenic emissions have relatively high $\delta^{13}\text{C}$ - CH_4 values (-45 to -55‰) with higher values normally associated with higher maturity gases (Schwietzke et al., 2016). Biogenic isotope signatures are controlled by the formation pathway. The reduction of CO_2 creates a $\delta^{13}\text{C}$ - CH_4 fractionation ($\delta^{13}\text{C} = <-100\text{‰}$; $\delta^2\text{H} = -150\text{‰}$ to -250‰), whilst the fermentation of reduced carbon sources (acetate and methanol) has larger fractionations in $\delta^2\text{H}$ - CH_4 ($\delta^{13}\text{C} = -50$ to -60‰ ; $\delta^2\text{H} = -300\text{‰}$ to -400‰) (Whiticar, 1999). Secondary, post formation effects, including methane oxidation to CO_2 , can cause isotope fractionations resulting in classical heavy isotope enrichment in the residual CH_4 pool (Whiticar, 1999). These processes can lead to misinterpretation of the residual CH_4 isotope values, where methane of biogenic origin can have isotopic signatures more reminiscent of thermogenic CH_4 .

Where care is taken, however, methane sources can be identified and characterised through stable isotope analysis of gas collections. This enables a ground truthing for emission sources and through this, better inputs into global emission estimate models (Fujita et al., 2020). An excellent example of this work by Menoud et al. (2022), highlights the divergence between top down (ground sampling) and bottom up (models) emission estimations and the requirement to close this gap through higher resolution real world collections and better understanding of source isotope composition (Schwietzke et al., 2016). Menoud et al. (2022) develop a more globalised dataset of methane isotope data through the integration of new European CH_4 data, collected from mobile vehicle, onboard aircraft and UAV, on foot, and soil chamber collections, with global literature and the comprehensive, but America-centric, data set of (Sherwood et al., 2017). In combination, these studies include thousands of spot measurements of methane isotope composition for 64 countries and identify isotopic ratios of all the major sources both natural and anthropogenic methane. This has led to a more comprehensive assessment of methane sources and clarified their average dual C-H isotope space, enabling better source identification (Fig. 2) (Menoud et al., 2022).

Whilst atmospheric pollution is a globally distributed problem, there are many local and regional issues driven by human activities. The remainder of this review will consider human impact on regional and local scales, with a specific focus on lakes as archives of palaeoenvironmental change and key sites of modern pollution. The following section reviews how stable isotope data can be used to trace the emergence of human activities, characterise natural conditions prior to major human impact, and identify the timing and nature of anthropogenic climate and environmental change at the regional-local level.

3.3. Archives of land use change and human impact

3.3.1. Carbon isotopes and C/N

Carbon isotopes have been widely used in palaeo archives to reconstruct natural climate variability over geological timescales (Mampuku et al., 2008; Richey et al., 2023; Zanchetta et al., 2018), as well as provide information about historical and contemporary human impact on the environment (Rubino et al., 2013). One of the main uses of carbon isotopes is to trace sources of organic matter preserved in paleo sequences. As plants assimilate atmospheric CO_2 during photosynthesis isotopic fractionation occurs, and the magnitude of the fractionation depends on the type of plant. Most plants use the C3 Calvin pathway and are associated with a $\delta^{13}\text{C}$ shift of approximately -20‰ from atmospheric $\delta^{13}\text{C}$ - CO_2 of currently -8.5‰ compared to a pre-industrial value of -6.5‰ (Graven et al., 2017). Organic matter produced by C3 plants

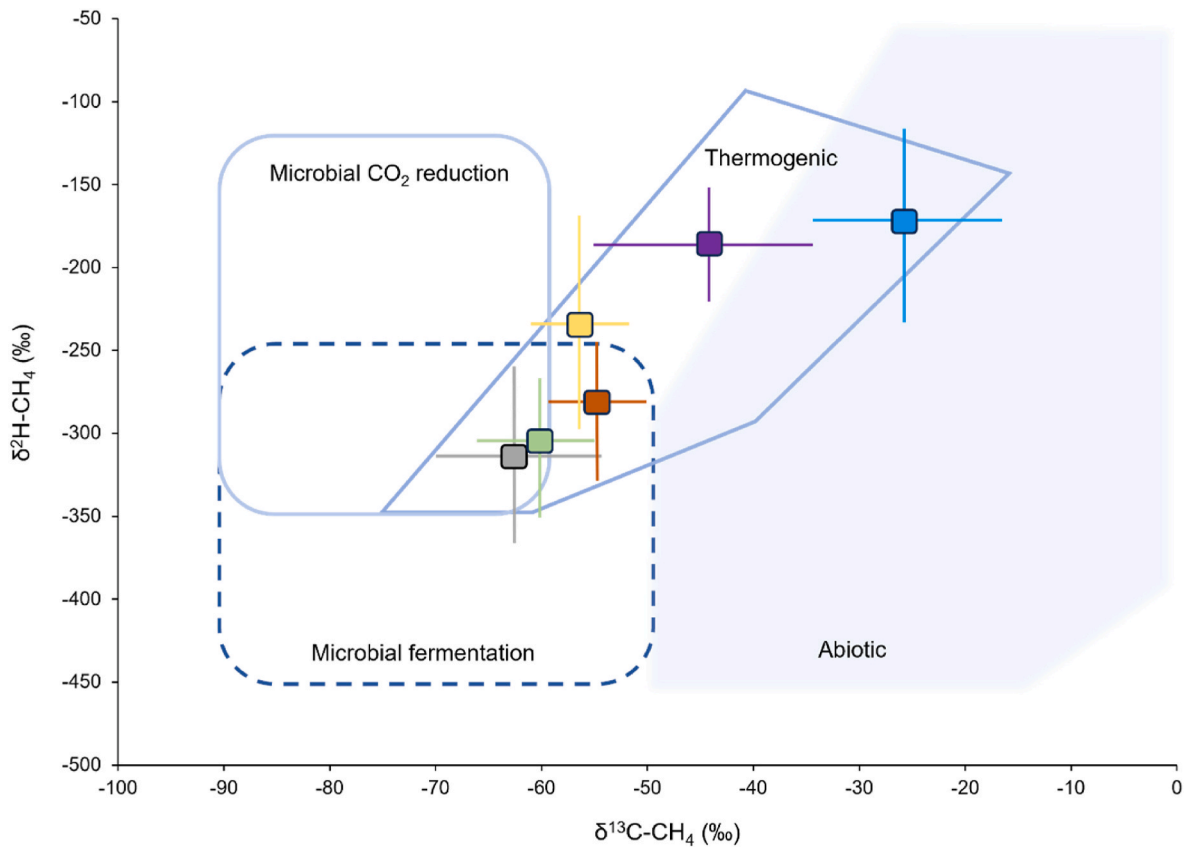


Fig. 2. Dual methane ($\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$) isotope plot adapted from Menoud et al. (2022), showing the differing methanogenic pathways as presented in Milkov and Etiope (2018). Squares represent the compiled mean and standard deviation values for: wetlands (grey), agriculture (green), waste (orange), other natural (yellow), fossil fuels (purple) and pyrogenic (blue) from the datasets of Menoud et al. (2022) and Sherwood et al. (2017).

