Is there an isotopic signature of the Anthropocene?

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Abstract

We consider whether the Anthropocene is recorded in the isotope geochemistry of the atmosphere, sediments, plants and ice cores, and the time frame during which any changes are recorded, presenting examples from the literature. Carbon and nitrogen isotope ratios have become more depleted since the 19th century, with the rate of change accelerating after ~AD 1950, linked to increased emissions from fossil fuel consumption and increased production of fertiliser. Lead isotope ratios demonstrate human pollution histories several millennia into the past, while sulphur isotopes can be used to trace the sources of acid rain. Radioisotopes have been detectable across the planet since the 1950s because of atmospheric nuclear bomb tests and can be used as a stratigraphic marker. We find there is isotopic evidence of widespread human impact on the global environment, but different isotopes have registered changes at different times and at different rates.

Keywords

Anthropocene, carbon, human impact, isotopes, lead, nitrogen, radioisotopes, Suess effect, sulphur

Introduction

The Anthropocene, the term used informally to denote the current interval where humans have become a dominant force of global environmental change (Crutzen, 2002; Crutzen and Stoermer, 2000), is contentious. There is no doubt that humanity has left its mark on the planet. For example, humans now transport more soil and rock around the surface of the Earth than natural processes do (Wilkinson, 2005), CO_2 levels have risen dramatically to the highest levels seen in at least 800,000 years (Keeling et al., 2005; updated: http://scrippsco2.ucsd.edu/data/in_situ_co2/monthly_mlo. csv; Lüthi et al., 2008) and humanity is implicated in causing rates of species extinctions to increase well beyond background levels (Barnosky et al., 2011). Consequently, a working group of the

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International Commission on Stratigraphy is set to present its preliminary findings in 2016 on whether the Anthropocene is distinctive and enduring enough to be defined as a new epoch and if so where the Holocene–Anthropocene boundary should be set (Foley et al., 2013; Gale and Hoare, 2012; Vince, 2011; Zalasiewicz et al., 2011). Ruddiman (2003, 2013) and Ruddiman et al. (2011, 2014) have argued the Anthropocene started in the early to mid Holocene, when they suggest land clearance and agriculture initiated changes in the composition of the atmosphere. Crutzen and Stoermer (2000), Crutzen (2002) and Steffen et al. (2011) have suggested a later date, in the late 18th or early 19th centuries, associated with the Industrial Revolution in Northern Europe. Alternatively, a 'Great Acceleration' in human impacts on the global environment has been suggested to have occurred ~AD 1950 (Steffen et al., 2007) and it has been proposed the Anthropocene could be defined as starting around this time (Zalasiewicz et al., 2014).

There is an urgent need to understand the impact humans have had on the global environment and when changes occurred. This review concentrates on wide-scale anthropogenic impact as recorded by isotope data from natural archives. Isotopes are different types of an element: they have the same number of protons but a different number of neutrons (e.g. Hoefs, 2009; Sharp, 2007). The ratio of one isotope of an element to another can vary through time depending on a host of environmental factors, meaning changes in isotope ratios can be used to reconstruct changes in, for example, climate, pollution and the composition of the atmosphere. In this review, we have selected the isotopes that previous studies have highlighted as important in tracking human impacts on the global environment. We show how isotopes record heavy metal contamination linked to technological innovations from Greek and Roman times onwards (lead isotopes), late-Holocene forest clearance and widespread fossil fuel burning since the onset of the Industrial Revolution (carbon isotopes), increased production and use of artificial fertilisers (nitrogen isotopes), acid rain (sulphur isotopes) and atmospheric nuclear weapons testing (caesium and plutonium isotopes). We consider how isotopes could contribute to the debate on where to set the Holocene–Anthropocene boundary.

Notation and standardisation of stable isotope data are summarised in Sharp (2007) and Hoefs (2009). $\delta^{13}C$ represents the ratio of $^{13}C/^{12}C$ and $\delta^{15}N$ the ratio of $^{15}N/^{14}N$ and are given in per mil (‰) relative to VPDB and AIR respectively. $\delta^{34}S$ represents the ratio of $^{34}S/^{32}S$ and is given in ‰ relative to VCDT. Lead isotopes are measured against a variety of standards as reviewed in Komárek et al. (2008). The abundance of ^{14}C ($\Delta^{14}C$) in a sample is given in ‰ relative to NIST oxalic acid activity corrected for decay (Stuiver and Polach, 1977). The abundance of radioisotopes such as ^{137}Cs and $^{239,240}Pu$ are measured in becquerel (Bq), with one Bq representing one decay per second (L'Annunziata, 2012).

