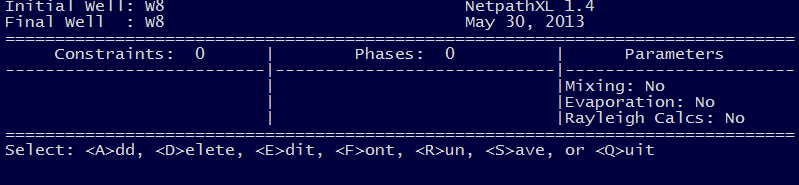
**Implementation of the Revised Fontes and Garnier radiocarbon adjustment model in NetpathXL**

An analysis of the radiocarbon adjustment model of Fontes and Garnier (1979) (F&G) shows an inadequate conceptualization in the formulation of the governing equations (Han and Plummer, 2013), resulting in underestimation of the initial 14C values (14Co) for groundwater systems that have undergone isotopic exchange. The degree to which 14Co is underestimated by the F&G model increases with the extent of isotopic exchange. A new model (Han and Plummer, 2013) revises the mass balance method of F&G by using a modified model conceptualization. The derivation yields a “global” model both for carbon isotopic exchange dominated by gaseous CO2 in the unsaturated zone, and for carbon isotopic exchange dominated by solid carbonate mineral in the saturated zone. The revised model requires different parameters for exchange dominated by gaseous CO2 as opposed to exchange dominated by solid carbonate minerals. The Revised F&G model has been implemented in NetpathXL (Parkhurst and Charlton, 2008); in turn, NetpathXL is based on NETPATH (Plummer and others, 1994). The revised model for exchange dominated by gaseous CO2 generates results similar to the model of Mook (Mook, 1976). In closed groundwater systems, the Revised F&G model produces results similar to that of Eichinger (1983). For groundwater systems where exchange occurs both in the unsaturated zone and saturated zone, the revised model can still be used; however, 14Co will be slightly underestimated (Han and Plummer, 2013). Finally, in carbonate systems undergoing complex geochemical reactions, such as oxidation of organic carbon, adjusted radiocarbon ages are best estimated by inverse geochemical modeling techniques.

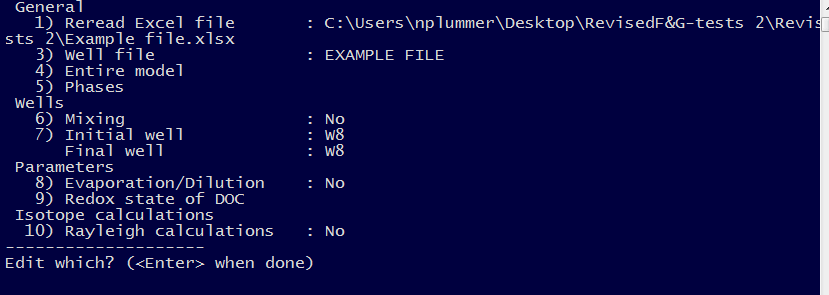
There are two ways to apply the Revised F&G model in NetpathXL: (a) radiocarbon dating of DIC in a single water sample, in which the initial and final water are defined as the same sample (“traditional” approach to radiocarbon dating without consideration of the geochemical mass balance reactions), and (b) radiocarbon dating of the final water when initial and final water samples are defined separately (in this case the Revised F&G model is applied to the initial water to estimate the pre-bomb 14C content in the initial water. In case (b), NetpathXL is then used to compute the carbon mass transfer to the final water sample and subsequently adjust the initial 14C content for geochemical reactions to estimate the 14C content of the final water (without radioactive decay).

Example

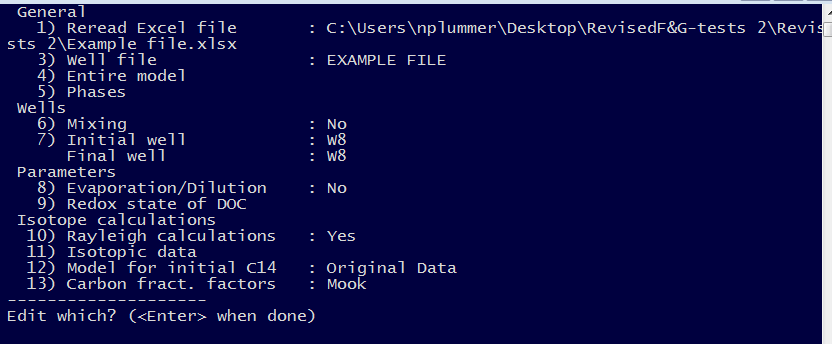
This example assumes the user has familiarity with radiocarbon dating of DIC in the NETPATH and NetpathXL environment. We begin by selecting initial and final water samples from the well file. In the example below, the initial and final waters are defined to be the same (case (a) above). There is no need to select phases or constraints in this case since the initial and final waters are the same. Having created a model (for either case (a) or case (b)) in NetpathXL, enter “e” to select <E>dit from the main screen



