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## A guide to radiocarbon units and calculations

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## **A guide to radiocarbon units and calculations**

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Kristina Eriksson Stenström<sup>1</sup>, Göran Skog<sup>2</sup>, Elisavet Georgiadou<sup>1</sup>, Johan Genberg<sup>1</sup>, Anette Johansson<sup>3</sup>

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## 1. Introduction

The first radiocarbon dating was performed in 1949 (Libby et al, 1949). At that time, and up until 1977, all radiocarbon measurements were performed by measuring the radioactive decay of  $^{14}\text{C}$ . Since then accelerator mass spectrometry (AMS) has entered the scene. AMS relies on counting the relative abundance directly in terms of isotope ratios. Even if only working with AMS, it is difficult to avoid the concept of activity measurement, as most definitions of the jungle of quantities and units that are used in radiocarbon measurements stems from the early days of radiocarbon dating.

In this paper we will review the basic calculations used in radiocarbon measurements and we will try to summarize the different quantities and units used. Unfortunately, some quantities have more than one definition, and we will make recommendations of how to use the different expressions.

## 2. Activity measurement

The basic information needed in a  $^{14}\text{C}$  measurement performed by decay counting is the measured specific activity of the sample ( $\tilde{A}_S$ ), a standard ( $\tilde{A}_{\text{stand}}$ ) and a background sample ( $\tilde{A}_b$ ). Specific activity equals the number of decays per time and mass unit, and can be expressed e.g. as counts per minute and gram C (cpm/g C) or as Bq/kg C (SI unit). To be representative, the standard and background should have undergone the same sample pre-treatment as the sample. The background arises both from a contamination of the sample by carbonaceous material (which can be of different specific activity) and from instrumental background.

The net specific  $^{14}\text{C}$  activity of the sample ( $A_S$ ) is a function of the measured specific  $^{14}\text{C}$  activities of the sample ( $\tilde{A}_S$ ) and of the background ( $\tilde{A}_b$ ), and for the standard,  $A_{\text{stand}}$  is a function of  $\tilde{A}_{\text{stand}}$  and  $\tilde{A}_b$ , that is

$$A_S = f_1(\tilde{A}_S, \tilde{A}_b) \quad (1)$$

$$A_{\text{s tan d}} = f_2(\tilde{A}_{\text{s tan d}}, \tilde{A}_b) \quad (2)$$

In the simplest case the net specific activities can be written as:

$$A_S = \tilde{A}_S - \tilde{A}_b \quad (3)$$

$$A_{\text{s tan d}} = \tilde{A}_{\text{s tan d}} - \tilde{A}_b \quad (4)$$

More information about background corrections when using AMS can be found e.g. in Donahue et al (1990) and Santos (2007).

### *Estimation of error*

The ratio

$$u = \frac{A_S}{A_{\text{s tan d}}} = \frac{\tilde{A}_S - \tilde{A}_b}{\tilde{A}_{\text{s tan d}} - \tilde{A}_b} \quad (5)$$

represents the sample activity relative to the standard. All these quantities involved are affected by errors (counting statistics as well as other, more unspecified). It is important to know how these quantities add up to a total error  $\sigma_u$ .

For a function  $u$  of several variables  $u(x,y,z,...)$  the following formula is used (propagation of error):

$$\sigma_u^2 \approx \left( \frac{\partial u}{\partial x} \right)^2 \sigma_x^2 + \left( \frac{\partial u}{\partial y} \right)^2 \sigma_y^2 + \left( \frac{\partial u}{\partial z} \right)^2 \sigma_z^2 + \dots \quad (6)$$

Thus,

$$\sigma_u^2 \approx \left( \frac{\partial u}{\partial \tilde{A}_S} \right)^2 \sigma_{\tilde{A}_S}^2 + \left( \frac{\partial u}{\partial \tilde{A}_{stand}} \right)^2 \sigma_{\tilde{A}_{stand}}^2 + \left( \frac{\partial u}{\partial \tilde{A}_b} \right)^2 \sigma_{\tilde{A}_b}^2 \quad (7)$$

Performing the partial derivatives yields

$$\begin{aligned} \sigma_u^2 &\approx \left( \frac{1}{\tilde{A}_{stand} - \tilde{A}_b} \right)^2 \sigma_{\tilde{A}_S}^2 + \left( -\frac{\tilde{A}_S - \tilde{A}_b}{(\tilde{A}_{stand} - \tilde{A}_b)^2} \right)^2 \sigma_{\tilde{A}_{stand}}^2 + \left( \frac{-1}{(\tilde{A}_{stand} - \tilde{A}_b)} + \frac{\tilde{A}_S - \tilde{A}_b}{(\tilde{A}_{stand} - \tilde{A}_b)^2} \right)^2 \sigma_{\tilde{A}_b}^2 \\ &= \left( \frac{1}{\tilde{A}_{stand} - \tilde{A}_b} \right)^2 \sigma_{\tilde{A}_S}^2 + \left( -\frac{\tilde{A}_S - \tilde{A}_b}{(\tilde{A}_{stand} - \tilde{A}_b)^2} \right)^2 \sigma_{\tilde{A}_{stand}}^2 + \left( \frac{\tilde{A}_S - \tilde{A}_{stand}}{(\tilde{A}_{stand} - \tilde{A}_b)^2} \right)^2 \sigma_{\tilde{A}_b}^2 \end{aligned} \quad (8)$$

