A NOTE ON REPORTING OF RESERVOIR ^{14}C DISEQUILIBRIA AND AGE OFFSETS

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Abstract. Reservoir age offsets are widely used to correct marine and speleothem ^{14}C age measurements for various calibration purposes. They also serve as a powerful tracer for carbon cycle dynamics. However, a clear terminology regarding reservoir age offsets is lacking, sometimes leading to miscalculations. This note seeks to provide consistent conventions for reporting reservoir ^{14}C disequilibria useful to a broad range of environmental sciences. We introduce the $F^{14}R$ and $\delta^{14}R$ metrics to express the relative ^{14}C disequilibrium between two contemporaneous reservoirs and the R metric as the associated reservoir age offset.

1. Introduction

Conventions for reporting of radiocarbon (^{14}C) data have been established in the seminal paper by Stuiver and Polach (1977) and later slightly revised and clarified by Mook and van der Plicht (1999) and Reimer et al. (2004). However, heretofore no conventions have been established for reporting ^{14}C disequilibria or age offsets between contemporaneous carbon reservoirs despite their necessity for calendar age determinations and broad use in reconstructing past carbon cycle dynamics. This lack of conventions may explain miscalculations that can be found in the scientific literature. This note aims to formalize the conventions for reporting of reservoir ^{14}C disequilibria and age offsets. We advocate the use of new metrics – $F^{14}R$ and $\delta^{14}R$ – as conservative isotopic tracers to characterize the ^{14}C disequilibrium between contemporaneous reservoirs. From these metrics we derive the corresponding reservoir age offset: R.

2. Reporting of reservoir ^{14}C disequilibria

2.1. General framework

The measured $\delta^{13}C$-normalized fraction modern (Fm_x) of an environmental sample (Stuiver and Polach, 1977; Mook and van der Plicht, 1999; Reimer et al., 2004) may be used to reconstruct that of its carbon source (e.g., reservoir *x*) at the time of its formation (T, years BP) via the Cambridge half-life (5730 years) and the law of radioactive decay, i.e., $Fm_x^T = Fm_x.exp(T/8267)$. Therefore, the ratio of Fm values from two contemporaneous carbon reservoirs (*x* and *y*) at time T [i.e.,Fm_x^T/Fm_y^T] is equal to that of two corresponding samples measured today and is defined here as the reservoir's "relative enrichment" ($F^{14}R_{x\text{-}y}$).

(1)
$$\boldsymbol{F^{14}R_{x-y} = \frac{Fm_x}{Fm_y}}$$

The reservoir's relative enrichment (Eq. 1) is conserved with the passage of time and therefore a fundamental measure of the relative disequilibrium between the ^{14}C inventories of two contemporaneous reservoirs. By convention, $F^{14}R$ is dimensionless and ranges from 0 to 1 by placing the more commonly enriched reservoir (*y*) in the denominator. For instance, under natural circumstances (pre-bomb epoch) the atmosphere is always enriched compared to all other carbon reservoirs and therefore would typically serve as reservoir *y*. Likewise, the surface ocean could serve as reservoir *y* when evaluating disequilibria with the deep ocean reservoir. Alternatively, the reservoir's relative enrichment can be expressed as the relative difference between the ^{14}C contents of reservoirs *x* and *y*, defined here as the reservoir's "relative deviation" ($\delta^{14}R_{x\text{-}y}$).

(2)
$$\boldsymbol{\delta^{14}R_{x-y} = \left(F^{14}R_{x-y} - 1\right) \times 1000‰}$$

Finally, the "reservoir age offset" ($R_{x\text{-}y}$) between two contemporaneous carbon reservoirs x and y can be easily calculated from $F^{14}R$ and the Libby half-life (5568 yr), and expressed in ^{14}C years.

(3) $$\boldsymbol{R_{x-y} = -8033 \times ln\left(F^{14}R_{x-y}\right)}$$

2.2. The atmospheric reference

Comparing relative disequilibria through time and space (e.g., in paleoceanography) requires a common reference. The atmosphere is the most logical reference because it is the most uniform and ^{14}C-enriched global carbon reservoir, with a ^{14}C concentration that is quite precisely known for the past 14,000 calendar years, and reasonably well known until 50,000 calendar years ago (Reimer et al., 2013a). Hence, in most cases, a reservoir's relative enrichment should be calculated relative to the atmosphere, thereby permitting unambiguous comparisons of reservoir ^{14}C disequilibria and age offsets through time and space.

