Stable Isotopes

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Volume 2, **The Earth system: biological and ecological dimensions of global environmental change**, pp 544–550

Edited by

Professor Harold A Mooney and Dr Josep G Canadell

in

Encyclopedia of Global Environmental Change
(ISBN 0-471-97796-9)

Editor-in-Chief

Ted Munn

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Stable isotopes *indicate those isotopes of an element which are stable and that do not decay through radioactive processes over time. Most elements consist of more than one stable isotope. For instance, the element carbon (C) exists as two stable isotopes,* ^{12}C *and* ^{13}C*, while the element oxygen (O) exists as three stable isotopes,* ^{16}O*,* ^{17}O*, and* ^{18}O*. As is the case with both carbon and oxygen, the more common stable isotope species typically contains the fewest number of neutrons for that element. Stable isotopes should not be confused with* radioactive isotopes *of an element. Radioactive isotopes have limited life times and undergo a decay to form a different element, although the time required for this decay may vary widely ranging from nanoseconds to thousands of years. For instance, carbon has six radioactive isotopes (*^{9}C, ^{10}C, ^{11}C, ^{14}C, ^{15}C*, and* ^{16}C*) of which* ^{14}C *is perhaps best known because of its utility in dating biological materials and as a tracer in metabolic studies.*

HOW COMMON ARE STABLE ISOTOPES?

A brief listing of the stable isotopes and their abundances for the elements most commonly used in global change research can be seen in Table 1.

Table 1 A brief listing of the stable isotopes and their abundances for the elements most commonly used in global change research

Element	Isotope	Abundance (%)
Hydrogen	^{1}H	99.985
	^{2}H	0.015
Carbon	^{12}C	98.89
	^{13}C	1.11
Nitrogen	^{14}N	99.63
	^{15}N	0.37
Oxygen	^{16}O	99.759
	^{17}O	0.037
	^{18}O	0.204
Sulfur	^{32}S	95.00
	^{33}S	0.76
	^{34}S	4.22
	^{36}S	0.014
Strontium	^{84}Sr	0.56
	^{86}Sr	9.86
	^{87}Sr	7.02
	^{88}Sr	82.56

HOW ARE STABLE ISOTOPE ABUNDANCES TYPICALLY MEASURED?

Of particular interest for global change studies are variations in the isotopic abundances of hydrogen, carbon, nitrogen, and oxygen isotopes. These relatively light elements are typically measured using a gas isotope rationing mass spectrometer. The mass spectrometer consists of a source to ionize the gas, a flight tube with a magnet to deflect the path of the ionized gas, and a detector system at the end of the flight tube to measure the different isotopic species. First, the element of interest must be converted to a gaseous form for introduction into the mass spectrometer. The most commonly used approaches involve introducing hydrogen as H_2, carbon as CO_2, nitrogen as N_2, and oxygen as CO_2. As the gas is introduced into the mass spectrometer, it is ionized by removal of an electron as the gas is bombarded by a source. Then as the ionized gas travels down the flight tube (under vacuum), the paths of light and heavy isotopic species are deflected differently by the magnet. Detectors are positioned at the end of the flight tube to measure the abundance ratios of the heavy and light isotopic species.

EXPRESSION OF STABLE ISOTOPE ABUNDANCES

The abundance of stable isotopes is typically presented in delta notation (δ), in which the stable isotope abundance is expressed relative to a standard (Equation 1):

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000‰ \quad (1)$$

where R is the molar ratio of the heavy to light isotopes, e.g., Equation (2):

$$R = \frac{^{13}\text{C}}{^{12}\text{C}} \text{ or } \frac{D}{H} \text{ or } \frac{^{18}\text{C}}{^{16}\text{O}} \quad (2)$$

For the most commonly used light isotopes, the internationally recognized standards are shown in Table 2.

