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RADIOCARBON IN GLOBAL TROPOSPHERIC CARBON DIOXIDE

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ABSTRACT. Since the 1950s, observations of radiocarbon (^{14}C) in tropospheric carbon dioxide (CO_2) have been conducted in both hemispheres, documenting the so-called nuclear “bomb spike” and its transfer into the oceans and the terrestrial biosphere, the two compartments permanently exchanging carbon with the atmosphere. Results from the Heidelberg global network of $\Delta^{14}\text{C}\text{-CO}_2$ observations are revisited here with respect to the insights and quantitative constraints they provided on these carbon exchange fluxes. The recent development of global and hemispheric trends of $\Delta^{14}\text{C}\text{-CO}_2$ are further discussed in regard to their suitability to continue providing constraints for ^{14}C -free fossil CO_2 emission changes on the global and regional scale.

KEYWORDS: anthropogenic $^{14}\text{CO}_2$ perturbations, bomb radiocarbon, global carbon cycle, tropospheric $^{14}\text{CO}_2$ data.

INTRODUCTION

Atmospheric nuclear weapon testing in the 1950s and 1960s in the Northern Hemisphere was a period of great anxiety, however, it had significant side effects for environmental sciences in many aspects. The artificial production of more than 6×10^{28} atoms or about 1.4 tons of radiocarbon (^{14}C) (Naegler and Levin 2006), led to a doubling of the $^{14}\text{C}/\text{C}$ ratio in tropospheric CO_2 of the Northern Hemisphere with a prominent spike in 1963 (Nydal and Lövseth 1983; Levin et al. 1985). This “bomb spike” that reached the Southern Hemisphere with some delay (Manning et al. 1990), has been used as a transient tracer in all compartments of the fast carbon cycle (e.g., Broecker et al. 1985; Levin and Heshshaimer 2000; Trumbore 2009), but also to study atmospheric dynamics, such as inter-hemispheric (e.g., Münnich and Vogel 1958, 1963; Czeplak and Junge 1974) and stratosphere-troposphere air mass exchange (e.g., Telegadas 1971; Heshshaimer and Levin 2000; Levin et al. 2010). As an indirect outcome of the weapon testing, a wealth of new insights into atmospheric and carbon cycle dynamics could be achieved in the decades following the nuclear test ban treaty in 1963.

Today, the transient bomb-radiocarbon signal has levelled off, and the anthropogenic input of radiocarbon-free fossil CO_2 into the atmosphere has become the dominant driver of the decrease of the $^{14}\text{C}/\text{C}$ ratio in global atmospheric CO_2 (Levin et al. 2010; Graven 2015). This $^{14}\text{CO}_2$ -free anthropogenic CO_2 flux from the burning of fossil fuels and cement production has increased globally by more than fourfold compared to the 1960s, and, together with ongoing land-use changes, has resulted in an increase of the atmospheric CO_2 burden by more than 5 PgC (1 PgC = 10^{15} gC) or $>0.5\%$ per year in the last decade (Friedlingstein et al. 2020). The fossil CO_2 emissions are not evenly distributed over the globe and because the biosphere and oceans today, in most regions, are sources of bomb

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Figure 1 Cooperative CO₂ background air sampling network for high-precision ¹⁴C analysis in the Heidelberg Radiocarbon laboratory.

¹⁴CO₂, the distribution of tropospheric $\Delta^{14}\text{C-CO}_2$ has undergone significant changes since the 2000s.

After a brief overview on the development in the last 60+ years of ¹⁴C in tropospheric CO₂, this paper reviews the insights from earlier studies that used bomb ¹⁴C for carbon cycle budgeting. Further, we present our extended high-precision $\Delta^{14}\text{C-CO}_2$ observations in background air at Alert, Jungfrauoch, Izaña, Cape Grim, Macquarie Island and the German Antarctic Neumayer station (Figure 1), and discuss these data in view of their potential to serve as additional constraints for global carbon fluxes. Finally, we provide a perspective on how ongoing changes of the distribution and trends of $\Delta^{14}\text{C-CO}_2$ in the background troposphere could potentially be used to constrain major components of the carbon cycle, including monitoring of anthropogenic CO₂ emission and their reductions in view of the Paris agreement from the regional to the global scale.

THE HISTORY OF ATMOSPHERIC $\Delta^{14}\text{C-CO}_2$ OBSERVATIONS

Shortly after Anderson and Libby (1951) published their first measurements of natural radiocarbon in various compartments of the Earth system, a number of Radiocarbon Laboratories have been established world-wide. First measurements of $\Delta^{14}\text{C-CO}_2$ in background air were conducted in 1954 in the Southern Hemisphere with sampling on the south-western coast of the Northern Island of New Zealand (NZ) close to Wellington (41.25°S, 174.69°E, 300 m asl; Rafter and Fergusson 1957). Münnich and Vogel (1963) collected their first atmospheric CO₂ samples for ¹⁴C analysis in 1959 at a number of stations in the Northern and Southern Hemisphere. Quasi-continuous sampling was finally established at Vermunt in the Austrian Alps (47.07°N, 9.57°E, 1800 m asl; Levin et al. 1985). In the early years, all samples were collected by passive absorption of atmospheric CO₂ in sodium hydroxide solution. CO₂ was then extracted in the laboratory from this basic solution by acidification. After purification of the extracted CO₂ the samples were analyzed by gas proportional counting (Kromer and Münnich 1992; Turnbull et al. 2017).