Changes in the global carbon cycle

Human activity has altered the concentration and isotopic composition of the gases in the atmosphere. Rises in atmospheric methane (CH_4) and carbon dioxide (CO_2) are captured in gas bubbles in ice cores (e.g. MacFarling Meure et al., 2006; Rubino et al., 2013) ~5000 years ago and ~8000 years ago, respectively. Ruddiman (2003, 2013) and Ruddiman et al. (2011, 2014) have argued these increases were caused by humans, and this has led to the Early Anthropogenic Hypothesis, which argues anthropogenic effects on global climate began millennia ago and had it not been for human-induced greenhouse gas increases leading to global warming the climate would have cooled substantially during recent millennia. A key part of their argument involves using carbon isotopes to trace the origins of these increases in CH_4 and CO_2 to wetland expansion, linked to rice production, and to widespread forest clearance. $\delta^{13}C$ of atmospheric CH_4 ($\delta^{13}CH_4$) from ice core bubbles

from the late Holocene have values ~−47‰ to −49‰ (Ferretti et al., 2005; Mischler et al., 2009). While some argue that these low values of $\delta^{13}CH_4$ could be explained by increased delivery of depleted (more negative) carbon from natural wetlands (e.g. Schmidt et al., 2004), Ruddiman et al. (2011) contend this would have been unlikely because of the drying in the late Holocene of northern monsoonal regions and the cooling of boreal regions, which would have reduced, not increased, CH_4 emissions of natural wetlands. Rather, they suggest that $\delta^{13}CH_4$ data could be explained by human emissions, with the observed mean of −48‰ satisfied by emissions from rice paddies (−63‰) and livestock (−60‰) and anthropogenic burning of grasses (−25‰). In terms of CO_2, Elsig et al. (2009) argue that the very small decrease in the $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}CO_2$) in the mid to late Holocene (before the Industrial Revolution), as atmospheric CO_2 concentrations were rising, would limit the net terrestrial contribution to atmospheric CO_2 during the last 7000 years to only ~5 ppm. Instead, there could have been large releases of CO_2 from the oceans (Broecker et al., 1999; Ridgwell et al., 2003). However, Ruddiman et al. (2011) argue that Elsig et al. (2009) underestimate carbon burial in boreal peat, and if burial in peat over the last 7000 years was greater than Elsig et al. (2009) calculated then it would require far greater anthropogenic emissions, via forest clearance, to balance the $\delta^{13}CO_2$ budget. The complexities of the carbon cycle mean the debate vis-à-vis the relative importance of human versus natural sources and sinks of carbon is complicated, and many researchers (e.g. Steffen et al., 2011) dismiss the plausibility of the Early Anthropogenic Hypothesis, but it is clear carbon isotopes are a key part of this debate.