Dividing Eq. 8 with  $u^2$  yields

$$\frac{\sigma_u^2}{u^2} \approx \frac{\sigma_{\tilde{A}_S}^2}{(\tilde{A}_S - \tilde{A}_b)^2} + \frac{\sigma_{\tilde{A}_{stand}}^2}{(\tilde{A}_{stand} - \tilde{A}_b)^2} + \left( \frac{\tilde{A}_S - \tilde{A}_{stand}}{(\tilde{A}_S - \tilde{A}_b)(\tilde{A}_{stand} - \tilde{A}_b)} \right)^2 \sigma_{\tilde{A}_b}^2 \quad (9)$$

Hence the relative error  $\sigma_u/u$  can be written as

$$\frac{\sigma_u}{u} = \sqrt{\left( \frac{\sigma_{\tilde{A}_S}}{\tilde{A}_S - \tilde{A}_b} \right)^2 + \left( \frac{\sigma_{\tilde{A}_{stand}}}{\tilde{A}_{stand} - \tilde{A}_b} \right)^2 + \left( \frac{\tilde{A}_S - \tilde{A}_{stand}}{(\tilde{A}_S - \tilde{A}_b)(\tilde{A}_{stand} - \tilde{A}_b)} \right)^2 \sigma_{\tilde{A}_b}^2} \quad (10a)$$

For “young” samples ( $\tilde{A}_S \gg \tilde{A}_b$ ) this expression is reduced to

$$\frac{\sigma_u}{u} = \sqrt{\left( \frac{\sigma_{\tilde{A}_S}}{\tilde{A}_S - \tilde{A}_b} \right)^2 + \left( \frac{\sigma_{\tilde{A}_{stand}}}{\tilde{A}_{stand} - \tilde{A}_b} \right)^2} \quad (10b)$$

### 3. Isotope fractionation

Isotope fractionation is a process that occurs during chemical reactions as well as during physical processes, and this effect needs to be taken into account in most radiocarbon measurements. The effect of isotope fractionation is a partial separation of the different isotopes and results in enrichment of one isotope relative to another. In chemical reactions the isotopic fractionation can be a result of slightly different equilibrium constants of the different isotopes for a particular chemical reaction. Evaporation, condensation and thermal diffusion may also result in significant fractionation.

In the carbon cycle isotope fractionation occurs when carbon is transferred from one part of the ecosystem to another. As an example, when  $\text{CO}_2$  is absorbed by the leaves of trees and in plants during the process of photosynthesis, relatively more  $^{12}\text{C}$  is absorbed than  $^{13}\text{C}$ , and  $^{13}\text{C}$  is absorbed to a higher degree than  $^{14}\text{C}$ . Compared to  $^{13}\text{C}$ ,  $^{12}\text{C}$  in cellulose in wood from trees is enriched by a factor of about 2 % during this process. The fractionation in this case is a kinetic effect: the heavier isotope proceeds

slower through the photosynthetic process and is therefore depleted. This also means that the specific activity of carbon in e.g. a leaf is lower than the specific activity of atmospheric CO<sub>2</sub> that the leaf absorbed its carbon from. Or, if speaking in terms of isotope ratios, the leaf will not have the same isotope ratio as the CO<sub>2</sub> that it grew in. Fractionation can also occur in the laboratory, i.e. in incomplete combustion or reduction.

In radiocarbon dating this effect needs to be taken into consideration to be able to compare the <sup>14</sup>C values of different materials, e.g. when comparing atmospheric CO<sub>2</sub> data to tree ring data. To find the age of a sample, the activity of the sample is, basically speaking, compared to the activity of tree rings of known ages and well-determined isotope fractionation. Therefore, the activity of a sample is translated to the activity that the sample would have had if it would have been wood with a particular stable isotope composition. The procedure, called normalisation, is described below. First, however, we need to introduce the quantity δ<sup>13</sup>C, which is a measure of isotope fractionation.

Instead of stating the <sup>13</sup>C/<sup>12</sup>C ratios directly, isotope fractionation is more conveniently expressed as δ<sup>13</sup>C, which is the relative deviation of the <sup>13</sup>C/<sup>12</sup>C ratio of the sample compared to that of a standard material, VPDB (Vienna Pee Dee Belemnite), expressed in per mil:

$$\delta^{13}\text{C} = \left( \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_S - \left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}}} \right) \cdot 1000\text{‰} \quad (11)$$

The original standard material was carbonate from a marine fossil collected from the Pee Dee Formation in South Carolina, USA. The fossil originated from an extinct squid-resembling organism called a Belemnite. This material, called PDB (Pee Dee Belemnite), had the <sup>13</sup>C/<sup>12</sup>C ratio of 1.12372‰. The high value reflects the marine origin of the material. The use of this standard therefore gives most natural materials negative δ<sup>13</sup>C values. The PDB material has been exhausted and replaced by the limestone standard VPDB (NBS19), which was manufactured from marble of unknown origin (Friedman et al, 1982).

Some typical δ<sup>13</sup>C values are shown in Table 1. The lower the δ<sup>13</sup>C value, the heavier discrimination of <sup>13</sup>C compared to <sup>12</sup>C in the material.