using atmospheric CO_2 therefore have an average $\delta^{13}\text{C}$ of around -28.5 ‰ and typically range between -31 ‰ and -23 ‰ (Kohn, 2010; Meyers and Lallier-vergés, 1999; O’Leary, 1988). However, the $\delta^{13}\text{C}$ of individual C3 plant species can vary by up to $+2$ ‰ with decreasing mean annual precipitation (Hartman and Danin, 2010; Kohn, 2010). Conversely, carbon fixation in C4 plants via the Hatch-Slack pathway is more complex and there is a smaller fractionation of between -6 ‰ and -4 ‰ and so the organic matter produced has higher $\delta^{13}\text{C}$ values around -14 ‰. Plants that use the CAM pathway have intermediate $\delta^{13}\text{C}$ values between C3 and C4. This difference in carbon isotope fixation by plants during photosynthesis has been crucial to uncovering the first anthropogenic impacts on landscape evolution, soil development, and erosional processes following the development of agriculture (Francke et al., 2019; Hillman et al., 2018; Kaplan et al., 2010; Kerr et al., 2020). In the Americas, sediment records show a shift to higher $\delta^{13}\text{C}$ after 4000 BP, indicating forest clearance and the introduction of C4 plants such as maize as a staple grain (Kennett et al., 2024), during the development of the Mayan civilisation (Beach et al., 2015; Johnson et al., 2007). Similarly, speleothem records from Japan trace a change from lower to higher $\delta^{13}\text{C}$ as forested landscapes were cleared from ca. 525 BP and replaced by grassland vegetation for agricultural use (Uchida et al., 2013). More recently, a shift to higher $\delta^{13}\text{C}$ over the last 100 years in soil profiles from central Queensland, Australia, indicates woodland removal and the initiation of European farming practices (Krull et al., 2005).

Whilst $\delta^{13}\text{C}$ can be used to distinguish between sources of C3 and C4 plants, sediments and soils may comprise multiple sources of organic matter and be complicated by overlapping $\delta^{13}\text{C}$ values within each C3 or C4 group (Fig. 3). The $\delta^{13}\text{C}$ of organic matter is also influenced by factors other than the vegetation type, such as productivity, water availability, and post-depositional change. In these cases, the use of C/N data can

provide complimentary information to differentiate between organic matter sources. For example, lakes in Ireland that have a majority of their catchment covered by plantations experienced a large expansion of algae following forest planting, driven by nutrient enrichment associated with forest fertilisation and terrestrial organic matter influx. This resulted in a shift to lower C/N and $\delta^{13}\text{C}$ values associated with phytoplankton (Stephenson, 2015). Fresh organic matter from algal sources has C/N values typically between 4 and 10, whilst terrestrial higher plants with cellulose-based supportive tissues produce organic matter with higher C/N values commonly above 20 (Fig. 3) (Meyers and Teranes, 2001).

There is now broad application of $\delta^{13}\text{C}$ and C/N in freshwater sediment records to reconstruct environmental change over past ~ 100 years, allowing us better understanding of both the timing and magnitude of human induced environmental change. Anthropogenic supply of key plant nutrients (N, P) to rivers and lakes has increased exponentially since 1950 driving enhanced primary production and carbon sequestration in lakes (Anderson et al., 2024). Nutrient enrichment from agricultural fertilisers, untreated wastewater effluents, and industrial pollution has accelerated the rate and magnitude of change towards eutrophic or hypereutrophic conditions, which has led to declining water quality and wide-ranging effects for carbon cycling in lakes (Anderson et al., 2014; Smith, 2003). The addition of excess nutrients drives strong primary productivity in lake surface waters, which progressively removes ^{12}C from the dissolved inorganic carbon pool, forcing a shift to higher $\delta^{13}\text{C}$ in phytoplankton. Several studies have demonstrated higher $\delta^{13}\text{C}$ in surface sediments from a eutrophic and hyper-eutrophic lakes compared to lower $\delta^{13}\text{C}$ in oligo-mesotrophic lakes, highlighting a correlation of $\delta^{13}\text{C}$ with lake trophic state associated with human pollution impacts (Routh et al., 2009; Torres et al., 2012). In lakes where CO_2 concentrations are not depleted, eutrophic conditions