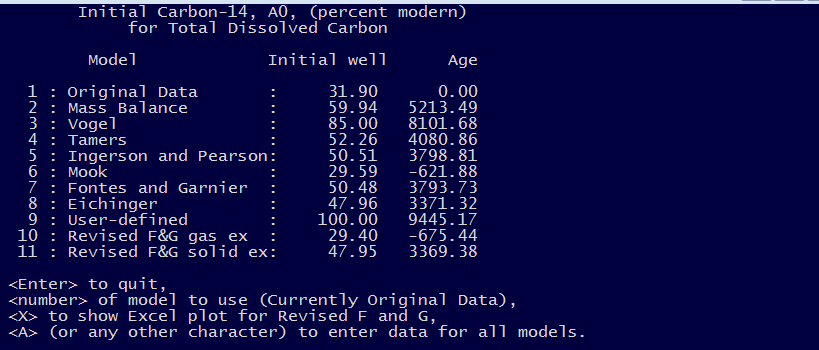
From the <E>dit menu, select option (10), “Rayleigh calculations”.



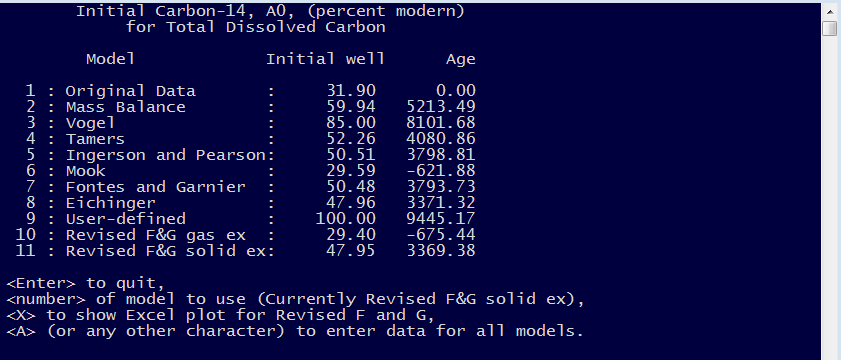
The prompt “Do Rayeligh calculations?” appears and answer “y”es. This expands the <E>dit menu to include options 11) Isotopic data, 12) Model for initial C14 (with “Original Data” as default, and 13) Carbon fractionation factors (default values from Mook). Select 12) “Model for initial C14”.



From the next screen, “Initial Carbon-14, A0, (percent modern) for Total Dissolved Carbon”, select either Model 10 or 11. If the sample to be dated is in the recharge zone, where open- (to CO2 gas) system conditions prevail, select Model 10 for CO2 gas dominated isotopic exchange. If the sample is from the saturated zone and isolated from the soil zone, select Model 11, for isotopic exchange with solid carbonate (calcite). Although NETPATH and NetpathXL treat the total dissolved carbon system, TDC, (TDC≡DIC+DOC+CH4), implementation of the Revised F&G model in NetpathXL treats only the inorganic carbon system, which is the most common application expected.



Here is the screen after selecting Model 11, “Revised F&G solid ex”



From this screen, one can type “X” which generates a Microsoft Excel spreadsheet that permits examination of all the samples from the originally selected well file (.xls or .xlsx). Typing the letter “A” permits editing all the isotopic values used in all the radiocarbon adjustment models programmed in NetpathXL.

Typing <X> to construct the Excel plot for the Revised F&G model

In the example above, for well W8, the Revised F&G model for CO2 gas dominated isotopic exchange leads to a negative age as does that of Mook. Model 11, for solid calcite isotopic exchange leads to a positive radiocarbon age. As the sample is from a well in the saturated zone, an initial guess would be to select Model 11, “Revised F&G solid exchange”. The following Excel spreadsheet is generated by NetpathXL. All samples from the selected well file are plotted as 14C (pmc) on the ordinate and δ13C (permil) on the abscissa. The larger red triangle represents the selected sample to be dated (W8). The rest of the samples from the well file are plotted as smaller green squares.