As recorded in direct measurements from the atmosphere, in gas bubbles trapped in ice cores and in natural archives including tree rings (February and Stock, 1999; Stuiver and Quay, 1981), corals (Nozaki et al., 1978; Swart et al., 2010), foraminifera (Al-Rousan et al., 2004; Black et al., 2011) and marine molluscs (Butler et al., 2009), there has been a more substantial change in the $\delta^{13}CO_2$ of the atmosphere since the 19th century, with the trend to lower values through the 19th century accelerating after ~AD 1950 (Figure 1), at the time of increased fossil fuel consumption that followed the Second World War (Steffen et al., 2007). The changes in $\delta^{13}C$ are of a different magnitude and the absolute values are different in tree rings, corals, foraminifera and direct measurements of the atmosphere or of gas bubbles in ice. This is because as organisms use carbon during growth, they preferentially take up one isotope over another, causing a change in the $\delta^{13}C$ from the source, a process known as fractionation (e.g. Hoefs, 2009; Sharp, 2007). However, assuming this fractionation is constant through time, it is still possible to track changes in the composition of the atmosphere using tree rings, corals and foraminifera. The classic graph from Mauna Loa shows $\delta^{13}CO_2$ declining (−7.6‰ in 1980 to −8.3‰ in 2011) as CO_2 concentrations in the atmosphere have risen (316 ppm in 1959 to 396 ppm in 2013) (Figure 2) (Keeling et al., 2005; updated: http://scripps-sco2.ucsd.edu/data/in_situ_co2/monthly_mlo.csv). There was also a decline in the amount of ^{14}C in atmospheric CO_2 ($\Delta^{14}CO_2$) in the first half of the 20th century (Levin et al., 2010; Stuiver and Quay, 1981), before the trend was interrupted in the 1950s and 1960s, followed by a decline again to the present day (Levin et al., 2013). These declines in $\delta^{13}CO_2$ and $\Delta^{14}CO_2$ (called the Suess Effect; Keeling, 1979; Suess, 1955) are linked to the burning of fossil fuels. Fossil fuels, such as the vast coal deposits of the Carboniferous period, are composed of the organic remains of organisms (mainly plants) that lived millions of years ago. Plants preferentially take up ^{12}C over ^{13}C so have low $\delta^{13}C$ (e.g. Farquhar et al., 1989), with most oil deposits having values of −32‰ to −21‰ and coal deposits −26‰ to −23‰ (Sharp, 2007). Consequently, CO_2 from fossil fuels contains on average 2% less ^{13}C per mole than atmospheric CO_2 (Keeling, 1979). Extraction and burning of these fossil fuel reserves releases this ^{12}C-enriched carbon back into the atmosphere, leading to a decline in $\delta^{13}CO_2$. Old carbon from fossil fuels is also virtually free of ^{14}C (Keeling, 1979), since the time between being deposited in the fossil record and burning is many thousands of half-lives
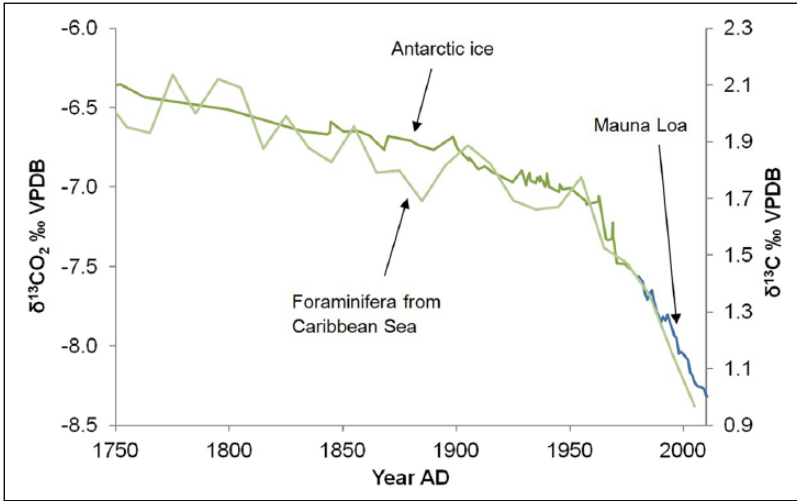
Figure 1. $\delta^{13}CO_2$ from Antarctic ice core record (Rubino et al., 2013), $\delta^{13}C$ record from foraminifera from the Caribbean Sea (Black et al., 2011) and $\delta^{13}CO_2$ from the Mauna Loa monitoring station (Keeling et al., 2005; updated: http://scrippsco2.ucsd.edu/data/in_situ_co2/monthly_mlo.csv). The former two records show a gradual depletion through the 19th century and an acceleration after ~AD 1950.
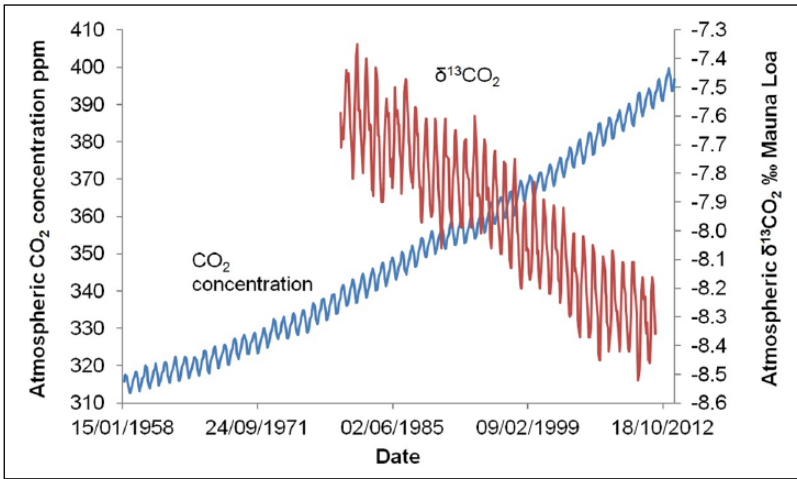