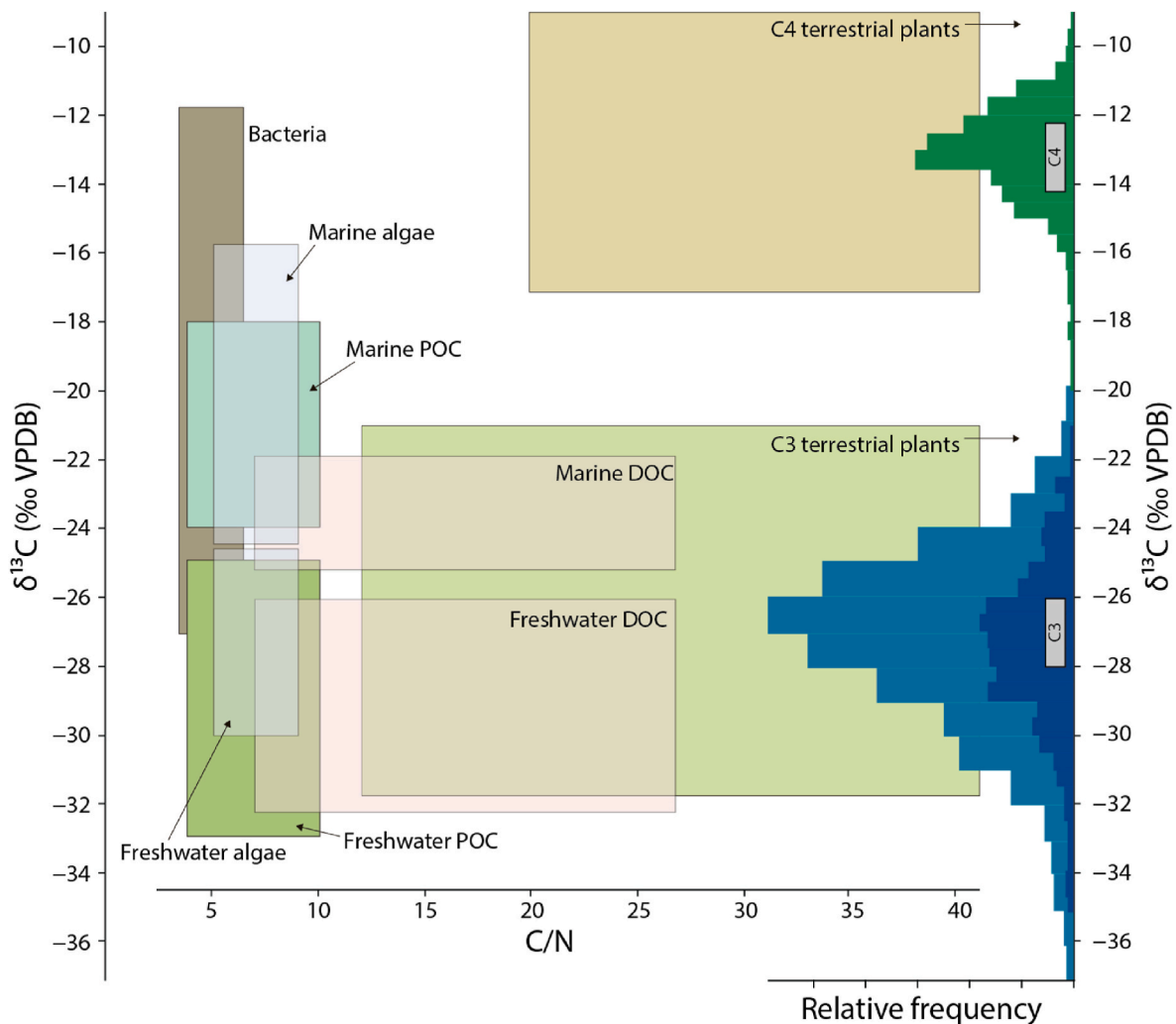


Fig. 3. Typical $\delta^{13}\text{C}$ and C/N ranges for organic matter inputs to terrestrial freshwater and coastal environments with histogram of the relative distribution of $\delta^{13}\text{C}$ for modern plants (adapted from Kohn, 2010; Lamb et al., 2006; O'Leary, 1988; Reiffarth et al., 2016).

promoting enhanced algal productivity can lead to a shift from higher $\delta^{13}\text{C}$ and C/N reflecting a mixed terrestrial and aquatic source of organic matter to lower $\delta^{13}\text{C}$ and C/N consistent with a primarily algal-dominated source. The sediments of hypereutrophic Rostherne Mere, UK, record a pronounced change to lower $\delta^{13}\text{C}$ and C/N following the construction of a sewage treatment works that discharged effluent upstream of the lake as well as agricultural run-off (Lacey et al., 2018). Even after the sewage works was closed, internal nutrient loading still promotes a high trophic state and low $\delta^{13}\text{C}$ and C/N values. Although algae preferentially utilise dissolved CO_2 (-8.5‰ if in equilibrium with atmospheric CO_2), reduced concentrations of CO_2 during periods of productivity can also cause algae to utilise the bicarbonate ion as a source of carbon (typically sourced from dissolution of catchment geological carbonate with $\delta^{13}\text{C} \sim 0\text{‰}$), which also leads to phytoplankton having higher $\delta^{13}\text{C}$. Lu et al. (2010a) illustrate that cultural eutrophication of Lake Erie and major water quality decline caused by external nutrient loading between 1800 and the 1970s is closely associated with changes to higher $\delta^{13}\text{C}$. In this record, the dissolved inorganic carbon pool fractionates strongly in response to P-driven phytoplankton productivity, and this forces higher $\delta^{13}\text{C}$ in both autochthonous organic matter as well as endogenic carbonate precipitated in the epilimnion.

Nutrient levels, as well as water and sediment retention, are also exacerbated by dam installation for hydropower, water level and flooding control, and water supply for irrigation and local populations. Dams have been shown to restrict carbon flows in and out of lakes as

well as enhance the rate organic matter degradation (Catalán et al., 2016; Maavara et al., 2017). In the Yangtze Basin, China, extensive hydrological modification to rivers due to dam and reservoir construction have led to stable water levels, improved water clarity, and reduced input of allochthonous organic material to floodplain lakes (Zeng et al., 2022). In lakes that had a restricted connection to the main Yangtze River channel, C/N values show less variability (6–8) compared to larger, hydrologically open lakes (3–13). These lakes have however responded to extensive secondary anthropogenic activity in the catchments which has promoted algal blooms and increased the proportion of autochthonous organic matter in the sediments leading to lower $\delta^{13}\text{C}$ and higher C/N when compared to the original allochthonous supply. Additionally, Briddon et al. (2020) highlight the impact of dam installation on a flood pulse wetland in Peninsular Malaysia. Lower values for both $\delta^{13}\text{C}$ and C/N were found after a dam was installed in 1995 due to an increase in algal productivity and reduced influence of allochthonous inputs from rivers. At this site, extensive oil palm plantations and mining in the catchment most likely are the source of external nutrients driving eutrophication of the lake.