In the 1970s, advancements in both the sampling and analysis systems occurred, e.g. the Heidelberg sampling system at Vermunt station was changed to actively flushing air through a rotating absorption column, now allowing quantitative (less fractionated) sampling of CO₂ over a well-defined time interval (Levin et al. 1980). At the NZ station, in addition to passive sampling, whole air flask samples started to be collected, and ¹⁴C analysis changed from gas counting to Accelerator Mass Spectrometric analysis (for details, see Turnbull et al. 2017, supplementary material). While in Heidelberg measurement of background air samples was and still is today by gas proportional counting, we changed our European background monitoring site in the Alps from Vermunt in Austria to Jungfrauoch in Switzerland (46.55°N, 7.98°E, 3450 m asl) in 1986. This seemed advantageous as the high elevation of Jungfrauoch provides better access to free tropospheric air. In addition, several continuous measurements of other atmospheric trace substances, including CO₂, are conducted at this site (Forrer et al. 2000).

The two pioneer stations in New Zealand and in the Austrian Alps, which document the largest excursions of bomb ¹⁴CO₂ in the Southern and the Northern Hemisphere troposphere, were supplemented by an increasing number of Δ¹⁴C-CO₂ observations world-wide, including the tropics and sub-tropics. The most comprehensive records were published by Nydal and Lövseth (1983, 1996) and by Meijer et al. (1995). These globally distributed data sets provided the opportunity to track the bomb ¹⁴CO₂ spike throughout the entire troposphere. Unfortunately, most of these sampling efforts were discontinued in the 1980s after bomb ¹⁴CO₂ had become well-mixed in both hemispheres.

Starting in 1983, when the German Antarctic Neumayer station became operational in Dronning Maud Land at the Antarctic coast (70.65°S, 8.25°E, 17 m asl), the Heidelberg Radiocarbon laboratory was granted the opportunity to start CO₂ sampling for ¹⁴C analysis at this remote Antarctic site. Soon after the first data became available, it was realized that the Δ¹⁴C-CO₂ level at Neumayer station was significantly influenced by a ¹⁴CO₂ disequilibrium flux with the Antarctic circumpolar surface water, originating from upwelling of about 800-year-old intermediate water of the Pacific Ocean, which, due to its age, is strongly depleted in (natural) ¹⁴C (Levin et al. 1987). This exciting feature of lower Δ¹⁴C-CO₂ levels in atmospheric CO₂ of Southern Hemisphere air when compared to the Northern Hemisphere had already been observed by Lerman et al. (1970) on tree rings. Their results were now confirmed by direct atmospheric observations. For us, this finding was the catalyst to re-start global monitoring of Δ¹⁴C-CO₂ in the atmosphere, i.e. during a period when other research agencies were terminating their ¹⁴CO₂ monitoring efforts. The potential of Δ¹⁴C-CO₂ observations as an ongoing constraint of gross carbon exchange fluxes between atmosphere, ocean and biosphere seemed obvious. However, unlike the situation immediately after the test ban treaty in 1963, being 20 years later, the spatial gradients and temporal variations of Δ¹⁴C-CO₂ in the atmosphere were more than two orders of magnitude smaller. To detect such small signals required increased precision in Δ¹⁴C-CO₂ analysis (about 2‰), and could only be achieved by gas proportional counting at that time. In the 1980s, we begun establishing a new network of Δ¹⁴C-CO₂ observations at a number of globally distributed stations, in cooperation with colleagues operating the Global Atmosphere Watch stations for continuous greenhouse gases observations (see map in Figure 1). Other investigations (Hesshaimer et al. 1994; Levin and Hesshaimer 2000), were also carried out using these data to close the atmospheric bomb ¹⁴C budget, and, in turn, determine the total input of anthropogenic ¹⁴C into the global carbon system (Naegler and Levin 2006).

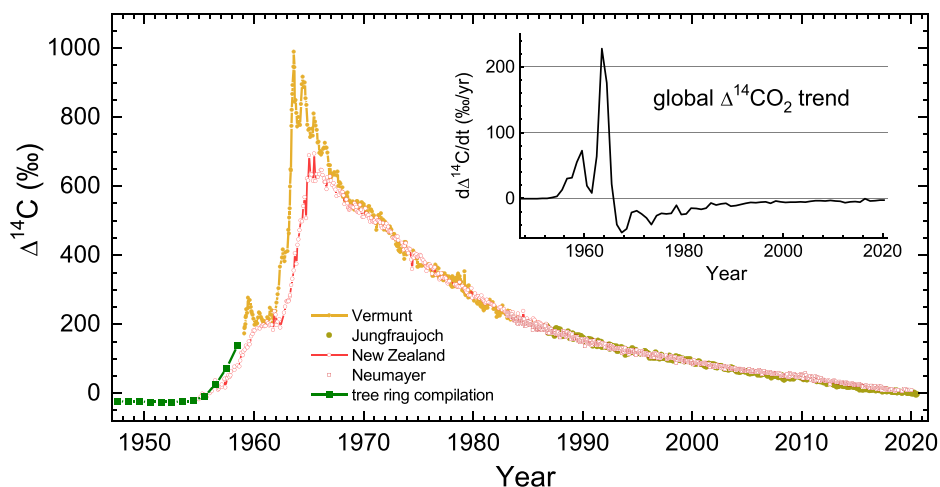


Figure 2 Development of tropospheric $\Delta^{14}\text{C-CO}_2$ in both hemispheres since the start of the atmospheric nuclear bomb tests. New Zealand data are from Turnbull et al. (2017). The inlay shows the derivative of annual mean $\Delta^{14}\text{C-CO}_2$.