(4) $$\boldsymbol{F^{14}R_{x-atm} = \frac{Fm_x}{Fm_{atm}}}$$

2.3. The case of speleothems

Speleothem (S) ^{14}C contents are usually lower than that of the contemporaneous atmosphere, mainly due to the incorporation of bedrock-derived ^{14}C-free ("dead") carbon during formation. The speleothem ^{14}C contents must be corrected for this dead carbon contribution in order to reflect the actual atmospheric ^{14}C content. A common correction, the "dead carbon proportion" (dcp) (Genty and Massault, 1997) or the equivalent "dead carbon fraction" (*dcf*) (Fohlmeister et al. 2011), can be defined using the $F^{14}R$.

(5) $$\boldsymbol{dcp = (1 - F^{14}R_{S-atm}) \times 100\%}$$

3. Discussion

The reservoir age offset metric (R) is almost always used to characterize reservoir ^{14}C disequilibria. This is historically linked to the fact that reservoir age offsets are extensively used to adjust ^{14}C dates to the atmospheric reservoir for various calibration purposes, e.g., construction of the "Intcal" calibration curves (corals and speleothem data, see Reimer et al., 2013b) or obtaining calendar chronologies from lacustrine/marine ^{14}C-dated archives (e.g., Toucanne et al., 2015). However, the metrics proposed here ($F^{14}R$, $\delta^{14}R$, R) are also well-suited for studying carbon dynamics and chemical processes in soils (Trumbore, 2000), inland waters (Keaveney and Reimer, 2012; Soulet et al., 2011), the ocean (DeVries and Primeau, 2010; Broecker et al., 1984), groundwater (Boaretto et al., 1998), and caves (Genty and Massault, 1997; Fohlmeister et al., 2011).

The $F^{14}R$, $\delta^{14}R$, and R metrics are easy to calculate, conserved with time, and thus clearer measures of both past and present reservoir ^{14}C disequilibria. For example, reservoir age offsets traditionally calculated as ^{14}C age differences are unsuitable for post-bomb samples (Fm >1) because the corresponding ages are reported qualitatively as ">*modern*" by convention (Stuiver and Polach, 1977). Thus post-bomb reservoir age offsets must be calculated directly from the fraction modern values using the reservoir's relative enrichment ($F^{14}R$) and equation (3) [see also Burr et al. (2009) and Keaveney and Reimer (2012)]. Likewise, $\Delta^{14}C$ nomenclature permits quantitative reporting of post-bomb ^{14}C measurements, but they, too, should be normalized to the contemporaneous atmosphere in order to unambiguously quantify temporal changes in disequilibria. As an example, the $\Delta^{14}C$ values of dissolved inorganic carbon (DIC) in surface waters of the Black Sea were similar in 1988 (57.3‰; Jones and Gagnon, 1994) and 2004 (62.5‰; Fontugne et al., 2009), whereas the contemporaneous atmospheric $\Delta^{14}C$ values were very different (175.0‰ and 70.4‰, respectively; Levin and Kromer, 2004). Thus, despite similar DIC $\Delta^{14}C$ values, the surface Black Sea was depleted by 100‰ relatively to the atmosphere in 1988 ($\delta^{14}R_{BS\text{-}atm}$=-100‰; $R_{BS\text{-}atm}$=850 ^{14}C yrs) but nearly equilibrated with the atmosphere in 2004 ($\delta^{14}R_{BS\text{-}atm}$=-7‰; $R_{BS\text{-}atm}$=60 ^{14}C yrs), suggesting two very different geochemical states.

Other measures of reservoir ^{14}C disequilibria have been proposed, such as the ΔΔ notation that reports differences between the Δ values of a reservoir and the atmosphere (Thornalley et al., 2011; Burke and Robinson, 2012).