Table 1. Typical δ<sup>13</sup>C values in nature (Stuiver and Polach, 1977)

Material	δ <sup>13</sup> C (‰)
Marine carbonates	0 (-4 to +4)
Atmospheric CO <sub>2</sub>	-9 (-11 to -6)
Grains, seeds, maize, millet	-10 (-13 to -7)
Marine organisms	-15 (-19 to -11)
Bone collagen, wood cellulose	-20 (-24 to -18)
Grains (wheat, oats, rice, etc)	-23 (-27 to -19)
Recent wood, charcoal	-25 (-30 to -20)
Tree leaves, wheat, straw	-27 (-32 to -22)

#### 4. Normalisation

Now let's look at the normalisation procedure, i.e. the translation of the measured activity to the activity that the sample would have had if it would have been wood with  $\delta^{13}\text{C} = -25\text{‰}$ .

For this purpose we introduce the  $^{13}\text{C}$  fractionation factor ( $\text{Frac}_{13/12}$ ):

$$\text{Frac}_{13/12} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{[\delta^{13}\text{C}=-25]}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_s} \quad (12)$$

The  $^{14}\text{C}$  fractionation factor ( $\text{Frac}_{14/12}$ ) is approximately given by the square of the  $^{13}\text{C}$  fractionation factor (Stuiver and Robinson, 1974):

$$\text{Frac}_{14/12} \approx \text{Frac}_{13/12} \cdot \text{Frac}_{14/13} \approx (\text{Frac}_{13/12})^2 \quad (13)$$

According to Stuiver and Robinson (1974) an exponent of 1.9 may be more correct. The normalised specific activity of the sample,  $A_{\text{SN}}$ , is thus given by

$$A_{\text{SN}} = A_s \cdot \text{Frac}_{14/12} \approx A_s \cdot (\text{Frac}_{13/12})^2 = A_s \left( \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{[\delta^{13}\text{C}=-25]}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_s} \right)^2 \quad (14)$$

Using the definition of  $\delta^{13}\text{C}$  (eq. 11), equation (14) above can be rewritten as

$$\begin{aligned} A_{\text{SN}} &= A_s \left( \frac{\left(1 - \frac{25}{1000}\right) \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}}{\left(1 + \frac{\delta^{13}\text{C}}{1000}\right) \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}} \right)^2 = A_s \left( \frac{\left(1 - \frac{25}{1000}\right)}{\left(1 + \frac{\delta^{13}\text{C}}{1000}\right)} \right)^2 = A_s \left( \frac{0.975}{\left(1 + \frac{\delta^{13}\text{C}}{1000}\right)} \right)^2 \\ &\approx A_s \left( 1 - \frac{2(25 + \delta^{13}\text{C})}{1000} \right) \end{aligned} \quad (15)$$

The last step in (eq. 11) is an approximation which renders an error of maximum 1 ‰ for  $\delta^{13}\text{C}$ -values between -35 and +3 ‰.



## 5. Standards

Radiocarbon measurements are performed relative to a standard of known activity (eq. 5). Due to the radioactive decay of  $^{14}\text{C}$  the specific activity of any  $^{14}\text{C}$  standard material decreases with time. Therefore *the absolute radiocarbon standard* has been established. The specific activity of this absolute radiocarbon standard ( $A_{\text{abs}}$ ) has been defined as (see e.g. Mook and van der Plicht, 1999):

$$A_{\text{abs}} = 226 \text{ Bq/kg C.} \quad (16)$$

$A_{\text{abs}}$  is intended to correspond to the hypothetical specific activity of atmospheric carbon of year 1950, measured in 1950, making the assumption that this hypothetical atmosphere is free from human perturbations and normalised to  $\delta^{13}\text{C} = -25 \text{ ‰}$ .  $A_{\text{abs}}$  can be written as:

$$A_{\text{abs}} = A_{1950[-25]} e^{\lambda_{\text{C}}(y-1950)} \quad (17)$$

where  $A_{1950[-25]}$  means the specific activity of the hypothetical 1950 atmosphere, normalised to  $\delta^{13}\text{C} = -25 \text{ ‰}$ , and decayed to the present. Please note that  $A_{1950[-25]}$  corresponds to an activity measured at the present, while  $A_{\text{abs}}$  refers to the value if measured in 1950. In the exponential  $\lambda_{\text{C}}$  is based on the Cambridge half-life<sup>1</sup> of  $(T_{1/2})_{\text{C}} = 5730 \pm 40$  years and  $y$  corresponds to the year of measurement: thus the exponential translates  $A_{1950[-25]}$  to the value that it would have had in 1950.

The “real-world” atmospheric  $^{14}\text{C}$  level in 1950 was lower than  $A_{\text{abs}}$  due to human influence. Since it was desirable that the hypothetical atmosphere should be free from the fossil fuel effects of the industrial revolution, wood from year 1890 (corrected for radioactive decay to 1950) was chosen to correspond to the absolute radiocarbon standard.