Table 2 Internationally recognized standards for the most commonly used light isotopes

H	SMOW[a]	$R = 0.0001558$
C	PDB[b]	$R = 0.0112372$
N	AIR[c]	$R = 0.0036765$
O	SMOW	$R = 0.0020052$
S	CDT[d]	$R = 0.0450045$

[a] Standard Mean Ocean Water (SMOW).
[b] Pee Dee Belemnite (PDB).
[c] Atmospheric air (AIR).
[d] Canyon Diablo Triolite (CDT).

HOW DOES NATURAL VARIATION IN STABLE ISOTOPES COME ABOUT?

Variations in the abundances of stable isotopes among different compounds arise because the chemical bonding is stronger in molecules containing heavier isotopic forms, making it more difficult to break up the molecule in a chemical reaction (often termed *kinetic fractionation*), or because of differences in the physical properties of molecules containing heavier isotopic forms (often termed *diffusive and equilibrium fractionation*). With kinetic fractionation, the rate of an enzymatic reaction is faster with substrates that contain the lighter isotopic form than in reactions involving the heavier isotopic form. As a consequence, there will be differences in the abundances of the stable isotopes between substrate and product. Such differences will occur unless, of course, all of the substrate were consumed, in which case there would be no difference in the isotopic composition of substrate and product. Expression of a significant kinetic fractionation in most biological reactions involves substrates at branch points in metabolism, such as the initial fixation of carbon dioxide in photosynthesis. Equilibrium fractionation events reflect the observation that during equilibrium reactions, such as the equilibration of liquid and gaseous water, molecules with the heavier isotopic species are typically more abundant in the lower energy state phase. Diffusive fractionation events reflect the observation that heavier isotopic forms diffuse more slowly than lighter isotopic forms.

WHAT IS THE NATURAL RANGE OF ISOTOPIC VARIATION IN NATURE?

The natural variations in isotopic abundance can be large. Figure 1 illustrates the natural variations found for materials frequently of interest in global change studies: waters, greenhouse gases, and biological materials. As a starting point, note that some atmospheric gases, such as CO_2, N_2, and O_2, exhibit limited variation, while N_2O and CH_4 exhibit wide isotopic variation. The larger isotopic ranges in the latter two gases reflect both significant isotopic fractionation by microbes as well as different biological substrates which are used to produce these gases.

Oceans, the largest volume of water on Earth, exhibit only small variation in isotopic abundance and most of this is associated with changes in salinity. However, once water evaporates from the oceans and later recondenses as precipitation, there are large isotopic variations that are dependent on both cloud temperature and the amount of residual moisture remaining within the cloud mass. Lakes and rivers reflect precipitation input values, but are often further enriched by evaporative processes, which favor the movement of lighter isotopic forms of water into the vapor phase.

There can be significant biological fractionation against carbon dioxide during photosynthesis, which results in plants being isotopically depleted relative to the carbon dioxide substrate. Animals largely reflect the carbon isotopic composition of their food resources, a useful tool for food web studies. However, the carbon in animal bones and teeth consists of carbonates, which are isotopically enriched relatively to the original carbon dioxide substrate (in this case respired food resources or animal tissues). In general, carbonates are both ^{13}C and ^{18}O enriched, relative to their substrates, carbon dioxide and water.

There is very limited isotopic variation in diatomic nitrogen. The microbial process of nitrogen fixation ($N_2 \rightarrow NH_4^+$) exhibits little isotopic fractionation and thus these products have a similar nitrogen isotope ratio as the atmosphere. Yet subsequent nitrogen transformation reactions exhibit strong isotopic fractionations. In general, the isotopic composition of animals within a trophic level are enriched by ~3‰ relative to their food substrate. The wide variations in nitrogen dioxide reflect the large differences associated with aerobic versus anaerobic processes and industrial versus stratospheric processes.

HOW ARE STABLE ISOTOPES USED IN GLOBAL CHANGE RESEARCH?