Features of the spreadsheet

1. Once generated, the spreadsheet stands alone, can be saved and used in future calculations, and is closed only manually, external to NetpathXL.
2. The table in the lower left part of the spreadsheet contains the δ13C and 14C data for all the samples in the well file [obtained from the NetpathXL Excel file (.xls or .xlsx) that is generated by using DBXL, see Parkhurst and Charlton, 2008], along with their inorganic carbon speciation computed from the WATEQ aqueous model of NetpathXL.
3. The example shows results for well W8 (data in the blue-shaded cells in line 3). To change to another sample, copy and paste a line from the sample table in the lower left part of the spreadsheet to the blue-shaded columns of line 3. However, changes made in the Revised F&G spreadsheet have no effect on the NetpathXL model definitions. However, changes made in the Revised F&G spreadsheet have no effect on the NetpathXL model definitions.
4. Column 10, line 3 is a switch used to define fractionation factors for CO2(g) and calcite as, “1” relative to the isotopic composition of HCO3-, and “0” relative to the average isotopic composition of the DIC in the sample, the latter accounting for sample pH and distribution of species.  In most cases the results will be similar, because HCO3- usually is the predominant inorganic carbon species in groundwater.  Switching to option “0” might be more appropriate for samples from systems with high or low pH where CO3-2 or CO2(aq) are relatively more important; for example, in a closed-system quartz-sand aquifer that contains minor calcite where the pH is still low, such that CO2(aq) predominates.  Here calcite-solution might be more appropriate than calcite-HCO3-. (See Wigley et al., 1978).
5. Cells L7-M9 contain user-defined values of δ13C (permil) and 14C pmc for the carbonate solid (usually calcite), the unsaturated zone CO2 gas, and an estimate of the combined uncertainty in the unsaturated zone gas isotopic composition and the solid carbonate minerals isotopic composition.
6. The yellow shaded fields of the spreadsheet are calculated within the spreadsheet. Fractionation factors are calculated at the sample temperature. Concentrations are in mmol per kg of water.



Features of the plot

1. Tamers Point is the approximate isotopic composition of a sample that has reached calcite saturation in a closed system. It is located at the crossing of Tamers lines X and Y. In the spreadsheet, Tamers Point is computed in cells Q5 and R5 from defined values of δ13C and pmc of calcite and soil gas CO2 (cells L7-M8). Tamers X and Tamers Y lines are vertical and horizontal extentions of the Tamers point.
2. Considering uncertainty in δ13C and 14C, Tamers area is the approximate region in δ13C - 14C space where Tamer’s model applies, and is shown as the blue rectangle on the plot. Tamers area is computed around the Tamers point by using the assigned uncertainty in isotopic composition of soil gas CO2 and calcite (cells L9 and M9). Tamer’s area extends to 0 pmc for samples that have aged, but are not affected by extensive isotopic exchange with solid carbonate minerals.
3. Zero-age line for systems open to soil gas CO2 (Mook model). This line is drawn from Tamer’s point to the isotopic composition of HCO3- (or TDIC, if Frxn fact is 0) in equilibrium with soil gas CO2. Points plotting along the line represent increasing exposure of a sample at the Tamers point to soil gas CO2. Samples have zero age along this line representing a positive correction in 14C to Tamer’s point and are consistent with the Mook model. As the isotopic composition of soil gas CO2 often is not measured, some guesswork is involved in establishing this line, choosing, by trial and error, a value of the isotopic composition of soil gas CO2 (and calcite, L7-M8) that results in the calculated zero-age line passing through the trend in sample points (if such a trend exists). Many data sets may not have samples plotting along this zero-age line. Samples plotting below the zero-age line (gas ex) have radiocarbon age. The zero-age line (gas exchange) is computed in cells Q30, R30, Q31, and R31.
4. Two other reference points are plotted: (1) the defined (assumed) isotopic composition of soil gas CO2, and (2) the isotopic composition of CO2 (aq) in equilibrium with soil gas CO2.
5. The plot also shows the zero-age line for samples undergoing isotopic exchange (and/or water-rock reaction) in a closed system, according to the Revised F&G model (zero-age (solid ex) line). This is drawn from the Tamer’s point (cells Q5, R5) to the isotopic composition of calcite (user defined), (cells L8,M8). In the example, limestone reacting with sample W8 is assumed to be 3.0 permil in δ13C and 0 pmc. The Revised F&G model is that of Tamers, if there is no isotopic exchange. Otherwise, it can be shown to be identical to that of Eichinger’s model (Eichinger, 1983), and very similar to the Pearson model (Ingerson and Pearson, 1964). [Note: Several typographical corrections to previous publications that discuss the Eichinger model are reported in Plummer and Glynn (2013)]. Samples plotting along this solid-exchange line have zero radiocarbon age, even though their 14C content decreases with increasing values of δ13C. Samples plotting below the zero-age line (solid ex) have radiocarbon age.
6. For the selected sample, W8, Ao and the radiocarbon ages from Tamers, Revised F&G, Gas exchange, and Revised F&G, Solid exchange are computed in cells L12-M14. For another sample, copy the values in the lower left table into the blue cells, C3 – H3.
7. Changing values in any of the blue cells will cause the chart and all of the calculated values (yellow cells) to be updated.