Figure 2. Monthly data from the Mauna Loa monitoring station (Keeling et al., 2005; updated: http://scrippsco2.ucsd.edu/data/in_situ_co2/monthly_mlo.csv) showing an increase in the concentration of CO_2 in the atmosphere from 1958 and a decline in $\delta^{13}CO_2$ from 1980 when monitoring of this began.

of ^{14}C, so the release of this old carbon will lead to a decline in $\Delta^{14}CO_2$ in the atmosphere. $\delta^{13}C$ changes in the atmosphere have been vital in allowing the Intergovernmental Panel on Climate Change (IPCC) to conclude there is a 'very high confidence' that the dominant cause of the observed increase in CO_2 concentrations in the atmosphere since the 19th century has been the human burning of fossil fuels (IPCC, 2013).
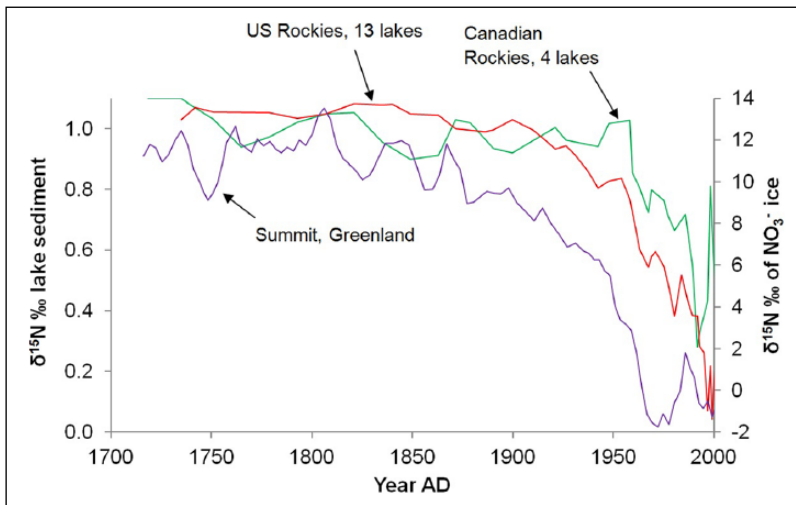
Figure 3. $\delta^{15}N$ from organic matter from lake sediments from the US and Canadian Rockies (three-point moving average) (Wolfe et al., 2013) and from nitrate in Greenland ice cores (Hastings et al., 2009). Depletion occurs after ~AD 1850, with an acceleration after ~AD 1950.

Changes to the nitrogen cycle

There have also been changes in the global nitrogen cycle, with increases in the amount of reactive nitrogen (nitrogen compounds such as nitrogen oxides that support biological growth) in the atmosphere, thought to be mainly due to the burning of fossil fuels and the use of fertiliser in agriculture (Galloway et al., 2004; Jaegle et al., 2005). As with carbon isotopes and the carbon cycle, $\delta^{15}N$ can be used to track changes in the nitrogen cycle and identify the sources of the nitrogen released. Anthropogenic reactive nitrogen sources, especially fertilised soils (Park et al., 2012; Pérez et al., 2001), but also fossil fuel emissions (Felix et al., 2012), are generally thought to be depleted in $\delta^{15}N$ relative to natural sources (although they can have highly variable values and some have argued $\delta^{15}N$ from fossil fuel emissions is unlikely to be lower than that from natural sources; Sharp, 2007; Geng et al., 2014). In organic matter from remote lake sediments from across North America and the Arctic (Holmgren et al., 2010; Holtgrieve et al., 2011; Wolfe et al., 2013), and in nitrate (NO_3-) from ice cores from Greenland (Hastings et al., 2009), there have been declines in $\delta^{15}N$ from ~AD 1850 (Figure 3). (Again, note that as a result of fractionation, the values and magnitudes of change of $\delta^{15}N$ in lake organic matter and ice core NO_3- differ, but they both shown a decline at similar times.) $\delta^{15}N$ values in Greenland NO_3- declined from +10.6‰ in AD 1716 to +0.8‰ in AD 2005 (Hastings et al., 2009). The trend in $\delta^{15}N$ may be because of the increase in isotopically depleted nitrogen from anthropogenic sources (fossil fuel combustion and fertilisers) (Felix and Elliott, 2013; Hastings et al., 2009; Holtgrieve et al., 2011), although Geng et al. (2014) have argued that the decline may be due to an equilibrium shift in gas-particle partitioning of atmospheric NO_3- caused by increasing atmospheric acidity resulting from anthropogenic emissions of nitrogen and sulphur oxides.