However, unlike $F^{14}R$, $\delta^{14}R$, or R, the ΔΔ metric will take different values for a given level of isotopic disequilibrium ($\delta^{14}R_{x-atm}$), depending on the initial atmospheric ^{14}C concentration (Fm^{T}_{atm}) since actually $\Delta\Delta_{x-atm} = Fm^{T}_{atm} \times \delta^{14}R_{x-atm}$. It is for this reason that recent papers advocated the use of the "*atmosphere normalized* $\Delta^{14}C$" ($\Delta^{14}C_{atm\ normalized}$; Burke et al., 2015) or the "*Initial* $\Delta^{14}C$ *corrected to a world with atmospheric* $\Delta^{14}C_{atm}=0$" ($\Delta^{14}C_{0,adj}$; Cook and Keigwin, 2015), both of which correspond to the reservoir's relative deviation ($\delta^{14}R$). Thus, $F^{14}R$ and its derived metrics (Eq. 1 – 4) would provide a clear and unified framework for expressing a host of marine ^{14}C 'ventilation metrics' that are found in the palaeoceanographic literature, including e.g., B-P (benthic-planktonic) offsets, B-Atm (benthic-atmosphere) offsets, Δ_x, and $\Delta\Delta_{x-atm}$. Similarly, the dead carbon proportion *dcp* (Eq. 5), which is currently exclusively applied to speleothems, would be equally useful as a measure of the 'hard water effect', which is actually a dilution of the inorganic ^{14}C pool by bedrock-derived dead carbon in lakes and rivers (Deevey et al., 1954; Keaveney and Reimer, 2012) rather than the result of limited exchange with the atmospheric carbon pool.

Finally, we have been careful not to overlap the marine ΔR metric (Stuiver et al., 1986) expressing the difference between the reservoir age offset of a regional part of the ocean and the expected value derived from the oceanic box model used to build the marine calibration curve (Stuiver and Braziunas, 1993; and e.g., Reimer et al., 2013a): $\Delta R = R_{x-atm} - R_{MarineXX-IntcalXX}$. By definition, ΔR is useful to calibrate marine ^{14}C ages using the marine calibration curve. However, unlike R, the definition of marine ΔR depends on the ocean box model used and its parameterization, including in particular the assumption of constant ocean circulation and carbon cycling (Stuiver et al., 1986). Hence, akin to Jull et al. (2013), reporting the actual measured values of R (i.e. R_{x-atm}, or the related metrics $F^{14}R_{x-atm}$ and $\delta^{14}R_{x-atm}$ defined above) would help to avoid any ambiguity.

4. Concluding remarks and recommendations

In this note we present a common framework for reporting ^{14}C disequilibria that is based upon the fundamental "relative enrichment" ($F^{14}R$) between two contemporaneous reservoirs. As the use these metrics are appropriate to a broad range of environmental sciences, we advocate quantifying ^{14}C disequilibria as a reservoir's "relative enrichment" ($F^{14}R$), "relative deviation" ($\delta^{14}R$), or "reservoir age offset" (R), with a clearly reported reference (e.g., "ocean-atmosphere relative enrichment", etc…) and a cautiously discussed causality [for reviews about various causes, see Jull et al., (2013) and Philippsen, (2013)]. The equations used to calculate these metrics are summarized in Table 1, and their uncertainties are detailed in the appendix.

Table 1. Summary of metrics used to report ^{14}C disequilibria between contemporaneous reservoirs *x* and *y*.

	$F^{14}R$	**$\delta^{14}R$**	**R**
Terminology	Relative enrichment	Relative deviation	Reservoir age offset
General equations	$F^{14}R_{x-y} = \frac{Fm_x}{Fm_y}$	$\delta^{14}R_{x-y} = \left(F^{14}R_{x-y} - 1\right) \times 1000‰$	$R_{x-y} = -8033 \times ln\left(F^{14}R_{x-y}\right)$
Units	Dimensionless	Dimensionless	^{14}C years
Reservoirs	All reservoirs, past and present, pre-bomb and post-bomb		
Applications	Physical oceanography, paleoceanography, limnology, paleolimnology, soil sciences, cave processes, calibration purposes		

Appendix

This short appendix provides the equations to be used to calculate the uncertainties of $F^{14}R$, $\delta^{14}R$, R, and dcp. These metrics implicitly assume strict synchrony between reservoirs. Two cases have to be considered.

Case 1: Pair of contemporaneous ^{14}C ages. For example, benthic and planktonic foraminifera picked from the same sediment layer may, in some cases, be assumed to be contemporaneous ^{14}C records of two distinct reservoirs. A similar example would be the ^{14}C dating of a shell and a piece of wood embedded in the same sediment layer. In such cases, the uncertainties (σ) on the reservoir's relative enrichment ($F^{14}R$), relative deviation ($\delta^{14}R$), dead carbon proportion (dcp), and reservoir age offset (R), are simple functions of the measured Fm values and their associated uncertainties (σ_x and σ_y).