Stable isotopes are useful for several important aspects of global change research. One major area is to use stable isotope ratios to reconstruct past environmental conditions, which is possible when a compound is laid down and preserved over time. Some common examples would include ice profiles, the shells of mollusks, and tree rings. Another major application of stable isotopes is to reconstruct diets of animals and ecosystem structure. The isotopic composition of an animal reflects its food source; while soft tissues and hair are lost after animals die, the bones and teeth can be used to reconstruct past diets. Similarly for ecosystems, the isotopic composition of soil organic matter reflects the plant material that occupied the surface in the past. Another very common application of stable isotopes is as a tracer to identify where materials had originated. This is a particularly powerful approach in atmospheric studies where the interest is in identifying which terrestrial surface (e.g., ocean versus land) or which terrestrial ecosystem (e.g., grassland versus forest) is contributing or removing a gas species from the atmosphere.

Below we provide several examples to illustrate how stable isotopes are used in global change research. However, because of space limitations, we will only consider examples involving hydrogen, carbon, and oxygen isotopes.

Reconstruction of Past Air Temperatures using Hydrogen Isotopes of Water in Ice Cores

The hydrogen and oxygen isotope ratios of water have been used to reconstruct temperature patterns. The basis for this observation is that the isotopic fractionation associated

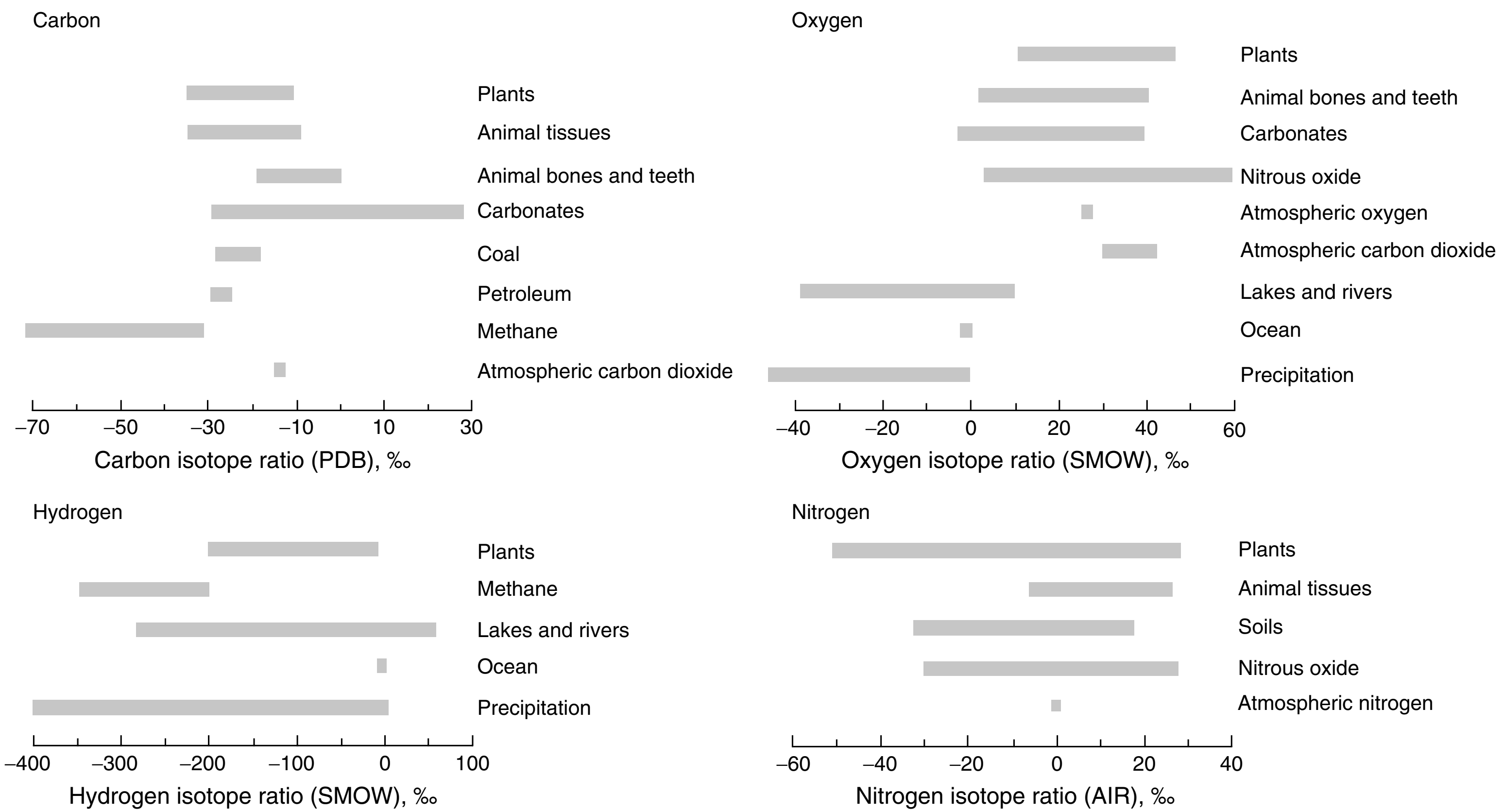

Figure 1 Variations in the carbon, oxygen, hydrogen, and nitrogen isotope ratios of materials of interest in global environmental change studies. (Data were collected from a very wide ranging series of studies)

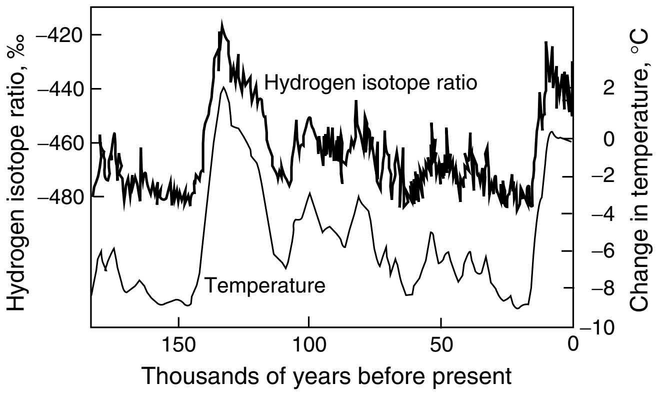