The principal radiocarbon standard is NIST<sup>2</sup> oxalic acid<sup>3</sup> I, also referred to as OxI, NBS<sup>4</sup> or SRM 4990 B ( $\delta^{13}\text{C}$  value close to  $-19 \text{ ‰}$ ). The OxI standard was made from a crop of 1955 sugar beet. At that time the  $^{14}\text{C}$  specific activity of the atmosphere had begun to rise due to the atmospheric testing of thermonuclear weapons<sup>5</sup>. Therefore  $A_{\text{abs}}$  is defined as 95% the specific activity, in AD 1950, of OxI (normalised to  $\delta^{13}\text{C} = -19 \text{ ‰}$  with respect to VPDB). In other words, the specific activity of OxI ( $A_{\text{OxI}}$ ) is first measured and normalised to  $\delta^{13}\text{C} = -19 \text{ ‰}$  giving the normalised sample activity  $A_{\text{ON}}$ :

$$A_{\text{ON}} = 0.95 A_{\text{OxI}} \left( \frac{1 - \frac{19}{1000}}{1 + \frac{\delta^{13}\text{C}}{1000}} \right)^2 \approx 0.95 A_{\text{OxI}} \left( 1 - \frac{2(19 + \delta^{13}\text{C})}{1000} \right) \quad (18)$$

This value is then corrected for decay since 1950 to obtain absolute international standard specific activity,  $A_{\text{abs}}$ :

$$A_{\text{abs}} = A_{\text{ON}} e^{\lambda_{\text{C}}(y-1950)} \text{ where } \lambda_{\text{C}} = \frac{1}{8267} \text{ yr}^{-1} \text{ and } y \text{ is the year of measurement.} \quad (19)$$

The OxI standard is no longer commercially available. Some other standards that are now available are listed in Table 2.

<sup>1</sup> For further information about half-lives, see section 9.

<sup>2</sup> National Institute of Standards and Technology; Gaithersburg, Maryland, USA

<sup>3</sup>  $\text{C}_2\text{H}_2\text{O}_4$

<sup>4</sup> From the former name of NIST: National Bureau of Standards

<sup>5</sup> These detonations resulted in the bomb effect, which peaked in 1963 when the atmospheric  $^{14}\text{C}$  level was about twice the natural level.

**Table 2.** Some common radiocarbon secondary standards

Standard	Material	$\delta^{13}\text{C}$ (‰)	pMC <sup>6</sup>
OxII (SRM 4990 C)	Oxalic acid	-17.8	134.08
IAEA-C6 (ANU)	Sucrose	-10.8	150.61
IAEA-C7	Oxalic acid	-14.48	49.53
IAEA-C8	Oxalic acid	-18.3	15.03

If using OxII, the equation of  $A_{\text{ON}}$  above (eq. 18) becomes (Donahue et al, 1990):

$$A_{\text{ON}} = A_{1950[-25]} = 0.95 A_{\text{OxI}} \left( \frac{1 - \frac{19}{1000}}{\delta^{13}\text{C}_{\text{OxI}} + \frac{1}{1000}} \right)^2 = 0.7459 A_{\text{OxII}} \left( \frac{1 - \frac{25}{1000}}{\delta^{13}\text{C}_{\text{OxII}} + \frac{1}{1000}} \right)^2 \quad (20)$$

In AMS isotope ratios ( $^{14}\text{C}/^{12}\text{C}$  and/or  $^{14}\text{C}/^{13}\text{C}$ ) are measured instead of specific activities. The specific  $^{14}\text{C}$  activity  $A$  of a natural sample is proportional to

$$\frac{N(^{14}\text{C})}{N(^{12}\text{C}) + N(^{13}\text{C}) + N(^{14}\text{C})} \approx \frac{N(^{14}\text{C})}{N(^{12}\text{C}) + N(^{13}\text{C})} \approx \frac{N(^{14}\text{C})}{N(^{12}\text{C})} \quad (21)$$

where  $N(^{12}\text{C})$ ,  $N(^{13}\text{C})$  and  $N(^{14}\text{C})$  is the number of nuclides of the different isotopes in the sample. According to Donahue et al (1990) the last approximation in (eq. 21) introduces an error of about 0.1‰ equivalent to approximately 1  $^{14}\text{C}$  year.

Using the approximation in (eq. 21), (eq. 20) can be rewritten in terms of the isotopic ration  $^{14}\text{C}/^{12}\text{C}$  (Donahue et al, 1990):

$$\left( \frac{^{14}\text{C}}{^{12}\text{C}} \right)_{1950[-25]} = 0.95 \left( \frac{^{14}\text{C}}{^{12}\text{C}} \right)_{\text{OxI}} \left( \frac{1 - \frac{19}{1000}}{\delta^{13}\text{C}_{\text{OxI}} + \frac{1}{1000}} \right)^2 = 0.7459 \left( \frac{^{14}\text{C}}{^{12}\text{C}} \right)_{\text{OxII}} \left( \frac{1 - \frac{25}{1000}}{\delta^{13}\text{C}_{\text{OxII}} + \frac{1}{1000}} \right)^2 \quad (22)$$

That is, for  $^{14}\text{C}/^{12}\text{C}$  measurements the term ( $^{14}\text{C}/^{12}\text{C}$ ) has simply substituted the specific activity  $A$ .

For  $^{14}\text{C}/^{13}\text{C}$  ratios the situation is somewhat different, as shown in Donahue et al (1990):

$$\left( \frac{^{14}\text{C}}{^{13}\text{C}} \right)_{1950[-25]} = 0.9558 \left( \frac{^{14}\text{C}}{^{13}\text{C}} \right)_{\text{OxI}} \left( \frac{1 - \frac{19}{1000}}{\delta^{13}\text{C}_{\text{OxI}} + \frac{1}{1000}} \right) = 0.7459 \left( \frac{^{14}\text{C}}{^{13}\text{C}} \right)_{\text{OxII}} \left( \frac{1 - \frac{25}{1000}}{\delta^{13}\text{C}_{\text{OxII}} + \frac{1}{1000}} \right) \quad (23)$$

<sup>6</sup> See definition below, (eq. 31)