3.3.2. Nitrogen isotopes

As seen in section 3.1 anthropogenic production of reactive nitrogen species and their circulation through the atmosphere, hydrosphere, and biosphere over the last 150 years has changed the global nitrogen cycle (Galloway et al., 2003), and translation via atmospheric nitrogen

loading is having global effects even in remote regions away from direct human activity (Fig. 1; Holtgrieve et al., 2011; Wolfe et al., 2013). However, the magnitude of $\delta^{15}\text{N}$ changes in sedimentary lake records and impacts on ecosystems at the local level can be even greater, due to a combination of point source and diffuse nitrogen pollution from urban development, wastewaters, industrial processes, agriculture, and subsequent internal loading that can each have characteristic $\delta^{15}\text{N}$ signatures. Anthropogenic nitrogen compounds readily enter the food chain as they are highly mobile and so can influence primary production and the $\delta^{15}\text{N}$ of organic matter deposited in lakes (Talbot, 2001). The $\delta^{15}\text{N}$ of bulk sediment is often compared to $\delta^{13}\text{C}$ and C/N to reconstruct past environmental change and human impact on the environment. However, due to nitrogen biogeochemical cycling being complex interpreting the $\delta^{15}\text{N}$ data can be more difficult and influenced by site specific controls on N (Hodell and Schelske, 1998; Meyers and Teranes, 2001). Bulk sediment $\delta^{15}\text{N}$ is influenced by the primary source of organic matter and the $\delta^{15}\text{N}$ of the nitrogen reservoir available to it, as well as fractionations associated with the assimilation of dissolved inorganic nitrogen (DIN), primary production, nitrogen fixation, and internal processing of the nitrogen pool by ammonification, nitrification, and denitrification (Talbot, 2001).

Typical $\delta^{15}\text{N}$ values for major sources of nitrogen in sediment archives include contributions from allochthonous organic material derived from land plants that have $\delta^{15}\text{N}$ close to 0 ‰ reflecting an atmospheric source of N_2 . Erosion and lateral transfer of terrestrial soils can give a broad range of potential $\delta^{15}\text{N}$ values depending on land use type (predominately 0 ‰ to +8 ‰), but higher $\delta^{15}\text{N}$ in soil organic matter is generally found in hot and dry ecosystems compared to cold or wet ecosystems (Craine et al., 2015) and at sites with greater land use intensity (Aranibar et al., 2008). Agricultural soils typically have higher $\delta^{15}\text{N}$ associated with enhanced mineralisation of soil organic nitrogen and the addition of fertiliser or animal waste (Heaton, 1986; Wang et al., 2018). Agricultural runoff and sewage have higher $\delta^{15}\text{N}$ due to loss of isotopically lighter ^{14}N during ammonia volatilisation (+10 ‰ to +25 ‰), and synthetic fertilisers produced by industrial nitrogen fixation have lower $\delta^{15}\text{N}$ reflecting that of atmospheric N_2 (-4 ‰ to +4 ‰; Heaton, 1986). Within a lake, aquatic plants and phytoplankton may have higher $\delta^{15}\text{N}$ as they commonly utilise dissolved NO_3^- that has $\delta^{15}\text{N}$ around +7 ‰ to +10 ‰ (Meyers and Teranes, 2001). Uptake of NO_3^- by phytoplankton can lead to fractionation of the remaining pool so algal $\delta^{15}\text{N}$ is typically lower than the $\delta^{15}\text{N}$ of total DIN. As eutrophication of water bodies increases, N-limitation and N_2 -fixing phytoplankton (cyanobacteria) become more prevalent which can drive lower $\delta^{15}\text{N}$ due to fixation of atmospheric N_2 . The $\delta^{15}\text{N}$ signature of allochthonous and autochthonous nitrogen sources can be further modified in the water column or during early diagenesis in sediments by denitrification, the reduction of NO_3^- to gaseous N_2 , under anoxic conditions or the loss of ammonium as NH_3 gas through ammonification, which both lead to isotope fractionation and higher $\delta^{15}\text{N}$ (Lehmann et al., 2003). This has been observed in sediments from Lake Erie, where increasing $\delta^{15}\text{N}$ (around +6 ‰) through the early-mid 20th century is attributed to increased denitrification in sediments related to the development of hypolimnetic anoxia associated with summer stratification (Lu et al., 2010b).

Although there are several fractionations that can occur during sedimentation and burial, the original $\delta^{15}\text{N}$ relationship between sources of heavily fractionated nitrogen should be largely preserved with degradational changes reported in the order of around 1 ‰–2 ‰ (Brahney et al., 2014; Gälman et al., 2009). In a study of 65 lakes in Quebec and Alberta, Canada, Botrel et al., 2014 showed a correlation between the concentration of total nitrogen in sediments with sedimentary $\delta^{15}\text{N}$ which has also been observed in surface sediments of 22 mountain lakes in Alberta (Bunting et al., 2010). Higher $\delta^{15}\text{N}$ in these northern hemisphere temperate lakes were found to generally occur alongside lower concentrations of total nitrogen suggesting degradational processes may have influenced the residual sediment $\delta^{15}\text{N}$ either

via microbial degradation in the water column or during early diagenesis. A significant relationship was also found between sediment $\delta^{15}\text{N}$ and the intensity of anthropogenic nitrogen loading to lakes.

There are now numerous palaeo studies that have investigated the timing and magnitude anthropogenic contamination of natural water bodies and the influence this has on nitrogen cycling and changes in sedimentary $\delta^{15}\text{N}$ values. Karthic et al. (2013) used a mixing model to show changes in the supply of nitrogen to Horseshoe Lake, USA, over the last ca. 335 years. Initial nitrogen supply to the lake was likely associated with biological fixation of nitrogen by cyanobacteria with $\delta^{15}\text{N}$ around 0 ‰. After 1920, nitrogen limitation reduced following the installation of a coke plant for steel manufacturing that discharged treated effluent with high $\delta^{15}\text{N}$ of up to +15 ‰ into the lake, which reduced the dominance of biological fixation. A third source from terrestrial runoff was present continuously throughout the sequence with $\delta^{15}\text{N}$ around 7 ‰–8 ‰. Routh et al. (2009) observed a pronounced shift to lower $\delta^{15}\text{N}$ from the early 1900s in the sediments of Lake Norrviken, Sweden in response to industrial and agriculture run-off into the lake. The $\delta^{15}\text{N}$ record traces a shift in the trophic status of the lake from eutrophic to hypereutrophic through this period, where transition to a cyanobacteria-dominated phytoplankton assemblage inferred from pigment analysis indicates the lower $\delta^{15}\text{N}$ is most likely related to an increase in nitrogen fixation from atmospheric N_2 . In the late 1900s, remediation efforts allowed the lake to return to mesotrophic conditions and $\delta^{15}\text{N}$ returns to higher values due to an expansion of non- N_2 fixing phytoplankton and utilisation of nitrogen from terrestrial sources. The trophic history of Lake Erie, USA, was also traced using $\delta^{15}\text{N}$ in sediment cores by Lu et al. (2010b), who documented the effects of eutrophication in response to accelerated external nutrient loading from catchment run-off. Variable $\delta^{15}\text{N}$ between 1950 and 1970 is interpreted as being the result of shifting sources of nitrogen, with agricultural and sewage waste driving shifts to higher $\delta^{15}\text{N}$ and blooms of N_2 -fixing cyanobacteria during periods of nitrogen depletion causing shifts to lower $\delta^{15}\text{N}$. An overall increasing trend in $\delta^{15}\text{N}$ values between 1910 and 1970 is thought to be related to the development of hypolimnetic anoxia during summer stratification in the central basin which promoted conditions suitable for denitrification and fractionation of the organic nitrogen pool towards higher $\delta^{15}\text{N}$ values.