Figure 2 The hydrogen isotope ratios of waters from segments of ice from the Vostok ice core in Antarctica and the calculated temperatures associated with those time periods for the past 200 000 years. (Adapted from Jouzel *et al.*, 1990)

with cloud vapor to precipitation formation is temperature dependent. Scientists have capitalized on this observation by analyzing deep ice profiles, such as the ice in Antarctica. Figure 2 shows the initial depth profile of hydrogen isotope ratios of ice water found in the Vostok ice core. The data shown reveal the isotopic oscillations observed during a glacial–interglacial cycle. When these isotopic values are converted to equivalent temperature differences, we see that the temperature at this location varied by 10 °C between glacial and interglacial periods. Of particular importance also are the smaller temperature cycles, which reflect oscillations in climate. Note also how rapid the change is from one temperature regime to another. The bottom of the Vostok ice core extends back to 420 000 years before present. By analyzing the ice records from different locations, scientists are able to reconstruct the spatial patterns of temperature changes and the extent to which climate oscillations were of regional versus global extent.

Carbon Isotopes in Fossils and Fossil Soils are used to Reconstruct Past Terrestrial Ecosystems

The carbon isotope difference between C_3 and C_4 vegetation can be exploited to determine ecological change in the past. C_3 and C_4 plants (*see* **C_3 and C_4 Photosynthesis**, Volume 2) have $\delta^{13}C$ values averaging approximately -27 and -12‰, respectively. The ratio of C_3 to C_4 plants in the ecosystem or in the diet of herbivores is recorded in fossil soils as organic carbon or as soil carbonate, and in mammalian tooth enamel. Organic matter preserved in soils has about the same $\delta^{13}C$ value as in the original soil, whereas soil carbonate and mammalian tooth enamel are both enriched by about 14‰ compared to the vegetation.