## 6. Radiocarbon quantities and units

There exist a number of different quantities and units in the field of radiocarbon measurements, and the suitable quantity to use is related to the particular type of measurement. In general there are three modes of reporting  $^{14}\text{C}$  activities:

- 1) absolute activity (i.e. the specific activity of  $^{14}\text{C}$  equal to the activity per kg of carbon, usually expressed as Bq/g C or dpm/g C)
- 2) activity ratio (the ratio between the absolute activities of a sample and the standard)
- 3) relative activity (the difference between the absolute activities of a sample and the standard relative to the absolute standard activity)

According to Mook and van der Plicht (1999) the basic definitions originate from decisions made at international radiocarbon conferences. Stuiver and Polach (1977) have tried to summarize what was used until 1977, and this paper is still frequently cited in the literature today. However, as also pointed out by Mook and van der Plicht (1999), some of these definitions can be confused and misinterpreted. An example is of percent modern, which in the Stuiver and Polach paper has two definitions (and an incorrect ‰ sign in Table 1 of the paper; it should be %). Therefore even more quantities, symbols and units have been introduced over the years, and it can be discussed if this has improved the situation or made it even harder to sort out what different symbols and units actually mean.

Donahue et al (1990) introduced the quantity fraction of modern, using the symbol F (which later has been denoted  $F_m$ ) as described in paragraph 6.5. Also this quantity has been widely used in the literature with another definition than the original. The aerosol community also use the term fraction modern, but use the symbol  $f_M$ , and unfortunately two slightly different definitions of  $f_M$  are in use. The aerosol field has also introduced the term fraction contemporary  $f_c$  (Currie et al, 1989), which can be found in some  $^{14}\text{C}$  source apportionment publications.

Mook and van der Plicht (1999) made an attempt clean up the mess by introducing new symbols and definitions. These have however not been widely adapted, perhaps due to the reluctance to adapt a new nomenclature that is not very transparent at a first glance (the symbols do not provide information that carbon is involved). Reimer et al (2004) have introduced a new symbol for fraction modern,  $F^{14}\text{C}$ , which is very useful for post-bomb calibrations. Among the most frequently quantities used, which are described below, are  $\Delta^{14}\text{C}$ , pMC,  $F_m$ ,  $f_M$ ,  $F^{14}\text{C}$  and specific activity A.

### 6.1. Per mil depletion or enrichment with regard to standard

These quantities and units do not take isotope fractionation into account (Stuiver and Polach, 1977):

$$d^{14}C = \left( \frac{A_S}{A_{ON}} - 1 \right) \cdot 1000\text{‰} \quad (24)$$

The term  $\delta^{14}C$  is used both with and without age correction (y=year of measurement; x=year of formation or year of growth,  $\lambda_C=(1/8267)$  years<sup>-1</sup>):

$$\delta^{14}C = \left( \frac{A_S}{A_{abs}} - 1 \right) \cdot 1000\text{‰} \quad (\text{without age correction}) \quad (25)$$

(Eq. 25) corresponds to the  $^{14}C$  content of the sample at the time of measurement.

(Eq. 26) below instead corresponds to the  $^{14}C$  content of the sample at the time of growth:

$$\delta^{14}C = \left( \frac{A_S e^{\lambda_C(y-x)}}{A_{abs}} - 1 \right) \cdot 1000\text{‰} = \left( \frac{A_S e^{\lambda_C(1950-x)}}{A_{ON}} - 1 \right) \cdot 1000\text{‰} \quad (\text{with age correction}) \quad (26)$$

Here it is obvious that it is very important to state if  $\delta^{14}C$  is with or without age correction!

### 6.2. Per mil depletion or enrichment with regard to standard normalised for isotope fractionation

When taking isotope fractionation into account the  $d^{14}C$  and  $\delta^{14}C$  above (eq. 24-26) become (Stuiver and Polach, 1977):

$$D^{14}C = \left( \frac{A_{SN}}{A_{ON}} - 1 \right) \cdot 1000\text{‰} \quad (27)$$

$$\Delta^{14}C = \left( \frac{A_{SN}}{A_{abs}} - 1 \right) \cdot 1000\text{‰} \quad (\text{without age correction}) \quad (28)$$

$$\Delta = \left( \frac{A_{SN} e^{\lambda_C(y-x)}}{A_{abs}} - 1 \right) \cdot 1000\text{‰} = \left( \frac{A_{SN} e^{\lambda_C(1950-x)}}{A_{ON}} - 1 \right) \cdot 1000\text{‰} \quad (\text{with age correction}) \quad (29)$$

(y=year of measurement; x=year of formation or growth,  $\lambda_C=(1/8267)$  years<sup>-1</sup>)

Here is a source of misinterpretations. As Reimer et al (2004) points out, there is a risk of confusion for  $\Delta$  and  $\Delta^{14}C$ .  $\Delta$  equals  $\Delta^{14}C$  only when the year of growth is the same as the year of measurement. Today, some authors actually mean  $\Delta$  (age corrected) but use the term  $\Delta^{14}C$  (called “age corrected  $\Delta^{14}C$ ” or “ $\Delta^{14}C$  corrected for decay”). As Reimer et al (2004) point out,  $\Delta^{14}C$  decreases with time and depends on the year of measurement. This means that a sample grown/formed e.g. in 1977 will give different  $\Delta^{14}C$  if measured today versus if it was measured in 1977.  $\Delta$  and  $D^{14}C$  do not change with time, since both the standard and the sample decay at the same rate.