As with $\delta^{13}C$, while there is a decline in $\delta^{15}N$ from the 19th century in many records, it is really after ~AD 1950 that the trend accelerates and becomes pronounced (Figure 3). The changes that have occurred in the last century in Sky Pond lake in the US Rockies, for example, are without
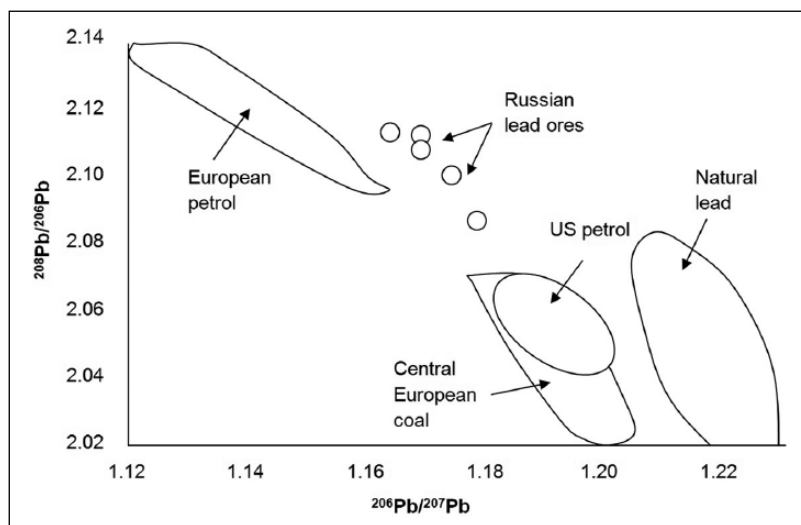
Figure 4. A $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ plot showing the different isotopic compositions of selected lead sources. Modified from Komárek et al. (2008).

precedent in the 14,000 year record (Wolfe et al., 2013). Although, as we have demonstrated, the real drivers of the $\delta^{15}N$ trend are debated, it is probable that a combination of anthropogenic processes are causing this decline, so $\delta^{15}N$ is a useful tool in tracing human impacts on the global nitrogen cycle.

Tracing pollution

As well as causing changes in the carbon and nitrogen cycles, human activity has caused pollution by remobilising certain elements. This can be traced using isotopes.

Lead isotopes

For millennia, humans have been mining and smelting lead ores, which has released vast quantities of lead into the atmosphere, causing widespread airborne pollution (Adriano, 2001; Settle and Patterson, 1980). There is evidence for lead contamination in Greenland ice cores, carried there in the atmosphere as microparticles, for over 2000 years (e.g. Hong et al., 1994; Rosman et al., 1997). Since different lead ores have different lead isotope ratios, it is possible to pinpoint where the lead was being mined. Rosman et al. (1997) showed that between ~150 BC and AD 50, 70% of the lead seen in Greenland ice cores originated from southern Spain, and historical records show the Romans mined the area at this time. As well as different lead ores, lead isotope ratios can be used to distinguish between pollution from different industrial processes. Komárek et al. (2008), using $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$, were able to distinguish between lead emitted from vehicles in Europe and the USA, coal burning in central Europe and natural sources (Figure 4). More recently it has been shown that lead in Greenland ice is increasingly from Chinese sources (Bory et al., 2014).