In the 2000s, the Scripps Institution of Oceanography (SIO) started analyzing ^{14}C on CO_2 extracted from flask samples collected from their global network of stations along the Pacific Ocean, stretching from Barrow, Alaska, down to the South Pole (Graven et al. 2012). These samples were analyzed with high precision Accelerator Mass Spectrometry. The data were included in a global atmospheric transport model (TM3, Heimann and Korner 2003) to investigate the spatial $\Delta^{14}\text{C-CO}_2$ distribution and document its changes since the 1990s. Unfortunately, $\Delta^{14}\text{C-CO}_2$ results from the SIO network since 2007 have not been published. In the 2000s, the Institute of Arctic and Alpine Research (INSTAAR) began measuring $\Delta^{14}\text{C-CO}_2$ on flask samples from the Global Monitoring Laboratory (GML) of the National Oceanic and Atmospheric Administration (NOAA/GML), primarily from aircraft flights and ground-based locations over North America (Turnbull et al. 2006; Miller et al. 2012). The primary focus of the INSTAAR program was to use these data to partition the ^{14}C -free fossil from the biogenic CO_2 component over the continent (Miller et al. 2012; Basu et al. 2020). $\Delta^{14}\text{C-CO}_2$ observations over continents have become the main focus of the carbon cycle community today, as ^{14}C is the most direct tracer to quantify the regional fossil CO_2 component (Levin et al. 2003; Turnbull et al. 2017; Graven et al. 2009). Also, in Europe, a new network of $\Delta^{14}\text{C-CO}_2$ monitoring stations was established as part of the atmospheric observational network of the Integrated Carbon Observation System (ICOS) Research Infrastructure (Levin et al. 2020). Since 2018 Jungfraujoch station has officially become part of this network, and the $\Delta^{14}\text{C-CO}_2$ analyses are conducted by the ICOS Central Radiocarbon Laboratory in Heidelberg (<https://www.iup.uni-heidelberg.de/research/kk/icos>).

TEMPORAL DEVELOPMENT OF $\Delta^{14}\text{C-CO}_2$ IN THE GLOBAL TROPOSPHERE

The long-term development of $\Delta^{14}\text{C}$ in tropospheric CO_2 in both hemispheres is displayed in Figure 2. The increase in the Southern Hemisphere (SH) since 1954 is documented by data from the New Zealand site close to Wellington (Turnbull et al. 2017). From 1983 onwards, we extended this record with data from the Neumayer station, Antarctica (Levin and Hammer

2021). In the Northern Hemisphere (NH) atmospheric, background observations are only available from 1959 onwards. In Figure 2 we extend the NH record back to the 1940s using annual mean values for 30°–90°N from the compilation by Graven et al. (2017), based on tree ring analyses. The Vermont record ended in 1985 when our Alpine background sampling site was moved to the Jungfraujoch station. For all stations, the results from individual atmospheric samples are shown in Figure 2. The data are available at the ICOS-ERIC Carbon Portal (Levin and Hammer 2021).

In the NH record, regular seasonal variations are clearly visible in the years of 1963–1968. This seasonality is caused by spring-time intrusion of stratospheric air into the troposphere (Telegadas 1971). During these initial years after the nuclear test ban treaty in 1963, a large share of bomb-produced ¹⁴CO₂ continued to reside in the stratosphere, which, in the course of the following years, was transported into the troposphere, mainly during spring (Tans 1981; Hesshaimer and Levin 2000). The subsequent transport of bomb ¹⁴CO₂ from the NH troposphere into the SH then caused a decrease of Δ¹⁴C-CO₂ in late summer. However, the approximately 1.5 years shift between Northern and Southern Hemisphere Δ¹⁴C-CO₂ curves provides the most direct measure of the interhemispheric exchange time. This atmospheric Δ¹⁴C-CO₂ dynamic during and shortly after the bomb tests has been used to calibrate or evaluate the validity of transport in atmospheric circulation models (e.g., Johnston 1989; Kjellström et al. 2000; Levin et al. 2010).

The inlay of Figure 2 shows the year-to-year change of global mean Δ¹⁴C-CO₂ values, calculated from the global compilation of Graven et al. (2017), extended with the most recent Heidelberg measurements from the NH and the SH. Unfortunately, no recent data from the tropics are available to calculate annual global means. We therefore extrapolated the tropical record with the annual mean trends observed in 2015–2020 for the extra-tropical latitudes. After the steep increase of tropospheric Δ¹⁴C-CO₂, reaching a maximum in the NH in 1963 and in the SH about 1.5 years later, we observe a fast decrease in both hemispheres. This decrease is caused by equilibration of the atmospheric bomb ¹⁴C disturbance with reservoirs exchanging CO₂ with the atmosphere, namely the ocean and the terrestrial biosphere. According to Levin et al. (2010: Figure 7) the largest net uptake of bomb ¹⁴C by the world oceans occurred in the 1970s and was about twice as high when compared to the net uptake by the biosphere. While the terrestrial biosphere acted as a net sink of anthropogenic ¹⁴C only until the 1980s (Naegler and Levin 2009), the oceans continued to be a sink of bomb ¹⁴C until around 2010.

