

NETPATH-WIN: An Interactive User Version of the Mass-Balance Model, NETPATH

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Abstract

NETPATH-WIN is an interactive user version of NETPATH, an inverse geochemical modeling code used to find mass-balance reaction models that are consistent with the observed chemical and isotopic composition of waters from aquatic systems. NETPATH-WIN was constructed to migrate NETPATH applications into the Microsoft WINDOWS[®] environment. The new version facilitates model utilization by eliminating difficulties in data preparation and results analysis of the DOS version of NETPATH, while preserving all of the capabilities of the original version. Through example applications, the note describes some of the features of NETPATH-WIN as applied to adjustment of radiocarbon data for geochemical reactions in groundwater systems.

Introduction

The computer program NETPATH (Plummer et al. 1994) is frequently used to construct quantitative models of the chemical evolution of waters along real or hypothetical flow paths in aquifers or other hydrologic systems using hydrochemical data. These models provide important information on geochemical processes and water-rock reactions that can be used to place constraints on numerical models of groundwater flow (Sanford et al. 2004).

NETPATH uses inverse geochemical modeling techniques (Plummer et al. 1983; Plummer 1985; Parkhurst and Plummer 1993; Glynn and Brown 1996; Nordstrom 2007) and equations of chemical mass balance, electron balance, and isotope mass balance to quantify all possible net geochemical reactions between the analyzed initial

and final water compositions along evolutionary paths in aquifers. The geochemical reactions are constrained to be consistent with the observed mineralogy, chemical, and isotopic data of the aquifer and groundwater system.

NETPATH has been used to investigate geochemical and isotopic reactions in a large number of hydrologic systems for more than 20 years (Plummer et al. 1990; Aravena et al. 1995; O'Brien et al. 1997; Malcolm and Soulsby 2001; Plummer and Sprinkle 2001; Cronin et al. 2005; Toth and Katz 2006; Lu et al. 2008; Noseck et al. 2009). The modeling concepts in NETPATH can be traced to geochemical mass-balance calculations originally demonstrated by Garrels and MacKenzie (1967), and have evolved through a series of theoretical and software contributions (Parkhurst et al. 1982; Plummer et al. 1983; Plummer et al. 1994; Parkhurst 1997; Glynn and Plummer 2005).

One of the most important applications of NETPATH is in radiocarbon dating in groundwater systems. Two approaches to radiocarbon dating in groundwater systems are considered in NETPATH: (1) application of traditional adjustment models (Fontes 1990; Kalin 1999), such as those of Tamers (1975), Ingerson and Pearson (1964), Mook (1972), Fontes and Garnier (1979), and Eichinger (1983) to a single water analysis (Figure 1); this approach is, for the most part, limited to some of the more important carbonate reactions that occur in groundwater systems

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Received April 2010, accepted October 2010.

Journal compilation © 2010 National Ground Water Association.

No claim to original US government works.

doi: 10.1111/j.1745-6584.2010.00779.x

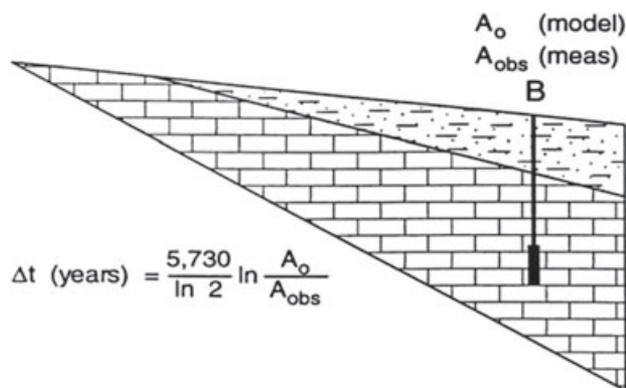


Figure 1. Conceptualization of application of “traditional” adjustment models in radiocarbon dating. The model, such as that of Tamers, Fontes and Garnier, Ingerson and Pearson, Eichinger, and others, is applied to a single water analysis in the system.