In comparison with larger water bodies, lakes with a smaller water volume can respond more rapidly to changes in external nutrient loading and environmental conditions, they are also less likely to stratify and may restrict post-depositional alteration of $\delta^{15}\text{N}$ by microbial recycling of organic matter. Moorhouse et al. (2014) found concomitant increases in $\delta^{15}\text{N}$ and cyanobacterial pigments in the sediments of Blelham Tarn, UK, that correlate strongly with increases in livestock grazing and sewage processing in the catchment. Sediments from Lake Igaliku, Greenland, record a gradual increase in $\delta^{15}\text{N}$ from around +1 ‰ to +2 ‰ over the last ca. 1000 years that remain stable until an abrupt rise to +4 ‰ in the last 30 years (Bichet et al., 2013). Local farming is indicated to start around 1010 CE based on increases in sediment flux to the lake and the gradual increase in $\delta^{15}\text{N}$ most likely reflects land clearance and the introduction of agricultural practices in the catchment. The change to higher $\delta^{15}\text{N}$ in recent years is opposite to the shift toward lower $\delta^{15}\text{N}$ found in other Arctic lakes due to atmospheric deposition of anthropogenic nitrogen (Fig. 1; Holtgrieve et al., 2011). Instead, higher $\delta^{15}\text{N}$ is thought to be connected to intensive agricultural practices with greater nitrogen input to the lake from manure and industrial fertilisers, highlighting the site-specific nature of interpreting $\delta^{15}\text{N}$ data from sediment records.

Rapid changes to nitrogen cycling in lakes can also occur with point source pollution and direct input of nutrients. The Guarapiranga Reservoir in Brazil supplies drinking water for two million people and became eutrophic between 1974 and 2010 due to urban population expansion, catchment deforestation, and specifically the transfer of untreated sewage. Investigation of sediment cores from the reservoir have shown that enhanced external nutrient loading resulted in a large

+8 ‰ shift in $\delta^{15}\text{N}$ and promoted algal productivity indicated by a trend to lower C/N values (Fontana et al., 2014). Aquaculture production has expanded dramatically in recent decades and is an intensive practice (FAO, 2020). Cage farming activities can provide large volumes of nutrients and suspended material to lakes through the transfer of uneaten food and faeces with high $\delta^{15}\text{N}$ (+10 ‰ to +15 ‰) into the water column and sediment (Go et al., 2023; Gondwe et al., 2012; Sarà et al., 2004; Wang et al., 2022). However, the complicated nature of nitrogen biogeochemical cycling, including control by lake morphometry (Botrel et al., 2014), is likely reflected in the application of $\delta^{15}\text{N}$ data to trace the environmental impacts of aquaculture and further work is needed to assess the longer-term influence of the practice on inland water bodies.

The utility of nitrogen isotopes in sediment archives has been shown as a faithful indicator of past changes in human impact on the environment, particularly for eutrophication studies and pollution tracing where $\delta^{15}\text{N}$ values are generally higher with increasing trophic status and greater human impact (Torres et al., 2012). Nitrogen isotope data have become an intrinsic part of the multi-proxy isotope toolkit and strongly compliment other geochemical (e.g. $\delta^{13}\text{C}$) and biological indicators (e.g. algal pigments) of past environmental change within sediments. To further enhance our understanding of the impact of anthropogenic activities we crucially also need to undertake contemporary monitoring to provide fundamental context for palaeo records and trace modern processes to characterise human impacts and the current state of the environment.

4. Modern freshwater pollution sources, processing, and impact

Palaeoclimate records from lakes can help to identify the timing and magnitude of change but modern tracing of key nutrients (NO_3 and PO_4) is required to fully understand the ongoing degradation of our freshwaters. A large number of studies now utilise stable isotope methods to understand how these key nutrients enter our environment and the subsequent impacts they are having, including their role in eutrophication of freshwater systems and pollution of groundwater aquifers (Davies et al., 2014; Goody et al., 2016; Kendall et al., 2007; Talbot, 2001). P and N inputs now feature heavily in updated Planetary boundary theory, with specific limits for their release from fertilisers into freshwaters suggested (Steffen et al., 2015b). Alongside the application and release of nutrient pollution it is also important to understand the role humans are having on altering the composition and location of freshwaters, with modelling studies showing the impact river damming, reservoir production and water course alteration has on the distribution and extent of natural freshwater bodies (Pekel et al., 2016). The following sections therefore aim to highlight how stable isotopes can help identify sources of pollutants, trace the transformations these sources undergo in nature, and highlight their impact over a range of scales within the environment.

4.1. The nitrogen cycle and modern water pollution

Some of the most acute environmental pressures now surround water resources. These are either global, related to changes in climate, or more often local, related to population increase, agricultural runoff, and sewage discharges. These local impacts are now routinely identified in scientific studies, baseline environmental monitoring programs, and reported widely in the media. Of particular concern are the rapid rates of nitrate (NO_3) and ammonium (NH_4) addition into fresh and groundwater resources, which can drive eutrophication and at times exceed nationally set limits for safe drinking waters (Canfield et al., 2010; Kendall et al., 2007). Sources of nitrate and ammonium pollution into river, lakes, and groundwater systems are, however, difficult to quantify using concentration data alone. Isotope analysis of dissolved species of nitrate ($\delta^{18}\text{O}\text{-NO}_3$, $\delta^{15}\text{N}\text{-NO}_3$) and ammonium ($\delta^{15}\text{N}\text{-NH}_4$) can start to resolve this source identification issue, either due to the distinct range of isotope values associated with individual sources (Hastings et al., 2013;

Kendall et al., 2007) or due to our ever-increasing understanding of how isotope fractionations can help to interpret nitrogen cycling (Venkiteswaran et al., 2019).