Starting in the mid-1990s, fossil CO₂ emissions into the global atmosphere became the dominant contribution to the decreasing global Δ¹⁴C-CO₂ trend. Levin et al. (2010) attempted to use the global Δ¹⁴C-CO₂ trend of the last decades as an independent constraint for the global fossil CO₂ emissions into the atmosphere. However, the uncertainty estimates were determined to be too large (25–30%) to be useful, due to the large uncertainties in the partitioned contributions from ocean and biosphere exchange fluxes to the Δ¹⁴C-CO₂ trend, compared to the global bottom-up fossil emission estimates, which were estimated to better than ±10% (Gilfillan and Marland 2021). Today though, with improved information on ocean and biosphere ¹⁴CO₂ fluxes, it may be a useful endeavor to repeat this exercise. However, for this purpose we would first need more representative high precision Δ¹⁴C-CO₂ observations at background stations that are compatible to better than ±0.5‰, in order to determine reliable global trends and hemispheric gradients, which today are only a few ‰ (see Figure 3). Better knowledge on

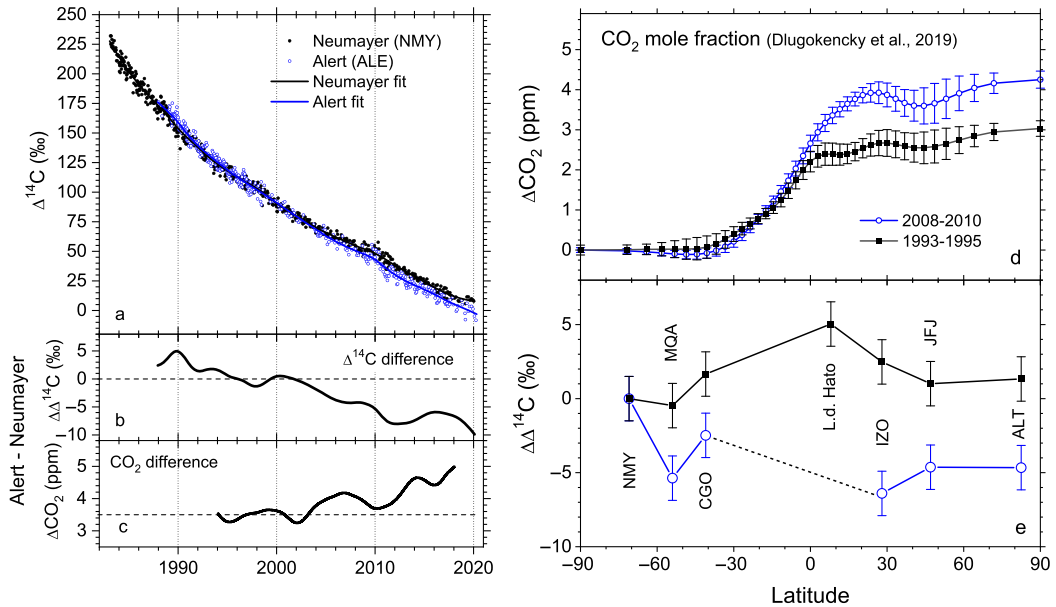


Figure 3 a: Long-term trend of $\Delta^{14}\text{C}$ - CO_2 at the two polar stations Alert (Arctic) and Neumayer (Antarctica) (Levin and Hammer 2021). The solid lines are de-seasonalised fitted curves through the individual data. Panel b displays the difference between both fitted $\Delta^{14}\text{C}$ - CO_2 curves, while c shows the differences of corresponding fitted curves through CO_2 concentration data from flask samples collected at the two stations (Weller et al. 2007; Worthy et al. 2021). d: Meridional distribution of three-year averages of CO_2 (Dlugokencky et al. 2019), and $\Delta^{14}\text{C}$ - CO_2 (e) for 1993–1995 in comparison to 2008–2010.

compatibility can only be achieved through frequent intercomparisons between those labs that contribute to this global $\Delta^{14}\text{C}$ - CO_2 background monitoring network. An earlier intercomparison between our low-level counting laboratory in Heidelberg (ICOS CRL) and 8 AMS laboratories yielded an overall agreement of better than $\pm 0.5\%$, but it was not conclusive concerning the compatibility within the AMS laboratories themselves (Hammer et al. 2017). More frequent regular intercomparisons are therefore urgently needed to achieve an overall compatibility of better than $\pm 0.5\%$. Then ^{14}C -based ffCO_2 estimates could provide an excellent independent top-down check on the global stocktake of the Paris Climate Accord (UNFCCC 2015).

SPATIAL VARIATION OF $\Delta^{14}\text{C}$ - CO_2 IN THE TROPOSPHERE

Because the bulk of the fossil CO_2 emissions are released in the NH, observed CO_2 concentrations in the Northern are higher than in the Southern Hemisphere (Dlugokencky et al. 2019). However, until the end of the last century, the north-south difference of $\Delta^{14}\text{C}$ - CO_2 was counterintuitively positive, with higher $\Delta^{14}\text{C}$ - CO_2 being observed in the North than in the South (Levin and Hesseshaier 2000). This latter north-south difference was caused by a strong ^{14}C -depleted flux with the $\Delta^{14}\text{C}$ -depleted surface water of the Southern Ocean around Antarctica (Levin et al. 1987). The sign of the observed north-south difference, however, changed in the mid-2000s, with lower $\Delta^{14}\text{C}$ - CO_2 being observed at high northern latitudes such as at Alert in the Arctic (82.45°N, 62.52°W, 185 m asl)

when compared to Neumayer, Antarctica. We calculated smoothed fitted curves (Nakazawa et al. 1997) through the individual data from the two polar stations and plot the long-term trends together with the individual data in Figure 3a. The difference between the two curves, fitting Alert and Neumayer $\Delta^{14}\text{C-CO}_2$ data, is shown in Figure 3b. It can be clearly seen that while the $\Delta^{14}\text{C-CO}_2$ difference was positive until the end of the 1990s, it decreased to about zero at the turn of the century and around 2003, it changed to negative values and continues in this manner until today. At the same time, the CO_2 concentration difference between the two polar stations increased from ca. 3.5 ppm in the 1990s to ca. 4–5 ppm in the last decade (Figure 3c).