The study of fossil soils and fossil tooth enamel from the Siwalik sediments in Pakistan illustrates how isotopes can be used to reconstruct past ecosystems. In Figure 3,

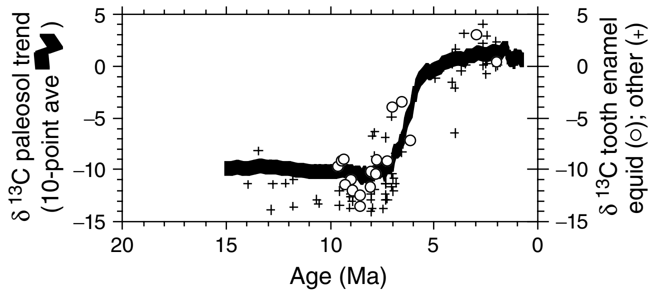

Figure 3 $\delta^{13}C$ values for soil carbonates from the Siwaliks in Pakistan shown as a 10 point running mean. $\delta^{13}C$ values for equids show that they had a C_3-dominated diet before 8 million years ago, but changed to a C_4 diet as the ecosystem underwent a change from C_3 dominated to C_4 dominated. (Adapted from Cerling *et al.*, 1998)

the fossil soil record shows that before eight million years ago, the local ecosystem was dominated by C_3 plants, and that they were gradually replaced by C_4 plants so that by five million years ago the ecosystem was dominated by C_4 plants. Fossil tooth enamel from the same region shows that equids and other mammals had a C_3-dominated diet before eight million years ago, but changed to a C_4-dominated diet as the ecosystem changed to become C_4-dominated. This change in vegetation is accompanied by a significant change in the $\delta^{18}O$ of local water of atmospheric origin indicating that the monsoon system may have undergone a significant change at this time. Recent studies have also shown that this was a time of major faunal turnover in the region (Cerling *et al.*, 1998).

Hydrogen and oxygen isotope ratios of water are used to determine current sources of plant water from within the soil, while those isotopes in cellulose of tree rings provide historical patterns. For plants, the primary sources of hydrogen and oxygen are from waters of atmospheric origins. Since the isotopic composition of precipitation will vary both seasonally and geographically, largely reflecting cloud condensation temperature, we have a tool for addressing ecological and global change questions. In plants, the isotopic composition of tree rings will in part reflect the isotopic composition of plant water sources, providing a tool for now understanding how precipitation patterns as reflected in tree rings may have changed during a plant's lifetime. For long-lived organisms, such as redwood trees, this provides a valuable tool for reconstructing climatic variations over periods of hundreds to thousands of years.

A second area in which isotopes of water are used in plant global change studies is for understanding the dynamics of water use by different species within a community, particularly for evaluating which species may or may not be competing for water. Figure 4 illustrates the hydrogen isotope ratios of different species at an arid site in western North America following intensive summer rains, which

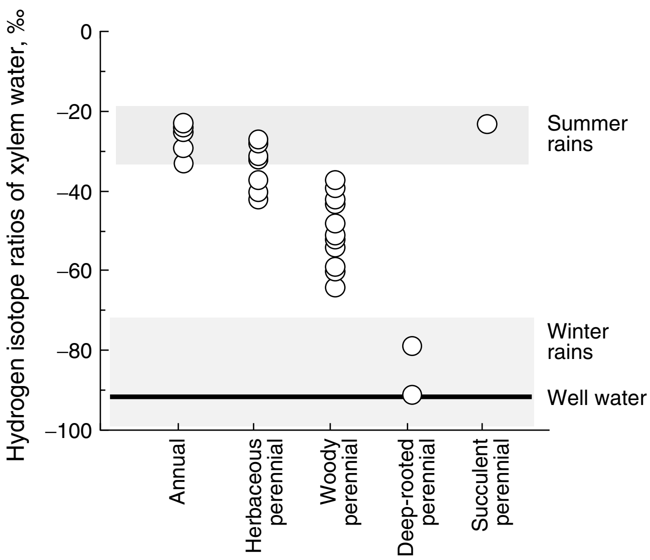

Figure 4 Hydrogen isotope ratios of water found in plants growing in the same arid land location in southern Utah following an intense summer rain event. Shown also are the observed variations in the isotopic composition of summer rains (upper depth soil moisture source) and winter rains (lower depth soil moisture sources). (Adapted from Ehleringer *et al.*, 1991)