$$\sigma_{F^{14}R} = F^{14}R \times \sqrt{\left(\frac{\sigma_x}{Fm_x}\right)^2 + \left(\frac{\sigma_y}{Fm_y}\right)^2}$$

$$\sigma_{\delta^{14}R} = \sigma_{F^{14}R} \times 1000‰$$

$$\sigma_{dcp} = \sigma_{F^{14}R} \times 100\%$$

$$\sigma_R = 8033 \times \sqrt{\left(\frac{\sigma_x}{Fm_x}\right)^2 + \left(\frac{\sigma_y}{Fm_y}\right)^2}$$

Case 2: Paired ^{14}C age and calendar age. This case is encountered when the ^{14}C age of the reservoir is associated to a calendar age that has significant measurement uncertainty. This is generally the case for speleothem *dcp* calculations (Southon et al., 2012), when dealing with ^{14}C and U/Th-dated corals (Druffel et al., 2008) or ^{14}C and chronostratigraphically dated foraminifera (Skinner et al., 2010). To calculate the $F^{14}R$, $\delta^{14}R$ and R, and their associated uncertainties, the use of the atmospheric calibration curve is required along with a methodology that propagates the uncertainties of the (i) ^{14}C measurements, (ii) calendar ages, (iii) and atmospheric calibration curve, as well as the calibration curve structures. As such, the resulting $F^{14}R$, $\delta^{14}R$, dcp and R probability density functions are not necessarily Gaussian. Instead, they may be asymmetric and multimodal. This *uncalibration-convolution process* has been recently developed for reservoir age offset calculations, and has been coded as the freely available "ResAge" program (Soulet, 2015) for the R statistical platform. The ResAge package has been updated and now includes function for $F^{14}R$, $\delta^{14}R$ and dcp calculations.

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References

Broecker W, Mix A, Andree M, Oeschger H. 1984. Radiocarbon measurements on coexisting benthic and planktic foraminifera shells: Potential for reconstructing ocean ventilation times over the past 20 000 years. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 5(2):331-339.

Boaretto E, Thorling L, Sveinbjörnsdottir AE, Yechieli Y, Heinemeier J. 1998. Study of the effect of fossil organic carbon on ^{14}C in groundwater from Hvinningdal, Denmark. *Radiocarbon* 40(2):915-920.

Burke A, Robinson LF. 2012. The Southern Ocean's role in carbon exchange during the last deglaciation. *Science* 335(6068)**:**557–61.

Burke A, Stewart AL, Adkins JF, Ferrari R, Jansen MF, Thompson AF. 2015. The glacial mid-depth radiocarbon bulge and its implications for the overturning circulation. *Paleoceanography* 30(7):1021-1039.

Burr GS, Beck JW, Corrège T, Cabioch G, Taylor FW, Donahue DJ. 2009. Modern and Pleistocene reservoir ages inferred from South Pacific corals. *Radiocarbon* 51(1):319-335.

Cook MS, Keigwin LD. 2015. Radiocarbon profiles of the NW Pacific from the LGM and deglaciation: evaluating ventilation metrics and the effect of uncertain surface reservoir ages. *Paleoceanography* 30(3):174-195.

Deevey ES, Gross MS, Hutchinson GE, Kraybill HL. 1954. The natural ^{14}C contents of materials from hard-water lakes. *Proceedings of the National Academy of Sciences of the United States of America* 40(5):285.

DeVries T, Primeau F. 2010. An improved method for estimating water-mass ventilation age from radiocarbon data. *Earth and Planetary Science Letters* 295(3):367-378.

Druffel ER, Robinson LF, Griffin S, Halley RB, Southon JR, Adkins JF. 2008. Low reservoir ages for the surface ocean from mid-Holocene Florida corals. *Paleoceanography* 23(2):PA2209.

Fohlmeister J, Kromer B, Mangini A. 2011. The influence of soil organic matter age spectrum on the reconstruction of atmospheric ^{14}C levels via stalagmites. Radiocarbon 53(1):99–115.

Fontugne M, Guichard F, Bentaleb I, Strechie C, Lericolais G. 2009. Variations in ^{14}C reservoir ages of Black Sea waters and sedimentary organic carbon during anoxic periods: influence of photosynthetic versus chemoautotrophic production. *Radiocarbon* 51(3):969-976.

Genty D, Massault M. 1997. Bomb ^{14}C recorded in laminated speleothems: calculation of dead carbon proportion. *Radiocarbon* 33(1):33–48.