### 6.3. Percent Modern (pM) and percent Modern Carbon (pMC)

pMC is frequently used for environmental samples and for post-bomb applications. Unfortunately, there are at least two definitions of percent Modern or percent Modern Carbon. In Stuiver and Polach (1977) it is stated: “The 8<sup>th</sup> International Conference on Radiocarbon Dating (Proceedings, 1972) accepted the replacement of D<sup>14</sup>C per mil by *percent Modern*, equated to the activity ratio  $A_{SN}/A_{ON} \times 100\%$ .” Then these authors introduced a new term, “absolute” percent Modern (pM) as:

$$pM = \frac{A_{SN}}{A_{abs}} \cdot 100\% \quad (30)$$

This ratio decreases with time and depends on the year of measurement, just like  $\Delta^{14}C$ .

In the abc program from NEC the following definition is used (the same as at the 8<sup>th</sup> International Conference on Radiocarbon Dating):

$$pMC = \frac{A_{SN}}{A_{ON}} \cdot 100\% \quad (31)$$

This ratio is constant over time, and thus the values of the standards in Table 2 are according to this definition. It would have been convenient if pM was only used for  $(A_{SN}/A_{abs}) \cdot 100\%$ , and pMC was reserved for  $(A_{SN}/A_{ON}) \cdot 100\%$ . This is however not the case: some authors use pMC as  $(A_{SN}/A_{abs}) \cdot 100\%$ . Although the difference between the two is rather small today ( $A_{abs}/A_{ON}$  is 1.0074 in 2011), it will become more important with time. Thus, we should always state what definition we use! Below we use the definition  $(A_{SN}/A_{ON}) \cdot 100\%$  (eq. 31).

### 6.4. Fraction of modern: $F$ , $F_m$ , $f_M$

Donahue et al (1990) introduce the term fraction of modern,  $F$ , as

$$F = \frac{\left( \frac{^{14}C}{^{13}C} \right)_{S[-25]}}{\left( \frac{^{14}C}{^{13}C} \right)_{1950[-25]}} \quad (32)$$

According to the equations in the section “Standards” (eq. 20, 22, 23) above this equals

$$F = \frac{\left( \frac{^{14}C}{^{13}C} \right)_{S[-25]}}{\left( \frac{^{14}C}{^{13}C} \right)_{1950[-25]}} = \frac{\left( \frac{^{14}C}{^{13}C} \right)_{S[-25]}}{0.9558 \left( \frac{^{14}C}{^{13}C} \right)_{OxI[-19]}} = \frac{A_{SN}}{A_{ON}} \quad (33)$$

Thus, using equations (27) and (31)

$$F = \frac{A_{SN}}{A_{ON}} = \frac{D^{14}C}{1000\text{‰}} + 1 = \frac{pMC}{100\%} = \frac{A_{SN}}{A_{abs} e^{(1950-y)/8267}} \quad (34)$$

In Donahue et al (1990) there is a discussion about background corrections, and the authors introduce the term  $F_m$  as the measured fraction modern, which should be subjected to background correction to

obtain the true fraction modern of the sample,  $F$ . Somehow, other authors have picked up  $F_m$  (or  $f_m$ ) instead of  $F$  as the term for true fraction modern of the sample. As stated by Reimer et al (2004) the term fraction modern has been used with and without  $\delta^{13}\text{C}$ -normalization of the sample activity, which is unfortunate.

Furthermore, in e.g. aerosol science the term fraction modern is associated to the symbol  $f_m$  and is if often unclear if the definition  $A_{\text{SN}}/A_{\text{ON}}$  or  $A_{\text{SN}}/A_{\text{abs}}$  has been used. E.g. in Currie et al (1989) it is stated (in the glossary at page 461):

“modern carbon – 0.95 times the  $^{14}\text{C}$  specific activity of SRM 4990B, normalized to  $\delta^{13}\text{C}=-19\text{‰}$  (PDB). Sample carbon is normalized to  $^{13}\text{C}=-25\text{‰}$  (PDB); the per mil difference of the normalized sample / modern-carbon ratio from unity is denoted  $\Delta^{14}\text{C}$ .”

This statement is confusing. The first sentence must refer to  $A_{\text{ON}}$  (eq. 20), otherwise it should have been added that it refers to the activity as if measured in 1950. Then the second statement does not agree with the Stuiver & Polach definition of  $\Delta^{14}\text{C}$  (eq. 28) (in this there is  $A_{\text{abs}}$  and not  $A_{\text{ON}}$ ). Either modern carbon should be the specific activity of SRM 4990B (OxI) as if measured in 1950, or it should be  $\Delta$  instead of  $\Delta^{14}\text{C}$ .

### 6.5. Fraction Modern, $F^{14}\text{C}$

Reimer et al (2004) highlight the problems with the different terms and symbols in radiocarbon measurements for post-bomb samples and propose

$$F^{14}\text{C} = \frac{A_{\text{SN}}}{A_{\text{ON}}} \quad (35)$$

$F^{14}\text{C}$ , like pMC (eq. 31),  $D^{14}\text{C}$  (eq. 27) and  $\Delta$  (eq. 29), do not change with time (does not depend on the year of measurement).  $F^{14}\text{C}$  has to our knowledge not been subjected to misinterpretations in the literature, and we recommend the use of this unit for post-bomb samples.