The use of isotopes for nitrate source identification is not a new development, with Heaton (1986) and references within, demonstrating distinct sources of nitrate using the nitrate nitrogen isotope value ($\delta^{15}\text{N}\text{-NO}_3$). However, these sources often have overlapping $\delta^{15}\text{N}\text{-NO}_3$ values reducing the source apportionment efficiency. The use of a biplot of nitrate oxygen ($\delta^{18}\text{O}\text{-NO}_3$) and $\delta^{15}\text{N}\text{-NO}_3$ then became common place as a diagnostic tool for identifying nitrate sources, as the combination of O and N provide a better differentiation between different sources (Fig. 4). Atmospheric nitrate isotope values have a large range ($\delta^{15}\text{N} = -15\text{‰}$ to $+15\text{‰}$, $\delta^{18}\text{O} = +20\text{‰}$ to $+70\text{‰}$), influenced by anthropogenic inputs, including proximity to pollution sources, chemical reactions within the atmosphere, and meteorological/seasonal conditions (Heaton, 1986; Jung et al., 2020). Synthetic nitrate fertilisers have a narrower isotope range ($\delta^{15}\text{N} = -4\text{‰}$ to $+4\text{‰}$, $\delta^{18}\text{O} = +19\text{‰}$ to $+25\text{‰}$), with the distinctive $\delta^{18}\text{O}\text{-NO}_3$ values associated with atmospheric O_2 isotope composition (average around $+23.5\text{‰}$) incorporated during their manufacture. Nitrates derived from the microbial nitrification of ammonium-based fertilisers have a wider $\delta^{15}\text{N}\text{-NO}_3$ range (-10‰ to $+8\text{‰}$) and lower $\delta^{18}\text{O}\text{-NO}_3$ values (-5‰ to $+15\text{‰}$), at least in well oxygenated soils (Kendall et al., 2007). Organic fertilisers derived from manure have a wide $\delta^{15}\text{N}\text{-NO}_3$ isotope range due to their diverse origins ($+2\text{‰}$ to $+30$) and $\delta^{18}\text{O}\text{-NO}_3$ values associated with within soil nitrification. Sewage and septic tank waste has similar $\delta^{15}\text{N}\text{-NO}_3$ isotope ranges, normally indistinguishable from animal waste (Jung et al., 2020). Soil nitrate values are characterised by a range of isotope values ($\delta^{15}\text{N} = -10\text{‰}$ to $+15\text{‰}$). In reality, these values represent a diverse range of sources and processes which act to pull the isotope value of the soil nitrate pool in several competing directions, often controlled by environmental conditions and anthropogenic pressures including the addition of fertilisers (Denk et al., 2017).

Whilst useful for generalisation, on a site specific scale this simplified biplot (Fig. 4) can lead to misinterpretation of nitrate sources in natural freshwater systems, especially where cycling of nitrate has occurred that overprints the initial nitrate source signatures (Jung et al., 2020). The predominant processes of nitrogen cycling within freshwaters are nitrification, assimilation, mineralisation, fixation, volatilisation, and denitrification. The relevant isotope effects of each of these processes are beyond the scope of this review but are now considered far more stringently in modern nitrogen pollution literature. Good reviews of these processes and expected isotope effects are given by (Denk et al., 2017; Jung et al., 2020; Kendall et al., 2007; Matiatos et al., 2021) and references within. Where a biplot style assessment of pollution sources is sought, the identification of local source endmember stable isotope values is now strongly recommended (Archana et al., 2016; Bateman and Kelly, 2007; Venkiteswaran et al., 2019).

Even considering all the potential factors that influence a bulk nitrate isotope signature, the nitrate isotope method has been applied widely and with great success to identify pollution sources and elucidate the often-complex processes of nitrogen cycling. Good examples can be found from studies investigating some of the world's largest river systems (Luu et al., 2020; Matiatos et al., 2021; Smith et al., 2024; Yue et al., 2017), pollution impacted watersheds (Matiatos et al., 2023), delicate groundwater aquifers (Karlović et al., 2023; Kazakis et al., 2020; Marković et al., 2022; Nikolenko et al., 2018), point sources of pollution, such as mine wastewater runoff (Nilsson and Widerlund, 2017), human wastewaters (Archana et al., 2016), the oceans (Thompson, 2022) and major lake systems (Hu et al., 2019; Mayer and Wassenaar, 2012).

In all these cases, stable isotope tracing has proved fundamental to our understanding of local and regional point sources of pollution and the role the nitrogen cycle plays in amplifying or reducing human induced pollution effects. Further work, especially in aquatic systems must now focus on high resolution sampling efforts due to the varying