The observed change in the sign in the north-south $\Delta^{14}\text{C-CO}_2$ difference has been previously reported by Graven et al. (2012). There are two reasons that may have caused this reversal: (1) The increase of the north-south gradient of CO_2 due to increasing fossil CO_2 emissions being more dominant in the NH, and in turn, causing an increasing dilution of the $^{14}\text{C}/\text{C}$ ratio in NH CO_2 , and (2) the decrease of the $\Delta^{14}\text{C-CO}_2$ disequilibrium between the atmosphere and surface waters in the circum Antarctic ocean (Graven et al. 2012). While the difference between atmospheric and surface ocean $\Delta^{14}\text{C-CO}_2$ in the late 1980 and 1990s was still about 200–300‰, it decreased by about 150‰ in the following decade, because atmospheric $\Delta^{14}\text{C-CO}_2$ decreased by this amount (Figure 2). If we assume that the increase of CO_2 difference from about 1994 to 2009 between Northern and Southern Hemisphere of about 1.5 ppm was caused by ^{14}C -free fossil CO_2 alone, this would have caused a change in the $\Delta^{14}\text{C-CO}_2$ north-south difference of approximately 3‰. The remaining difference of more than 2‰ must therefore be due to other reasons. The right panels of Figure 3 show the mean meridional distributions of CO_2 concentration (d) and $\Delta^{14}\text{C-CO}_2$ (e) in the period of 1993–1995 compared to the 15 years later period of 2008–2010. The change in $\Delta^{14}\text{C-CO}_2$ relative to Neumayer (NMY) station and CO_2 concentration relative to South Pole is observed throughout the Northern Hemispheric sites. CO_2 and $\Delta^{14}\text{C-CO}_2$ are rather homogeneously distributed from polar regions (Alert) to the subtropics at Izaña (Tenerife Island, 28.3°N, 16.48°W, 2373 m asl) with variations smaller than 1.5‰ in $\Delta^{14}\text{C-CO}_2$ and 1 ppm in CO_2 . In contrast, corresponding latitudes of the Southern Hemisphere show a significant $\Delta^{14}\text{C-CO}_2$ dip at Macquarie Island (54.5°S, 158.97°E, 6 m asl), which is not accompanied by a significant variation in CO_2 concentration. In this region of the Southern Ocean around Macquarie Island (MQA) with depleted ^{14}C the $^{14}\text{CO}_2$ disequilibrium flux is largest, also because large wind velocities enhance air-sea gas exchange.

As is the case for the long-term trend, changes in the north-south $\Delta^{14}\text{C-CO}_2$ difference can also provide a constraint on the predominantly Northern Hemispheric fossil CO_2 emissions. But keeping in mind that there are uncertainties in the other components contributing to the meridional $\Delta^{14}\text{C-CO}_2$ difference as well as uncertainties associated in atmospheric model transport limits the uncertainty of the fossil emissions constraint to around 25–30% (Levin et al. 2010).

A special feature can be seen in the data of the tropical station Llano del Hato (Venezuela, 8.78°N 70.87°W, 3600 m asl). Here we observed a regional $\Delta^{14}\text{C-CO}_2$ maximum in the 1990s, which we attributed to a signal of net bomb $^{14}\text{CO}_2$ released by heterotrophic respiration from the tropical biosphere. Naegler and Levin (2009) calculated from their global bomb- ^{14}C budget that the global biosphere switched from a net sink of anthropogenic $^{14}\text{CO}_2$ to a net source to the atmosphere around the 1980s. Small fossil CO_2 emissions or atmosphere ocean disequilibrium fluxes could be the reason why this

bomb- ^{14}C signal from the biosphere is visible at these latitudes. Unfortunately, due to logistics problems, sampling at this important tropical site was terminated in 1997. Graven et al. (2012) also found about 3–6‰ higher $\Delta^{14}\text{C-CO}_2$ in 2005–2007 at two tropical stations in the Pacific Ocean when compared to mid-latitude sites in the NH. Continuing observations in the tropics could possibly provide independent constraints on the turnover times of carbon in the terrestrial biosphere, an important parameter to assess the sustainability of the currently observed net uptake of anthropogenic CO_2 emissions by the terrestrial biosphere.

CONCLUSIONS AND PERSPECTIVES

$\Delta^{14}\text{C-CO}_2$ in the troposphere over the last 60+ years serves as an excellent transient tracer to study atmospheric and global carbon cycle dynamics. However, despite the wealth of information that is buried in the observed global distribution and trend of $\Delta^{14}\text{C-CO}_2$, only the first few decades of the existing records have yet been used to constrain global and regional exchange fluxes between the main compartments of the carbon cycle. This may be due to the sparsity of representative observations, for example, in the very heterogeneous terrestrial biosphere. But also for the much more homogenous global oceans, representative continuous monitoring of ^{14}C is incomplete. Further, only in the last decade, has ^{14}C been fully implemented in global models such as in the National Center for Atmospheric Research Community Earth System model (Koven et al. 2013; Jahn et al. 2015). Concerning atmospheric tracer transport modeling of CO_2 , including ^{14}C in global and regional inversions is still at its infancy (e.g., Turnbull et al. 2009; Basu et al. 2020). Here, not only do the ocean and biosphere “boundary conditions” need to be well defined, but reliable atmospheric modeling of $^{14}\text{CO}_2$ also requires stratosphere-troposphere air mass exchange to be represented correctly in the model. Contrary to the stable isotopes in CO_2 , where the tropospheric variability is governed by sources and sinks located at the Earth surface, the $^{14}\text{CO}_2$ cycle has a natural production source in the upper troposphere and lower stratosphere. All these challenges need to be accounted for in order to disentangle the small gradients and trends, particularly those observed in the last decade. However, most important are long-term high-precision measurements at key stations themselves. Models can always be improved in the future, but the atmosphere at present can only be sampled today.