### 6.6. Fraction contemporary, $f_c$

In some papers using  $^{14}\text{C}$  for source apportionment of organic aerosols the term fraction contemporary  $f_c$  is used (e.g. Currie et al, 1989, Szidat et al. 2004), and is defined as the ratio between fraction modern in the sample and fraction modern in contemporary carbon in the year of sampling. The  $f_c$  this method render is however only correct if all modern carbon in the sample has the same fraction modern as the atmosphere the year of sampling. Atmospheric organic aerosol may however originate from biomass which has accumulated  $^{14}\text{C}$  over decades with varying atmospheric  $F^{14}\text{C}$  values.

Lewis et al (2004) has combined the atmospheric  $^{14}\text{C}$  values with a growth function of a tree to calculate how the  $^{14}\text{C}$  concentration varies with the age of the tree. In their paper the calculation is done for trees harvested in 1999. They used the equation:

$$F^{14}C_{bb} = \int_{t_1}^{t_2} F^{14}C_A(t) w(t) dt / \int_{t_1}^{t_2} w(t) dt$$

where  $F^{14}\text{C}_A$  is the fraction modern carbon in the atmospheric  $\text{CO}_2$  at time  $t$ .  $w$  is a weighting function to determine the incorporation of carbon into the biomass as a function to time.

$w$  is calculated by deriving the Chapman-Richards growth model presented in Lewis et al. (2004):

$$V = A * (1 - e^{-(t-t_0)/\tau})^m$$

In the equation  $V$  is the volume of the tree or the biomass of a community.  $t$  is the year of measurement and  $t_0$  is year when the tree starts to grow.  $A$ ,  $\tau$  and  $m$  are selected to fit the growth of the biomass. Lewis et al. (2004) used  $\tau = 50$  and  $m = 3$ . The value of  $A$  is irrelevant once the function has been derived.

Using the same equation and parameters to calculate  $F^{14}C_{bb}$  - using values from atmospheric measurements by Levin et al. (2008 and personal communication) and Stuiver and Quay (1981) - the  $F^{14}C_{bb}$  value depends on age of the tree and when it was harvested. For trees harvested in 2007 the effect is most important for trees which are between 60 and 70 years old where the values range between 1.21 and 1.23. For a 30 year old tree the  $F^{14}C$  value is, according to the model, 1.09. A “standard tree” has to be assumed in order to derive the  $F^{14}C$  content in biomass burning.

The value to derive  $f_c$  is because of different sources of the particles hard to do. We therefore recommend that  $f_c$  is only used then there is one source of modern carbon or the sources have the same  $^{14}C$  concentration. As always it must be stated whether  $f_c$  was calculated using normalised  $^{14}C$  data and if absolute or relative standard is being used. In the paper by Szidate et al. (2004) neither is to be found.

## 7. Specific activity and its relation to pMC and $F^{14}C$

In measurements of enhanced  $^{14}C$  radioactivity (nuclear industry, biomedical research) the specific activity of the sample is required:

$$A = \frac{A_s}{A_{abs}} \cdot 226 \text{ Bq/kg C} \quad (36)$$

From the AMS measurements we get (pMC according to eq. 31):

$$pMC = \frac{A_{SN}}{A_{ON}} \cdot 100\% = \frac{A_{SN}}{A_{abs} e^{\lambda_C (1950-y)}} \cdot 100\% \quad (37)$$

Thus we need to “de-normalise” the sample activity  $A_{SN}$  (eq. 15) to achieve  $A_S$ :

$$A_{SN} = A_S \left( \frac{0.975}{\left( 1 + \frac{\delta^{13}C}{1000} \right)} \right)^2 \quad (38)$$

Now pMC can be written as:

$$pMC = \frac{A_s}{A_{abs} e^{\lambda_C (1950-y)}} \cdot \left( \frac{0.975}{\left( 1 + \frac{\delta^{13}C}{1000} \right)} \right)^2 \cdot 100\% \quad (39)$$

Therefore the ratio of  $A_S/A_{abs}$  that we need to calculate the specific activity  $A$  is given by:

$$\frac{A_s}{A_{abs}} = \frac{pMC}{100\%} \cdot \left( \frac{1 + \frac{\delta^{13}C}{1000}}{0.975} \right)^2 \cdot e^{\lambda_c(1950-y)} \quad (40)$$

Finally, we can now write specific activity A as:

$$\begin{aligned} A &= \frac{pMC}{100\%} \cdot \left( \frac{1 + \frac{\delta^{13}C}{1000}}{0.975} \right)^2 \cdot e^{\lambda_c(1950-y)} \cdot 226 \text{ Bq/kg C} \\ &= \frac{pMC}{100\%} \cdot \left( \frac{1 + \frac{\delta^{13}C}{1000}}{0.975} \right)^2 \cdot e^{(1950-y)/8267} \cdot 226 \text{ Bq/kg C} \\ &= F^{14}C \cdot \left( \frac{1 + \frac{\delta^{13}C}{1000}}{0.975} \right)^2 \cdot e^{(1950-y)/8267} \cdot 226 \text{ Bq/kg C} \end{aligned} \quad (41)$$

## 8. Relation between different units

Table 2 summarizes some of the definitions of the different quantities used to express the  $^{14}C$  content of a sample.