Hoffmann DL, Beck JW, Richards DA, Smart PL, Singarayer JS, Ketchmark T, Hawkesworth CJ. 2010. Towards radiocarbon calibration beyond 28ka using speleothems from the Bahamas. *Earth and Planetary Science Letters* 289(1):1–10.

Ishikawa NF, Tayasu I, Yamane M, Yokoyama Y, Sakai S, Ohkouchi N. 2015. Sources of Dissolved Inorganic Carbon in Two Small Streams with Different Bedrock Geology: Insights from Carbon Isotopes. *Radiocarbon* 57(3):439-448.

Jones GA, Gagnon AR. (1994). Radiocarbon chronology of Black Sea sediments. *Deep Sea Research Part I: Oceanographic Research Papers* 41(3):531-557.

Jull AJ, Burr GS, Hodgins GW. 2013. Radiocarbon dating, reservoir effects, and calibration. *Quaternary International* 299: 64–71.

Keaveney EM, Reimer PJ. 2012. Understanding the variability in freshwater radiocarbon reservoir offsets: a cautionary tale. *Journal of Archaeological Science* 39(5):1306-1316.

Levin I, Kromer B. 2004. The tropospheric $^{14}CO_2$ level in mid latitudes of the Northern Hemisphere. *Radiocarbon* 46(3):1261-1272.

Mook WG, van der Plicht J. 1999. Reporting ^{14}C activities and concentrations. *Radiocarbon* 41(3):227–39.

Philippsen B. 201. The freshwater reservoir effect in radiocarbon dating. *Heritage Science* 1(1):24.

Reimer PJ, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck CE, Cheng H, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hafidason H, Hajdas I, Hatté C, Heaton TJ, Hoffmann DL, Hogg AG, Hughen KA, Kaiser KF, Kromer B, Manning SW, Niu M, Reimer RW, Richards DA, Scott EM, Southon JR, Staff RA, Turney CSM, van der Plicht J. 2013a. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55(4):1869–87.

Reimer PJ, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Brown DM, Buck CE, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Haflidason H, Hajdas I, Hatté C, Heaton TJ, Hogg AG, Hughen KA, Kaiser KF, Kromer B, Manning SW, Reimer RW, Richards DA, Scott EM, Southon JR, Turney CSM, van der Plicht J. 2013b. Selection and treatment of data for radiocarbon calibration: an update to the International Calibration (IntCal) criteria. Radiocarbon 55(4), 1923-1945.

Reimer PJ, Brown TA, Reimer RW. 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3):1299-1304.

Skinner LC, Fallon S, Waelbroeck C, Michel E, Barker S. 2010. Ventilation of the deep Southern Ocean and deglacial CO_2 rise. *Science* 328(5982):1147–51.

Soulet G. 2015. Methods and codes for reservoir–atmosphere ^{14}C age offset calculations. *Quaternary Geochronology 29*:97-103.

Soulet G, Ménot G, Garreta V, Rostek F, Zaragosi S, Lericolais G, Bard E. 2011. Black Sea "Lake" reservoir age evolution since the Last Glacial—Hydrologic and climatic implications. Earth and Planetary Science Letters 308(1):245–58.

Southon JR, Noronha AL, Cheng H, Edwards RL, Wang Y. 2012. A high-resolution record of atmospheric ^{14}C based on Hulu Cave speleothem H82. *Quaternary Science Reviews* 33:32–41.

Stuiver M, Braziunas TF. 1993. Modeling atmospheric ^{14}C influences and ^{14}C ages of marine samples to 10,000 BC. *Radiocarbon* 35(1):137–89.

Stuiver M, Pearson GW, Braziunas T. 1986. Radiocarbon age calibration of marine samples back to 9000 cal yr BP. *Radiocarbon* 28(2B):980-1021.

Stuiver M, Polach HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Thornalley DJR, Barker S, Broecker WS, Elderfield H, McCave IN. 2011. The Deglacial Evolution of North Atlantic Deep Convection. *Science* 331(6014):202–5.

Toucanne S, Soulet G, Freslon N, Jacinto RS, Dennielou B, Zaragosi S, Eynaud F, Bourillet JF, Bayon G. (2015). Millennial-scale fluctuations of the European Ice Sheet at the end of the last glacial, and their potential impact on global climate. *Quaternary Science Reviews* 123:113-133.

Trumbore S. 2000. Age of soil organic matter and soil respiration: radiocarbon constraints on belowground C dynamics. *Ecological Applications* 10(2), 399-411.