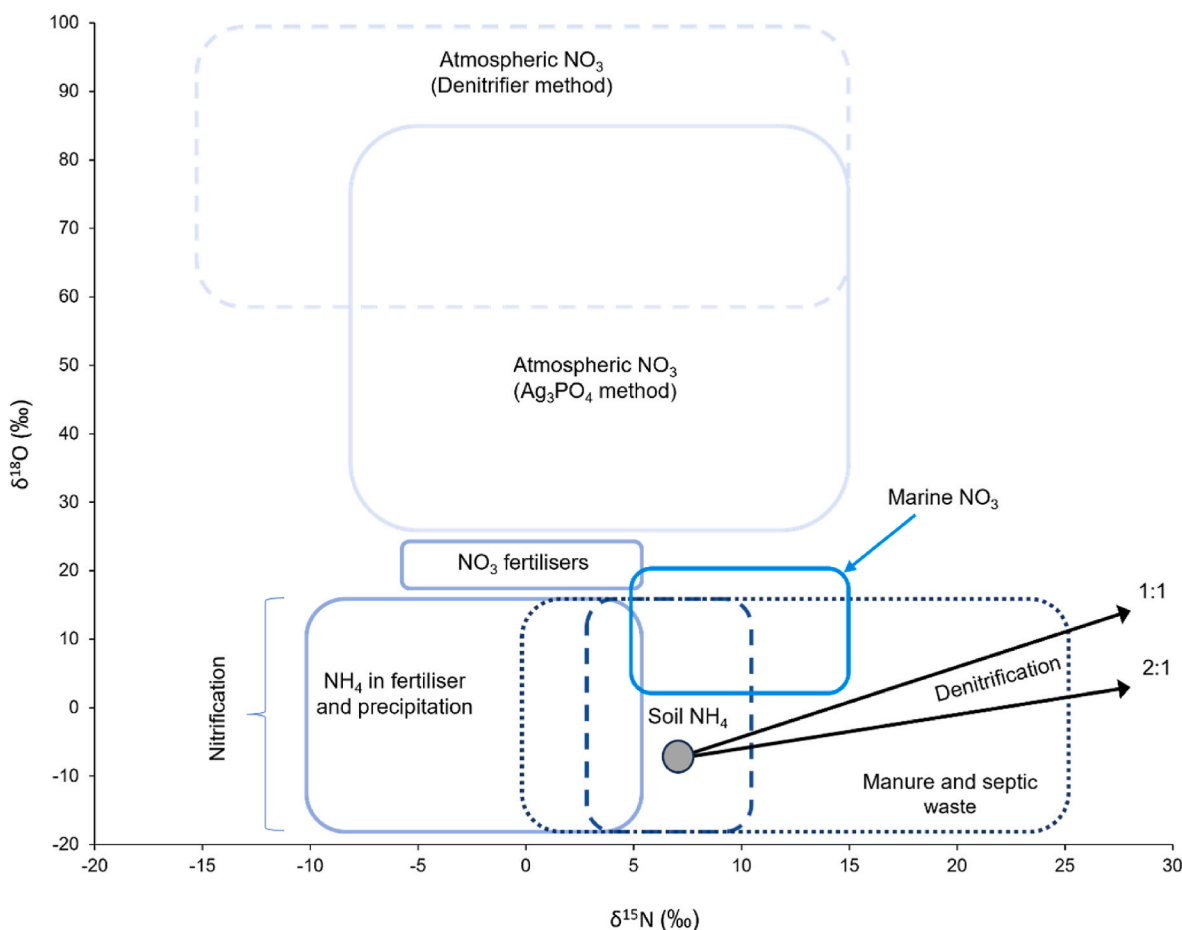


Fig. 4. Dual nitrogen and oxygen isotope plot showing average source $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values and the theoretical impact of denitrification. The diagram is modified using the source values and figures of Kendall et al. (2007) and Jung et al. (2020).

temporal and spatial pressures these systems face (Matiatos et al., 2021). In addition, efforts to understand the impacts of nutrient pollution on local and regional scales need to go further than just considering nitrogen. Multi-nutrient, stable isotope assessments are now needed to further expand our understanding of heavily impacted systems (Goody et al., 2016) and, where possible, both modern sources and potential legacy pollutants should be considered.

4.2. Tracing phosphate using oxygen isotopes

The tracing of phosphorus within the environment has historically been far more complicated than tracing nitrogen and carbon, predominantly due to the inability to apply a stable isotope method. Where both carbon and nitrogen have two stable isotopes, phosphorus only has one (^{31}P). In the early 2000's, researchers started to explore the potential for stable isotope tracing in modern systems using the isotope composition of oxygen bound to phosphorus within the phosphate mineral ($\delta^{18}\text{O-PO}_4$) (Blake et al., 2001; McLaughlin et al., 2004). This method relies on the fact that once formed, the P-O bond is stable under Earth surface conditions in the absence of biological activity (Davies et al., 2014; Pfahler et al., 2022).

The only ways to alter this starting isotope signature are through 1) the sorting of heavier and lighter isotopologues or 2) enzymatically mediated cleaving of the P-O bond. Relatively small isotope fractionations have been reported for this first process during P uptake by biota (Blake et al., 1997) and during the inorganic sorption/desorption of P into metal oxides (Jaisi et al., 2010). The active cleaving of the P-O bond by enzymes however, leads to much larger isotope fractionations (Chang and Blake, 2015; Pfahler et al., 2022). The most ubiquitous of these

enzymes is inorganic pyrophosphatase which catalyses the hydrolysis of pyrophosphate into phosphate, creating a temperature dependent isotopic equilibrium (Equation (2) and Fig. 5) (Chang and Blake, 2015; Pistocchi et al., 2017).

$$\text{EQ}\delta^{18}\text{O-PO}_4 = -0.17 T + 26.5 + \delta^{18}\text{Ow} \quad \text{Equation 2}$$

Where $\text{EQ}\delta^{18}\text{O-PO}_4$ is the $\delta^{18}\text{O-PO}_4$ value of phosphate at equilibrium with oxygen in the ambient water in ‰, T is the ambient temperature in °C and $\delta^{18}\text{Ow}$ is the isotopic composition of O in water in ‰.

This process completely overprints the original source $\delta^{18}\text{O-PO}_4$ value and is thought to be so prevalent in natural systems as to normally swamp any other enzyme derived isotope fractionations. In practice, this leads to a two-endmember scenario. Firstly, the original oxygen isotopic composition of the source phosphate and secondly, the expected isotopic equilibrium ($\text{EQ}\delta^{18}\text{O-PO}_4$), if the whole phosphate pool had been overturned by enzymatic activity. As equilibrium can be theoretically calculated, as long as temperature and water $\delta^{18}\text{O}$ are known, it is critically important to accurately derive possible source endmembers $\delta^{18}\text{O-PO}_4$ to support conclusions on the possible sources of environmental pollution or the extent of PO_4 cycling (Fig. 5) (Smith et al., 2021a).