**Table 2.** Some common expressions of  $^{14}C$  content

Expression	Comment
$A_{abs} = A_{ON} e^{(y-1950)/8267}$	(eq. 19)
$D^{14}C = \left( \frac{A_{SN}}{A_{ON}} - 1 \right) \cdot 1000\text{‰}$	(eq. 27)
$\Delta^{14}C = \left( \frac{A_{SN}}{A_{abs}} - 1 \right) \cdot 1000\text{‰}$	Without age correction (eq. 28)
$\Delta = \left( \frac{A_{SN} e^{\lambda_c(y-x)}}{A_{abs}} - 1 \right) \cdot 1000\text{‰} = \left( \frac{A_{SN} e^{\lambda_c(1950-x)}}{A_{ON}} - 1 \right) \cdot 1000\text{‰}$	With age correction (eq. 29)
$pMC = \frac{A_{SN}}{A_{ON}} \cdot 100\%$	(eq. 31)



Below follows some useful conversions between units (y=year of measurement; x=year of growth, A=specific activity in Bq/kg C).  $F^{14}C$  can be written as

$$\begin{aligned}
 F^{14}C &= \frac{A_{SN}}{A_{ON}} = \frac{D^{14}C}{1000\text{‰}} + 1 = \frac{pMC}{100\%} = \frac{A_{SN}}{A_{abs} e^{(1950-y)/8267}} = \left( \frac{\Delta^{14}C}{1000} + 1 \right) e^{(y-1950)/8267} \\
 &= \left( \frac{\Delta}{1000} + 1 \right) e^{(x-1950)/8267} = \frac{A}{226 \text{ Bq/kg C}} \cdot \left( \frac{0.975}{\left( 1 + \frac{\delta^{13}C}{1000} \right)} \right)^2 \cdot e^{(y-1950)/8267} \quad (42)
 \end{aligned}$$

Not normalized to  $^{13}C$  fractionation should be written with minuscules (small letters) to differentiate them from units using normalized  $^{14}C$  concentrations which should be written with majuscules (capital letters), e.g.:

$$d14 = \left( \frac{A_s}{A_{ON}} - 1 \right) \cdot 1000\text{‰}$$

$$\delta 14 = \left( \frac{A_s}{A_{abs}} - 1 \right) \cdot 1000\text{‰}$$

## 9. Radiocarbon age

The radioactive decay law states:

$$N(t) = N_0 e^{-\lambda t} \quad (43)$$

where  $N(t)$  is the number of nuclides at time  $t$  and  $N(t=0)=N_0$ . This is equivalent to

$$A_{SN} = A_{ON} e^{-\lambda t} \quad (44)$$

and we have

$$F^{14}C = \frac{A_{SN}}{A_{ON}} = e^{-\lambda t} \quad (45)$$

By convention 1950 AD equals 0 BP (Before Present) is set to  $t=0$ . By another convention the decay constant, called the Libby decay constant ( $\lambda_L$ ), is set to  $\lambda_L=1/8033 \text{ yr}^{-1}$ . Please note that this value is not the same as the Cambridge decay constant ( $\lambda_C=1/8267 \text{ yr}^{-1}$ ). The “conventional” radiocarbon age is given by

$$T_{14\text{C-years}} = -\frac{1}{\lambda_L} \ln \frac{A_{SN}}{A_{ON}} = -8033 \ln \frac{A_{SN}}{A_{ON}} = -8033 \ln F = -8033 \ln F^{14}C \quad (46)$$

The *Libby half-life*<sup>7</sup> is then given by

$$(T_{1/2})_L = -8033 \ln \frac{1}{2} = 5568 \text{ yr} \quad (47)$$

Then a sample with  $A_{SN}=A_{ON}/2$  has the radiocarbon age 5568 BP. Equations (46) and (6) give the error  $\Delta t$ :

$$\Delta t^2 = \left( -8033 \cdot \frac{1}{F^{14}C} \right)^2 \cdot (\Delta F^{14}C)^2 \quad (48)$$

A relative error of 1% thus gives  $\Delta t=8033 \cdot 0.01$  radiocarbon years =80 radiocarbon years.

A useful expression for  $\Delta$  (or “age corrected  $\Delta^{14}C$ ”) is given by combining (eq. 29) and (eq. 46).

$$\begin{aligned} \Delta &= \left( \frac{A_{SN} e^{\lambda_C (1950-x)}}{A_{ON}} - 1 \right) \cdot 1000\text{‰} = \left( e^{-\lambda_L \cdot T_{14\text{C-years}}} \cdot e^{\lambda_C (1950-x)} - 1 \right) \cdot 1000\text{‰} \\ &= \left( e^{-\frac{T_{14\text{C-years}}}{8033}} \cdot e^{\frac{T_{\text{cal-years}}}{8267}} - 1 \right) \cdot 1000\text{‰} \end{aligned} \quad (49)$$

<sup>7</sup> This half-life was estimated by Libby. Later on (1960ies) an improved value of the half-life came into use, the Cambridge half-life,  $(T_{1/2})_C=5730 \pm 40$  years. Even though the Libby half-life is not correct, it is still used to obtain radiocarbon age (which is further converted to calendar years: this process is called calibration). Moreover, neither the Cambridge half-life may be entirely correct (Chiu et al, 2007).

## **10. Recommendations**

- In your papers use a proper reference in for quantities, units and symbols, and make sure that the definition cannot be subjected to misinterpretations (in particular pMCΔ <sup>14</sup>C and fraction modern)
- For post-bomb samples use F<sup>14</sup>C with (Reimer et al, 2004) as reference.

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