saturate the upper soil layers while the remaining winter moisture exists only in deeper soil layers. Shown also are isotopic ratios expected for rains falling in summer versus winter months. Note that species utilize different moisture sources, suggesting a strong sensitivity of each species to whether rain falls in winter or summer. Strong interannual variations in precipitation are associated with El Niño events and this will influence the growth and competitive dynamics of plants in those regions of the globe impacted by El Niño Southern Oscillation (ENSO). While analyses of water within stems of modern plants can be used to immediately assess the impact of ENSO on plant performance, tree ring analyses can be used to reconstruct the periodicity and extent of the impact over historical periods.

Reconstruction of Animal Migration Routes using Hydrogen and Oxygen Isotope Ratios of Feathers

In global change studies, it is often useful to know if animals have changed their migration routes, reflecting some change in the quality of an environment. Or for animals that congregate in a common winter location, such as the monarch butterflies that winter in central Mexico, where did these individuals originate? The isotopic composition of butterfly wings and of bird feathers have been shown to reflect the isotopic composition of water at the location where that tissue was initially formed. Thus, isotopes provide a powerful tool for identifying where an individual might have originated from. In the case of

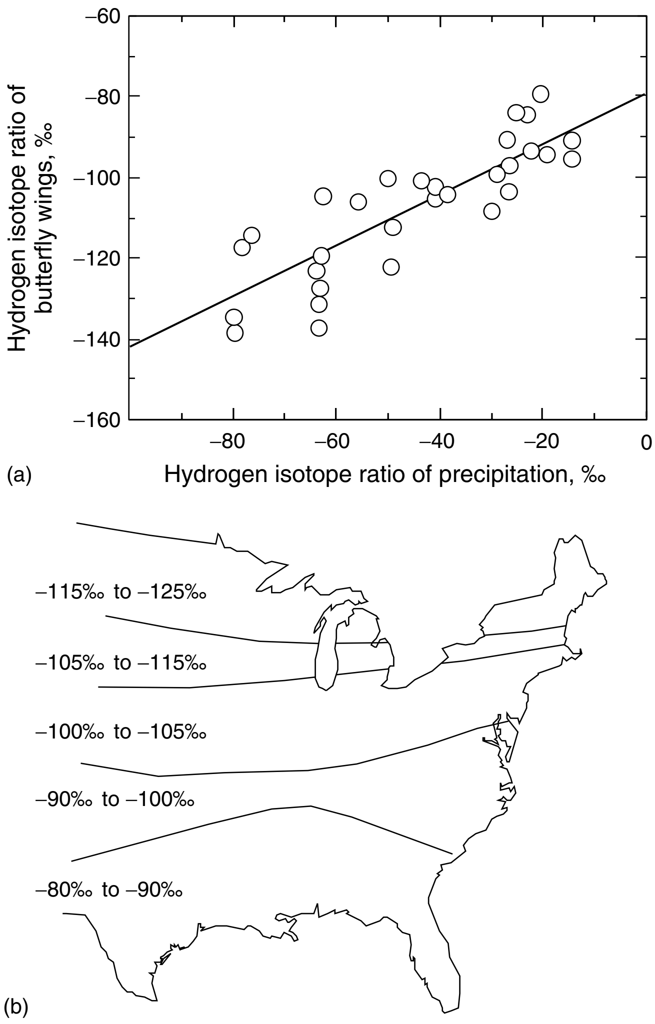

Figure 5 (a) The relationship between hydrogen isotope ratios of wings of field-raised monarch butterflies and of weighted mean growing-season precipitation. (b) Geographic patterns of hydrogen isotope ratios of precipitation across the eastern US. (Adapted from Hobson *et al.*, 1999)