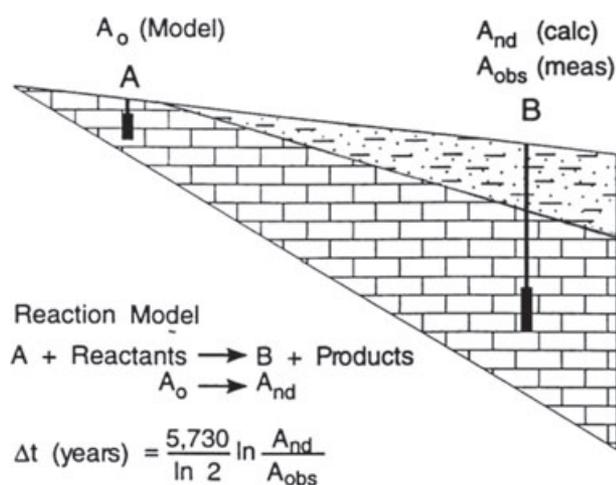


Figure 2. Conceptualization of the generalized approach to radiocarbon dating of DIC (or TDC) in NETPATH. Two evolutionary waters are selected: the initial, A, and final, B. A and B typically are on a flow path, but are only required to be representative of evolutionary pairs. A_o is modeled, measured, or estimated in water from the initial well. NETPATH constructs geochemical adjustment models to estimate the ^{14}C activity of TDC in water from well B, without radioactive decay, A_{nd} . The piston-flow travel time between A and B is calculated from the decay equation.

and (2) a generalized quantitative approach to radiocarbon dating that adjusts the ^{14}C content in the initial water for all the predominant water-rock reactions, redox reactions, mixing processes, and isotope exchange processes, thus developing a radiocarbon adjustment model tailored to an individual reaction path in the aquifer (Figure 2). In either case, the radiocarbon dating analysis of NETPATH utilizes data on total dissolved carbon (TDC) (dissolved inorganic carbon, DIC; dissolved organic carbon, DOC; and dissolved methane, CH_4). Previous traditional approaches to radiocarbon dating, as in Figure 1, only accounted for inorganic carbon and a somewhat limited number of reaction possibilities. NETPATH is unique among geochemical modeling codes in its handling of radiocarbon

dating, utilizing TDC, inverse geochemical modeling, and Rayleigh distillation equations (Wigley et al. 1978) to model isotope fractionation processes.

The use of NETPATH involves an iterative approach that can require multiple calculations with varying initial conditions and constraints. The inverse-modeling process is nonunique, but often can eliminate some reaction and mixing possibilities. Originally, NETPATH and an associated database program, DB, were written in FORTRAN 77 for operation in a DOS environment.

PHREEQC (Parkhurst 1995, 1997; Parkhurst and Appelo 1999) is another widely used geochemical modeling code that has inverse-modeling capability. Some of the advantages of PHREEQC in inverse geochemical modeling applications over that of NETPATH (and NETPATH-WIN) are: (1) treatment of uncertainty in chemical data and (2) calculation of what are called “minimal models”, that is, geochemical mass-balance reaction models that include only the reactants and products that, within the uncertainty in the chemical and isotopic data, must be included to account for the observed chemical and isotopic data.

The most important capability that distinguishes NETPATH (and NETPATH-WIN) from PHREEQC is in the treatment of radiocarbon dating of dissolved carbon in groundwater samples. Capabilities of NETPATH (and NETPATH-WIN) that are not currently available in PHREEQC include (1) application of well-known radiocarbon adjustment models to water samples and (2) solving the Wigley et al. (1978) isotope evolution equations, automatically calculating the relevant isotopic compositions of exsolving or precipitating phases, and allowing the calculation of ^{14}C geochemical dilution and isotope fractionation adjustments in radiocarbon dating of dissolved carbon.

Recently the data-handling functions of NETPATH were replaced with a new version, NetpathXL that uses Microsoft Excel[®] (Parkhurst and Charlton 2008) for data entry. Similar spreadsheet capabilities are available in NETPATH-WIN. Because of the spreadsheet data entry capabilities of NetpathXL and NETPATH-WIN, it is now possible to run the exact PHREEQC model in NetpathXL and NETPATH-WIN to explore isotope compositions and ages. NetpathXL is otherwise identical to NETPATH, and runs in a DOS environment. Although NetpathXL has made it easier to use NETPATH in today’s computing environment, the lack of a graphical user interface has limited the use of this software in general. NETPATH-WIN has therefore been constructed to overcome this difficulty by migrating NETPATH and NetpathXL applications into the Microsoft WINDOWS[®] environment.

Features of NETPATH-WIN and DB-WIN

The purpose of the graphical user interface for NETPATH is to facilitate data entry and interactive use of the code for testing and accepting various model results. Detailed model-use procedures, description of input variables and terms, and test cases are documented in the

original NETPATH report (Plummer et al. 1994), which is included in the NETPATH-WIN package. Two complete data sets are included with the NETPATH-WIN distribution package: (1) test cases associated with the original NETPATH (Plummer et al. 1994) and (2) geochemical models with radiocarbon dating from a study by Plummer and Sprinkle (2001). The user should be familiar with the model, its limitations and assumptions, and data requirements.