Trends in lead isotope ratios (especially $^{206}Pb/^{207}Pb$) can also be used to track changes in pollution through time. For example, in Sweden, background $^{206}Pb/^{207}Pb$ is thought to be around 1.5, whereas atmospheric lead pollution derived from smelting, leaded petrol and burning of coal has a
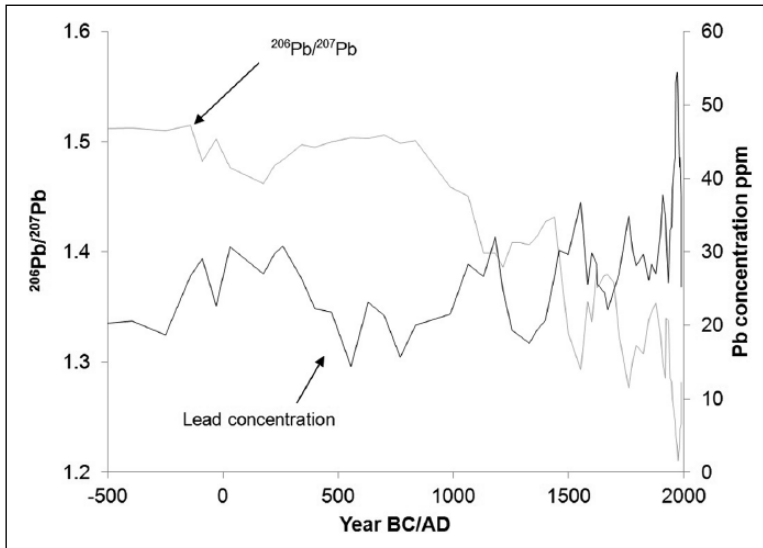
Figure 5. Trends in [206]Pb/[207]Pb and lead concentrations from Lake Koltjärn in Sweden, with a depletion in the ratio taken to represent increased anthropogenic lead pollution (Renberg et al., 2002).

[206]Pb/[207]Pb value of ~1.2 (Renberg et al., 2002). Lake sediments show there was a decline in the ratio in Roman times (to ~1.46), and then an increase to higher values in the Dark Ages ~AD 500–800 (~1.50) (Renberg et al., 2002). Minimum [206]Pb/[207]Pb ratios (~1.22) were reached in the 1970s when leaded petrol consumption peaked (Figure 5). With the phasing out of leaded petrol in Europe there has been an increase in the ratio (currently ~1.28). The low [206]Pb/[207]Pb in Roman times, related to lead mining, as seen in Greenland and Sweden, could be used to support the argument made by others (Certini and Scalenghe, 2011; Ellis et al., 2013; Ruddiman, 2003) using different proxies that substantial human impacts on the environment were occurring millennia before the Industrial Revolution.

Sulphur isotopes

Sulphur isotope ratios can be used to track fossil fuel burning and to trace the sources of pollution because, as with lead isotopes, natural and anthropogenic sources often have different isotope ratios (e.g. Krouse et al., 1984; Lim et al., 2014). Sulphur released into the atmosphere has the potential to cause acid rain. Concerns over widespread ecosystem damage resulting from acid rain first gained prominence in Europe in the late 1950s. Tracing the sources of sulphur pollution is particularly important given sulphur compounds produced and released into the atmosphere in one country can travel across borders and cause acid rain in another (Metcalfe and Derwent, 2005). Yu et al. (2007) demonstrated how the $\delta^{34}S$ of sulphate in meteoric waters from Chuncheon in South Korea vary from +2.6 to +7.5‰, which is significantly different from the $\delta^{34}S$ of sulphate from locally combusted coal (−4.5 to −0.7‰). This was taken to suggest that sulphur implicated in acid rain in that region was not the result of local pollution. A decline in emissions over time from brown coal power stations in eastern Germany has been recorded in an increase in $\delta^{34}S$ of rain in Wroclaw in Poland, demonstrating the effectiveness of measures taken to reduce acid rain resulting from anthropogenic emissions (Jędrysek, 2000). Indeed, global sulphur emissions are showing an
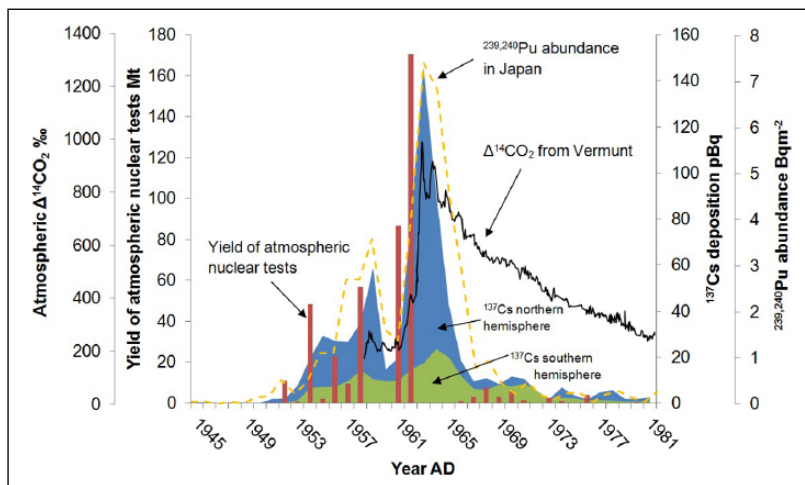
Figure 6. Yield of atmospheric nuclear tests per year shown by bars (UNSCEAR, 2000), ^{137}Cs deposition in Northern and Southern Hemispheres represented by areas (UNSCEAR, 2000), ^{239,240}Pu deposition in Japan shown by the dashed line (Hirose et al., 2000) and $\Delta^{14}CO_2$ measured at Vermunt, Austria shown by the solid line (Levin et al., 1985). The yield of atmospheric nuclear tests in the atmosphere peaked in 1962. $\Delta^{14}CO_2$ at Vermunt, ^{239,240}Pu in Japan and ^{137}Cs deposition in the Northern Hemisphere peaked in 1963 and ^{137}Cs in the Southern Hemisphere in 1964.