Developments in the extraction and purification of phosphate for isotope analysis (McLaughlin et al., 2004; Pfahler et al., 2022; Rieckmann et al., 2024; Tamburini et al., 2010) have enabled researchers to isolate dissolved, sedimentary, and plant phosphates more efficiently. These advancements have led to a growth in research applying the $\delta^{18}\text{O-PO}_4$ tracer to understand sources of environmental phosphate (Fig. 5), including bedrocks (Smith et al., 2021a), wastewater treatment

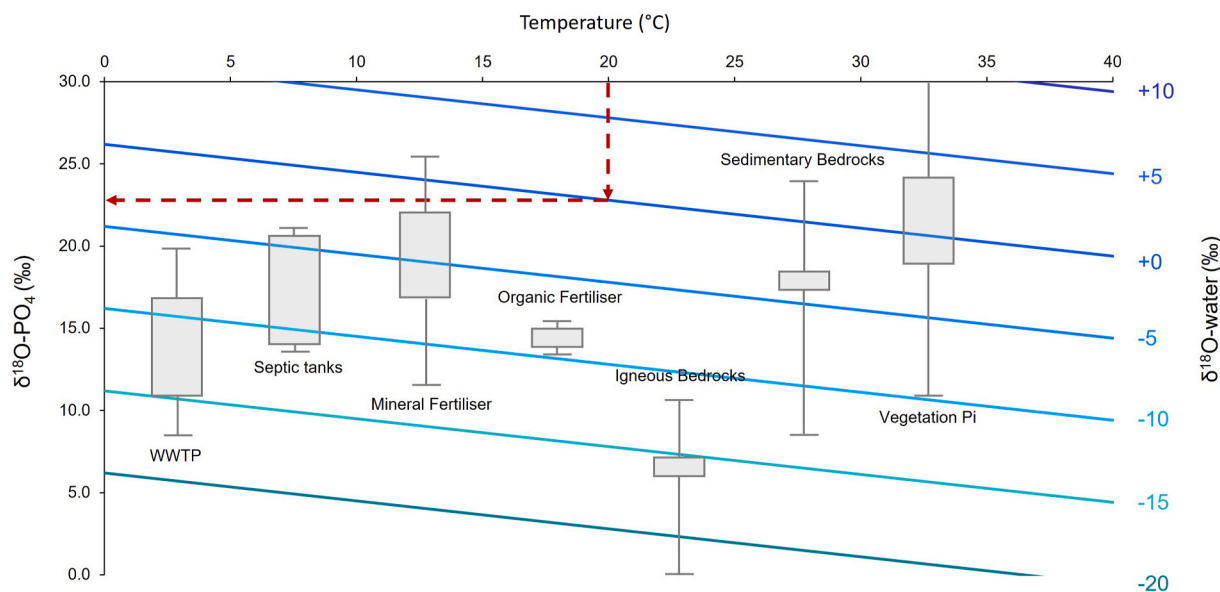


Fig. 5. Grey boxes present $\delta^{18}\text{O-PO}_4$ values for a range of common source endmembers, bedrock data from [Smith et al. \(2021a\)](#), other common source data from [Pfähler et al. \(2022\)](#) and references therein. Blue lines represent expected phosphate oxygen isotope equilibrium ($\text{EQ}\delta^{18}\text{O-PO}_4$) at a range of different water oxygen isotope values and temperatures, following the equation of ([Chang and Blake, 2015](#)). The red dashed line offers an example of $\text{EQ}\delta^{18}\text{O-PO}_4$ ($= -22.8\text{‰}$) at a measured temperature of 20 °C and a water oxygen isotope value of 0‰ .

plant discharges ([Goody et al., 2018](#); [Gruau et al., 2005](#)) and fertilisers and manure ([Granger et al., 2018](#); [Gruau et al., 2005](#); [Yang et al., 2023](#)). By analysing the $\delta^{18}\text{O-PO}_4$ of local phosphate sources and utilising the expected equilibration ($\text{EQ}\delta^{18}\text{O-PO}_4$) value, new areas of phosphate tracing research have developed; including soils ([Helfenstein et al., 2018](#); [Tamburini et al., 2014](#); [Zohar et al., 2010](#)), agricultural and grassland systems ([Pfähler et al., 2020](#); [Wells et al., 2022](#)), lake and river sediments ([Goldhammer et al., 2011](#); [Jin et al., 2023](#); [Pistocchi et al., 2017](#); [Wang et al., 2021](#)), application to extreme or extraterrestrial environments ([Blake et al., 2001](#); [Shen et al., 2020](#)), plants ([Pfähler et al., 2013](#); [Tamburini et al., 2014](#)) and pollution within aquatic systems and drinking waters ([Davies et al., 2014](#); [Elsbury et al., 2009](#); [Goody et al., 2015](#)).

When trying to trace sources of environmental pollution, some of the best examples now employ a multi-isotope framework, coupling the $\delta^{18}\text{O-PO}_4$ method with nitrate and ammonium isotope tracing. [Goody et al. \(2016\)](#) is a prime example of this multi-isotope framework approach, applying this toolkit when tracing eutrophication to the River Beult, UK. They identify nutrient inputs from wastewater treatment works and agriculture and utilise the stable isotope composition of river waters alongside nutrient concentrations to investigate biogeochemical processes associated with nutrient removal. Interestingly, the study captures high and low flow conditions, which have different nutrient concentrations but similar isotope values, indicating similar nutrient sources regardless of flow rate and concentration.

Whilst this study undertakes two sampling rounds (high and low flow), future work must attempt to capture even higher resolution stable isotope datasets, especially in seasonally impacted systems such as agricultural systems, lakes or drinking water reservoirs. Combatting eutrophication requires a complex, seasonally resolved understanding of nutrient sources, their uptake, cycling and deposition within natural environmental systems. This type of high-resolution work, coupled to palaeo records of nutrient pollution, offers us the best opportunity to accurately resolve environmental degradation within aquatic systems. This greater level of source and process understanding will then lead to far more effective mitigation and environmental remediation measures.

5. Conclusions

Regardless of scale, stable isotope analysis is one of the key components of the geochemical toolkit when tracing human impact on the environment. Whether considering the release and global transport of greenhouse gasses or trying to elucidate the causes of direct pollution of local aquatic systems, stable isotope analysis has a key role to play. This review has highlighted a range of isotope systems, some routinely applied, such as $\delta^{13}\text{C}$ within atmospheric records of carbon dioxide, and others which are only now becoming more common place, including $\delta^{18}\text{O}$ of phosphate, as well as the importance of considering anthropogenic environmental change over a range of spatial and temporal scales. Stable isotopes in palaeo archives can provide a better understanding of the initiation, nature, and timing of anthropogenic impact and environmental change through time, in addition to highlighting the relative magnitude of these changes in relation to baseline or natural background conditions. Isotope tracing methods and modern monitoring can then be employed more strategically, to investigate the sources and cycling of key pollutants within these environmental systems. Through a combined palaeo and contemporary monitoring method and by employing a multi-isotope framework, researchers have far greater power to investigate the often-complex range of anthropogenic pressures at regional and local scales, which can lead to environmental degradation.

Author contributions

ACS and JHL co-researched and authored the review.

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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Data availability

No data was used for the research described in the article.

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