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DATA AVAILABILITY

Individual $\Delta^{14}\text{C}$ - CO_2 data from Alert, Jungfraujoch, and Neumayer stations are available at the ICOS-ERC Carbon Portal (Levin and Hammer 2021).

REFERENCES

- Anderson EC, Libby WF. 1951. World-wide distribution of natural radiocarbon. *The Physical Review* 81(1):64–69.
- Basu S, Lehman SJ, Miller JB, Andrews AE, Sweeney C, Gurney KR, Xue X, Southon J, Tans PP. 2020. Estimating US fossil fuel CO_2 emissions from measurements of ^{14}C in atmospheric CO_2 . *PNAS* 117(24):13300–13307. doi: [10.1073/pnas.1919032117](https://doi.org/10.1073/pnas.1919032117).
- Broecker WS, Peng TH, Östlund G, Stuiver M. 1985. The distribution of bomb radiocarbon in the ocean. *J. Geophys. Res.* 90(C4):6953–6970. doi: [10.1029/JC090iC04p06953](https://doi.org/10.1029/JC090iC04p06953).
- Czeplak G, Junge C. 1974. Studies of interhemispheric exchange in the troposphere by a diffusion model. *Adv. Geophys.* 18:57–72.
- Dlugokencky EJ, Thoning KW, Lang PM, Tans PP. 2019. NOAA Greenhouse gas reference from atmospheric carbon dioxide dry air mole fractions from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Data ftp://afftp.cmdl.noaa.gov/data/trace_gases/co2/flask/surface/Network. Last accessed 8.5.2021.
- Forrer J, Rüttimann R, Schneiter D, Fischer A, Buchmann B, Hofer P. 2000. Variability of trace gases at the high-Alpine site Jungfraujoch caused by meteorological transport processes. *J. Geophys. Res.* 105:12241–12251. [https://doi:10.1029/1999JD901178](https://doi.org/10.1029/1999JD901178).
- Friedlingstein P, O'Sullivan M, Jones MW, Andrew RM, Hauck J, Olsen A, Peters GP, Peters W, Pongratz J, Sitch S, et al. 2020. Global carbon budget 2020. *Earth Syst. Sci. Data* 12:3269–3340. doi: [10.5194/essd-12-3269-2020](https://doi.org/10.5194/essd-12-3269-2020).
- Gilfillan D, Marland G. 2021. CDIAC-FF: global and national CO_2 emissions from fossil fuel combustion and cement manufacture: 1751–2017. *Earth Syst. Sci. Data* 13:1667–1680. doi: [10.5194/essd-13-1667-2021](https://doi.org/10.5194/essd-13-1667-2021).
- Graven HD. 2015. Impact of fossil fuel emissions on atmospheric radiocarbon and various applications of radiocarbon over this century. *Proceedings of the National Academy of Sciences* 112:9542–9545. doi: [10.1073/pnas.1504467112](https://doi.org/10.1073/pnas.1504467112).
- Graven HD, Allison CE, Etheridge DM, Hammer S, Keeling RF, Levin I, Meijer HAJ, Rubino M, Tans PP, Trudinger CM, Vaughn BH, White JWC. 2017. Compiled records of carbon isotopes in atmospheric CO_2 for historical simulations in CMIP6. *Geoscientific Model Development* 10(12):4405–4417. doi: [10.5194/gmd-10-4405-2017](https://doi.org/10.5194/gmd-10-4405-2017).
- Graven HD, Guilderson TP, Keeling RF. 2012. Observations of radiocarbon in CO_2 at seven global sampling sites in the Scripps flask network: Analysis of spatial gradients and seasonal cycles. *J. Geophys. Res.* 117(D02303). doi: [10.1029/2011JD016535](https://doi.org/10.1029/2011JD016535).
- Graven HD, Stephens BB, Guilderson TB, Campos TL, Schimel DS, Campbell JE, Keeling RF. 2009. Vertical profiles of biospheric and fossil fuel-derived CO_2 and fossil fuel CO_2 : CO ratios from airborne measurements of ^{14}C , CO_2 and CO above Colorado, USA. *Tellus B* 61:536–546. doi: [10.1111/j.1600-0889.2009.00421.x](https://doi.org/10.1111/j.1600-0889.2009.00421.x).
- Hammer S, Friedrich R, Kromer B, Cherkinsky A, Lehman SJ, Meijer HA, Nakamura T, Palonen V, Reimer RW, Smith AM, Southon JR, Szidat S, Turnbull J, Uchida M. 2017. Compatibility of atmospheric $^{14}\text{CO}_2$ measurements: comparing the Heidelberg low-level counting facility to international accelerator mass spectrometry (AMS) laboratories. *Radiocarbon* 59(3):875–883. doi: [10.1017/RDC.2016.62](https://doi.org/10.1017/RDC.2016.62).
- Heimann M, Korner S. 2003. The Global Atmospheric Tracer Model TM3. Model description and users manual release 3.8a. Tech. Rep. 5. Max Planck Inst. for Biogeochem., Jena, Germany.
- Hesshaimer V, Heimann M, Levin I. 1994. Radiocarbon evidence for a smaller oceanic carbon dioxide sink than previously believed. *Nature* 370:201–203. doi: [10.1038/370201a0](https://doi.org/10.1038/370201a0).
- Hesshaimer V, Levin I. 2000. Revision of the stratospheric bomb $^{14}\text{CO}_2$ inventory. *J. Geophys. Res.* 105(D9):11,641–11,658.
- Jahn A, Lindsay K, Giraud X, Gruber N, Otto-Bliessner BL, Liu Z, Brady EC. 2015. Carbon isotopes in the ocean model of the Community Earth System Model (CESM1). *Geoscientific Model Development* 985 8:2419–2434. doi: [10.5194/gmd-8-2419-2015](https://doi.org/10.5194/gmd-8-2419-2015).
- Johnston HS. 1989. Evaluation of excess carbon-14 and strontium-90 data for suitability to test two-dimensional stratospheric models. *J. Geophys. Res.* 94:18 485–18 493.
- Kjellström E, Feichter J, Hoffmann G. 2000. Transport of SF_6 and $^{14}\text{CO}_2$ in the atmospheric general circulation model ECHAM. *Tellus* 52B:1–18. doi: [10.1034/j.1600-0889.2000.00882.x](https://doi.org/10.1034/j.1600-0889.2000.00882.x).
- Koven CD, Riley WJ, Subin ZM, Tang JY, Torn MS, Collins WD, Bonan GB, Lawrence DM, Swenson SC. 2013. The effect of vertically resolved soil biogeochemistry and alternate soil C and N