the monarch butterfly, Figure 5(a) illustrates the strong correlation between the hydrogen isotope ratios of precipitation at a location and the subsequent hydrogen isotope ratios observed for organic matter in the butterfly wings. Since virtually all of the hydrogen in organisms (both plants and animals) originates from precipitation, the strong correlation is expected. The offset from a 1 : 1 relationship reflects biological fractionation processes during synthesis of the wing. The basis for geographical variations in isotopic composition of precipitation reflects temperature differences in the clouds at the time of precipitation. Colder storms are found at higher latitudes. As shown on Figure 5(b), there is a variation of ~45% in hydrogen isotopes across the eastern portions of the US allowing sufficient variation for scientists

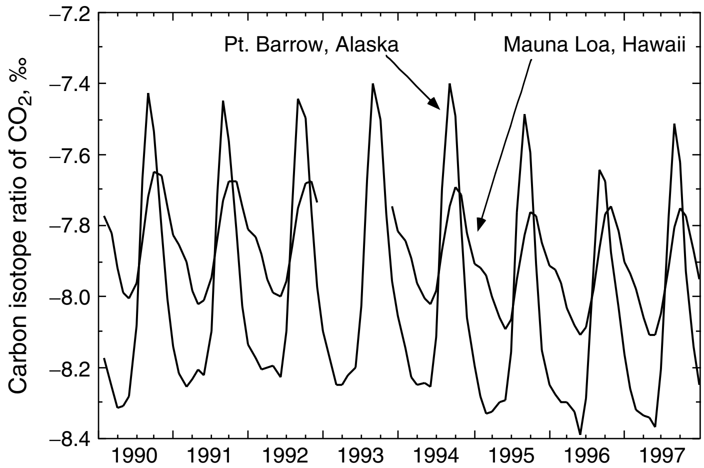

Figure 6 Seasonal changes in the carbon isotope ratios of atmospheric CO_2 at Point Barrow (Alaska) and Mauna Loa (Hawaii) between 1990 and 1997. The seasonal changes are driven by differences in the relative rates of photosynthesis and respiration by ecosystems at these latitudes. The enhanced amplitude at northerly latitudes reflects the shorter growing season. (Adapted from the National Oceanic and Atmospheric Administration – Climate Monitoring and Diagnostics Laboratory Monitoring Program; data courtesy of Jim White and Pieter Tans)

to identify regions from which a monarch butterfly might have come.

Dissecting the Global Carbon Cycle Today with Carbon and Oxygen Isotopes in Carbon Dioxide

The carbon isotope ratios of fossil fuels are depleted in ^{13}C relative to the atmosphere (Figure 1). Since the increases in atmospheric CO_2 are largely associated with fossil fuel emissions, there has been a long-term trend of progressive decreases in the average carbon isotope ratio of atmospheric carbon dioxide from −6.5‰ to −8‰ today.

On an annual basis, variations in the carbon isotope ratio analyses of atmospheric carbon dioxide are used to understand seasonal dynamics on the land surfaces. In Figure 6, the monthly average carbon isotope ratio, for atmospheric carbon dioxide at Point Barrow, Alaska (latitude 71 °N) and Mauna Loa, Hawaii (latitude 19 °N) are shown for the period 1990–1997. The strong seasonal cycles reflect the addition of carbon dioxide during periods when ecosystem respiration exceeds photosynthesis, resulting in a net loss of carbon dioxide from the ecosystem. In contrast, during periods when photosynthetic activity is high, the carbon isotope ratio of the atmosphere increases as photosynthetic processes discriminate against the heavier $^{13}CO_2$. By analyzing these time trends, it is possible to detect changes in the length of the growing season over time and to address carbon cycle questions, such as the extent to which terrestrial versus oceanic surfaces are responsible for absorbing anthropogenically produced carbon dioxide.

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