overall decline (Klimont et al., 2013). This demonstrates that some anthropogenic impacts on the environment, in this case acid rain linked to sulphur emissions as recorded by $\delta^{34}S$, have peaked, at least in some parts of the world.

Radioisotopes

Some isotopes (e.g. ^{137}Cs, ^{239}Pu and ^{240}Pu) occur on Earth almost entirely because of their production and release into the atmosphere from nuclear reactors and especially atmospheric nuclear weapons testing. They provide a rather precise stratigraphic point in geological archives, with detectable levels first apparent ~AD 1952, and peak abundance ~AD 1963/1964 after a large number of atmospheric nuclear tests were carried out in AD 1962 before the Partial Nuclear Test Ban Treaty came into effect (Figure 6) (Hirose et al., 2000; United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 2000). ^{14}C is produced naturally in the atmosphere through the interaction of neutrons with nitrogen atoms, but as discussed above the burning of fossil fuels had been leading to a decline in $\Delta^{14}CO_2$ in the atmosphere. This trend was interrupted as neutrons released by atmospheric nuclear tests increased the production of ^{14}C in the atmosphere, with a peak at a similar time to the peaks in ^{137}Cs, ^{239}Pu and ^{240}Pu (Figure 6) (Graven et al., 2012; Levin and Kromer, 2004; Levin et al., 1985; Naegler and Levin, 2009), before a decline again to the present day, producing a time-dependent distribution pattern that is referred to as the 'bomb curve'. This is seen in archives such as tree rings (Hua et al., 2000) and corals (Roark et al., 2006).

Conclusion

Changes in isotope geochemistry demonstrate that humans are having an impact on the global environment. Different isotopes have recorded different anthropogenic impacts, and changes have

occurred at different times and different rates. $\delta^{13}C$ and $\Delta^{14}C$ show the input of fossil fuel-derived CO_2 into the atmosphere, $\delta^{15}N$ records reveal a change in the global nitrogen cycle, lead and sulphur isotopes are tracers of human pollution histories and radioisotopes record the point at which humans mastered nuclear weapons technology. Some of the isotopes that we use to demonstrate human impacts, especially carbon and nitrogen isotopes, could also be influenced in similar ways by natural processes. This complexity has led to the Early Anthropogenic Hypothesis debate. On the other hand, other isotopes, especially radioisotopes, but arguably also lead isotopes, show a clear human imprint: in the case of certain radioisotopes their occurrence is almost entirely due to human-induced nuclear reactions and in the case of lead isotopes the ratios are changed in ways unlikely to be due to natural processes.

As for whether isotopes can contribute to the debate on where to set the Holocene–Anthropocene boundary, we have shown there is a clear acceleration in the trend to lower $\delta^{13}C$ and $\delta^{15}N$ after ~AD 1950, at the time of the 'Great Acceleration' in human activities (Steffen et al., 2007), and a decade later there was a near synchronous, worldwide peak in radioisotopes related to atmospheric nuclear weapons testing that could be useful as a unique stratigraphic marker to define the boundary (Zalasiewicz et al., 2014). However, it has been argued that carbon isotopes show (smaller) changes in the global composition of the atmosphere hundreds to thousands of years before AD 1950 and other isotopes, such as lead, also show human impacts on the environment millennia ago. Therefore, while there *is* an isotopic signature of the Anthropocene, and isotope geochemistry can play a role in the decision of the International Commission on Stratigraphy regarding whether to define a new geological epoch, it is not clear from isotopes alone *where* to set the Holocene–Anthropocene boundary.

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