- models on C dynamics of CLM4. *Biogeosciences* 10(11):7109–7131. doi: [10.5194/bg-10-7109-2013](https://doi.org/10.5194/bg-10-7109-2013).
- Kromer B, Münnich KO. 1992. CO₂ gas proportional counting in radiocarbon dating—review and perspective. In: Taylor RE, Long A, Kra RS, editors. *Radiocarbon after four decades*. New York: Springer. p. 184–197.
- Lerman J, Mook W, Vogel J. 1970. C14 in tree rings from different localities. In: Olsson IU, editor. *Radiocarbon variations and absolute chronology*. Proceedings, XII Nobel Symposium. New York: Wiley. p. 275–301.
- Levin I, Hammer S. 2021. Supplementary data to Levin et al. (2021), Radiocarbon in global tropospheric carbon dioxide, ICOS-ERIC Carbon Portal. <https://doi.org/10.18160/K6P6-WBH5>.
- Levin I, Heshaimer V. 2000. Radiocarbon—a unique tracer of global carbon cycle dynamics. *Radiocarbon* 42:69–80. doi: [10.1017/S0033822200053066](https://doi.org/10.1017/S0033822200053066).
- Levin I, Karstens U, Erritt M, Maier F, Arnold S, Rzesanke D, Hammer S, Ramonet M, Vítková G, Conil S, Heliasz M, Kubistin D, Lindauer M. 2020. A dedicated flask sampling strategy developed for ICOS stations based on CO₂ and CO measurements and STILT footprint modelling. *Atmos. Chem. Phys.* 20:11161–11180. doi: [10.5194/acp-20-11161-2020](https://doi.org/10.5194/acp-20-11161-2020).
- Levin I, Kromer B, Schmidt M, Sartorius H. 2003. A novel approach for independent budgeting of fossil fuels CO₂ over Europe by ¹⁴C observations. *Geophys. Res. Lett.* 30(23):2194. doi: [10.1029/2003GL018477](https://doi.org/10.1029/2003GL018477).
- Levin I, Kromer B, Schoch-Fischer H, Bruns M, Münnich M, Berdau D, Vogel JC, Münnich KO. 1985. 25 years of tropospheric ¹⁴C observations in central Europe. *Radiocarbon* 27:1–19. doi: [10.1017/S0033822200006895](https://doi.org/10.1017/S0033822200006895).
- Levin I, Kromer B, Wagenbach D, Münnich KO. 1987. Carbon isotope measurements of atmospheric CO₂ at a coastal station in Antarctica. *Tellus B* 39B(1–2):89–95. doi: [10.1111/j.1600-0889.1987.tb00273.x](https://doi.org/10.1111/j.1600-0889.1987.tb00273.x).
- Levin I, Münnich KO, Weiss W. 1980. The effect of anthropogenic CO₂ and ¹⁴C sources on the distribution of ¹⁴CO₂ in the atmosphere. *Radiocarbon* 22:379–391. doi: [10.1017/S003382220000967X](https://doi.org/10.1017/S003382220000967X).
- Levin I, Naegler T, Kromer B, Diehl M, Francey RJ, Gomez-Pelaez AJ, Steele LP, Wagenbach D, Weller R, Worthy DE. 2010. Observations and modelling of the global distribution and long-term trend of atmospheric ¹⁴CO₂. *Tellus B* 62(1):26–46. doi: [10.1111/j.1600-0889.2009.00446.x](https://doi.org/10.1111/j.1600-0889.2009.00446.x).
- Manning MR, Lowe DC, Melhuish WH, Sparks RJ, Wallace G, Brenninkmeijer CAM, McGill RC. 1990. The use of radiocarbon measurements in atmospheric studies. *Radiocarbon* 32(1): 37–58. doi: [10.1017/S0033822200039941](https://doi.org/10.1017/S0033822200039941).
- Meijer HAJ, van der Plicht J, Gislefoss JS, Nydal R. 1995. Comparing long term atmospheric ¹⁴C and ³H records near Groningen, the Netherlands with Fruholmen, Norway and Izana, Canary Islands ¹⁴C stations. *Radiocarbon* 37(1):39–50. doi: [10.1017/S0033822200014776](https://doi.org/10.1017/S0033822200014776).
- Miller JB, Lehman SJ, Montzka SA, Sweeney C, Miller BR, Karion A, Wolak C, Dlugokencky EJ, Southon J, Turnbull JC, Tans PP. 2012. Linking emissions of fossil fuel CO₂ and other anthropogenic trace gases using atmospheric ¹⁴CO₂. *J. Geophys. Res.* 117:D08302. doi: [10.1029/2011JD017048](https://doi.org/10.1029/2011JD017048).
- Münnich KO. 1963. Der Kreislauf des Radiokohlenstoffs in der Natur. *Naturwissenschaften* 50(6):212–218.
- Münnich KO, Vogel J. 1958. Durch Atomexplosionen erzeugter Radiokohlenstoff in der Atmosphäre. *Naturwissenschaften* 45(14):327–329.
- Münnich KO, Vogel J. 1963. Investigations of meridional transport in the troposphere by means of radiocarbon measurements. In: Symposium on radioactive dating. Proc.: IAEA Vienna.
- Naegler T, Levin I. 2006. Closing the global radiocarbon budget 1945–2005. *J. Geophys. Res.* 111:D12311. doi: [10.1029/2005JD006758](https://doi.org/10.1029/2005JD006758).
- Naegler T, Levin I. 2009. Biosphere-atmosphere gross carbon exchange flux and the δ¹³C₂ and Δ¹⁴C₂ disequilibria constrained by the biospheric excess radiocarbon inventory. *J. Geophys. Res.* 114:D17303. doi: [10.1029/2008JD011116](https://doi.org/10.1029/2008JD011116).
- Nakazawa T, Ishizawa M, Higuchi K, Trivett NBA. 1997. Two curve fitting methods applied to CO₂ flask data. *Environmetrics: The official journal of the International Environmetrics Society* 8.3:197–218.
- Nydal R, Lövsøth K. 1983. Tracing bomb ¹⁴C in the atmosphere 1962–1980. *J. Geophys. Res.* 88:3621–3642.
- Nydal R, Lövsøth K. 1996. Carbon-14 measurements in atmospheric CO₂ from Northern and Southern Hemisphere sites, 1962–1993. ORNL/CDIAC-93, NDP-057. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 67 p. doi: [10.3334/CDIAC/atg.ndp057](https://doi.org/10.3334/CDIAC/atg.ndp057).
- Rafter TA, Fergusson GJ. 1957. “Atom Bomb Effect”—recent increase of carbon-14 content of the atmosphere and biosphere. *Science* 126(3273):557–558.
- Tans PP. 1981. A compilation of bomb ¹⁴C data for use in global carbon model calculations. In: Bolin B, editor. SCOPE 16, carbon cycle modelling. Chichester, New York, Brisbane, Toronto: Wiley. p 131–157.
- Telegadas K. 1971. The seasonal atmospheric distribution and inventories of excess carbon-14 from March 1955 to July 1969. HASL report 243, Health and Safety Lab., U.S. At. Energy Comm., New York.