Further explanation regarding the Han and Plummer plot

The zero-age line is represented by line A2-O-B in the Han and Plummer Plot (see following figure, green dashed line). This line can be calculated by the Revised F&G equation:

 (1)

(See Han and Plummer, 2013 for definition of terms, and Han and others, 2012 for examples using this diagram). The first term in Eqn. (1) is Tamers’ point (point O) (Tamers, 1967; Tamers, 1975; Tamers and Scharpenseel, 1970). Based on the δ13C value, the second term (correction term) either corrects 14C0 to higher values (Mook line (Mook, 1976)) or lower values (Pearson (Ingerson and Pearson, 1964) or Eichinger line (Eichinger, 1983)) compared with the Tamers’ value. This equation considers geochemical dilution effects, but not decay of 14C. Thus, by using each value of δ13C, ranging from ca. -17 per mil to ca. 0 per mil, one obtains line A2-O-B (“O” is Tamer’s Point, and “B” is at point 0,0) (of course other parameters have to be correctly guessed in order to calculate 14C0 using the equation). Because on the left side of Eqn. (1) we have 14C0, this line is the zero-age line (i.e. 14C0 line). It shows the 14C0 value after dilution without decay. The values can also plot above the 50 pmc line (see one of the green triangles).

The part of Pearson’s line that plots left to Tamers’ point (line A1-O) does not exist in most situations. The reason is: If carbonate minerals are not present, the DIC will plot at point A1 (The water contains only dissolved CO2, i.e. CO2(aq)). On the other hand, however, if carbonate minerals are present, the DIC isotopic composition will jump to Tamers’ point. A point on Pearson’s line left to Tamers’ point would mean that only part of the CO2(aq) has reacted with carbonate minerals (e.g. the DIC is a mixture of CO2(aq) with HCO3-). It is difficult to imagine that after perhaps hundreds of years, the reaction is still incomplete. The vertical red arrows on the diagram below are all 14C decay lines.

Mook’s model tells us that after CO2(aq) has reacted with carbonate (originally at Tamers’ point) the system was not closed immediately. Rather, the system has been open to soil CO2 for some time before becoming closed. The Mook line represents the water that is still open to soil CO2 (or has been closed but no measurable change in 14C). The longer the system remains open the closer is the point to A2 (depending on infiltration speed). Many waters become closed before reaching A2. Thus, a point below the Mook line above 50 pmc may be an aged sample (e.g. the green triangle with ca. 70 pmc). A point below the Mook line higher than 50 pmc may be an aged sample. For example the 14C in both of the two samples represented by green triangles in the diagram below have decayed after becoming closed (see the red decay lines below Mook’s line). Sample points plotting above the Mook line may contain fractions of bomb-14C CO2, or have reacted with calcite enriched in 13C more than that of defined in cell C5.

All points along the green dashed line (see figure below) have zero age. Their 14C values represent the initial values, calculated from Eqn. (1) for the Revised F&G model (14C0=*f*(δ13C)). As seen from the green triangles in the figure, the ages interpreted by using Mook’s model are older than those from Eichinger’s and Pearson’s (left part) model. Because samples rarely plot along Eichinger’s or Peason’s line left of Tamers’ point, it is preferable to use Mook’s line for all data plotting left of Tamers’ point, ignoring the Eichinger’s and Pearson’s line. In the Tamers’ rectangle (the blue rectangle), all decay lines (red arrows) start from 50 pmc instead of starting from the green dashed zero-age line, considering the uncertainty in δ13C.



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