- Turnbull JC, Miller JB, Lehman SJ, Tans PP, Sparks RJ, Southon J. 2006. Comparison of ¹⁴CO₂, CO, and SF₆ as tracers for recently added fossil fuel CO₂ in the atmosphere and implications for biological CO₂ exchange. *Geophys. Res. Lett.* 33:L01817. doi: [10.1029/2005GL024213](https://doi.org/10.1029/2005GL024213).
- Turnbull JC, Lehman SJ, Miller JB, Sparks RJ, Southon JR, Tans PP. 2007. A new high precision ¹⁴CO₂ time series for North American continental air. *J. Geophys. Res. Atmos.* 112(D11). doi: [10.1029/2006JD008184](https://doi.org/10.1029/2006JD008184).
- Turnbull J, Rayner P, Miller JB, Naegler T, Ciais P, Cozic A. 2009. On the use of ¹⁴CO₂ as a tracer for fossil fuel CO₂: quantifying uncertainties using an atmospheric transport model. *J. Geophys. Res.* 114(D22). doi: [10.1029/2009JD012308](https://doi.org/10.1029/2009JD012308).
- Turnbull JC, Mikaloff Fletcher SE, Ansell I, Brailsford GW, Moss RC, Norris MW, Steinkamp K. 2017. Sixty years of radiocarbon dioxide measurements at Wellington, New Zealand: 1954–2014. *Atmos. Chem. Phys.* 17:14771–14784. doi: [10.5194/acp-17-14771-2017](https://doi.org/10.5194/acp-17-14771-2017).
- Trumbore SE. 2009. Radiocarbon and soil carbon dynamics. *Annual Review of Earth and Planetary Sciences* 37:47–66. doi: [10.1146/annurev.earth.36.031207.124300](https://doi.org/10.1146/annurev.earth.36.031207.124300).
- UNFCCC. 2015. The Paris Agreement. http://unfccc.int/files/essential_background/convention/application/pdf/english_paris_agreement.pdf.
- Weller RI, Levin I, Wagenbach D, Minikin A. 2007. The air chemistry observatory at Neumayer stations (GvN and NH-II) Antarctica. *Polarforschung* 76(1–2):39–46.
- Worthy DE et al. 2021. Results of a long-term international comparison of greenhouse gas and isotope measurements at the Global Atmosphere Watch (GAW) Station in Alert, Nunavut, Canada. In preparation.