DB-WIN

DB-WIN is an interface for the database program DB (Plummer et al. 1994) that allows entering and editing of chemical and isotopic data for a set of water analyses. DB-WIN permits entry, storage, and editing of up to 50 analyses of water samples for a single file (*file.lon*), calculates mineral saturation indices, and creates the input file (*file.pat*) to be used for constructing reaction models in NETPATH-WIN. All of the features of the original DB program (Plummer et al. 1994) are retained in DB-WIN. New in DB-WIN is the ability to import and/or export data to/from Microsoft Excel[®] spreadsheets using the CSV format. Previously constructed data sets from earlier DOS applications can be read by DB-WIN, and if desired, exported to Microsoft Excel[®] spreadsheets. DB-WIN documentation can be accessed through an interactive Instruction tab from the main screen of DB-WIN.

NETPATH-WIN

NETPATH-WIN includes the interface for NETPATH (Plummer et al. 1994), which, given a set of chemical and isotopic constraints, and a set of possible reactant and product minerals and gases, finds all the geochemical mass-balance models that are consistent with the analyzed initial and final water compositions along evolutionary paths in aquifers. All of the original features of NETPATH are retained in NETPATH-WIN. Documentation is provided through an Instruction tab from the main screen of NETPATH-WIN. Some of the modeling features of NETPATH include: (1) possible mixing of up to five initial waters with or without further geochemical reaction, (2) inclusion of oxidation-reduction reactions, (3) treatment of the TDC system (DIC-DOC-CH₄), and (4) isotopic evolution (N₂, S, Sr, and C) including radiocarbon dating.

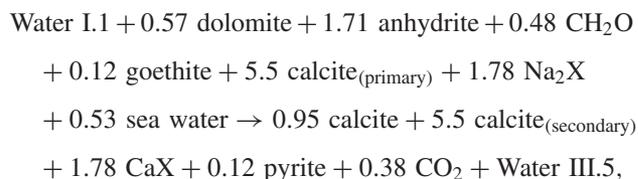
Example Using DB-WIN and NETPATH-WIN

As an example, we compare (1) the unadjusted radiocarbon age, (2) radiocarbon ages calculated from selected traditional radiocarbon adjustment models (as in Figure 1), and (3) radiocarbon age adjusted from a more complete evaluation of the geochemical reactions (as in Figure 2) from a part of the Floridan aquifer of Florida, USA, as originally investigated by Plummer and Sprinkle (2001). In this brief example, radiocarbon dating is applied to water from well III.5 (well 5 on flow path III, Figure 3). All of the data for this example are

available in the distribution files of NETPATH-WIN and in Plummer and Sprinkle (2001). Details on using DB-WIN and NETPATH-WIN in this example are in the Supporting Information.

From the measured ¹⁴C of DIC, 0.23 pmc, and correcting for a small amount of DOC with an assumed ¹⁴C of 0 pmc, the unadjusted radiocarbon age of TDC in water from well 3.5 is 50,600 years. Applying a series of traditional adjustment models (as in Figure 1), we find from Tamers (1975), 44,600 years; Ingerson and Pearson (1964), 36,800 years; Mook (1972), 49,100 years; Eichinger (1983), 28,800 years; and Fontes and Garnier (1979), 34,800 years.

Considering the overall geochemical evolution of recharge water (well I.1, Figure 3) to water of well III.5, the net mass-balance reaction, as in Figure 2, is:



where the reaction coefficients are in mmols per kg of water. The part of the overall reaction pertaining to calcite recrystallization, 5.5 mmol/kg calcite_(primary) → 5.5 mmol/kg calcite_(secondary), represents recrystallization of an estimated mass of 5.5 mmols of calcite (of marine origin, δ¹³C_{calcite} ≡ 2 per mil) per kg water to form 5.5 mmols of secondary calcite (accounting for isotopic fractionation in calcite precipitation) in fresh water, an amount of recrystallization needed for the calculated δ¹³C of DIC to match the observed. The adjusted radiocarbon age of TDC at well III.5 is 22,800 years, as in Plummer and Sprinkle (2001).

By correcting for a rather complete set of geochemical reactions affecting the chemical and isotopic evolution of water III.5, the adjusted age (22,800 years) is considerably younger than the unadjusted age, and those adjusted radiocarbon ages calculated utilizing the traditional adjustment models.

The unadjusted radiocarbon age has been shown applicable in some siliciclastic aquifers (Plummer et al. 2004) where there are few carbonate reactions that can affect the initial ¹⁴C content. Selected traditional adjustment models are best suited for geochemical systems undergoing relatively simple water-rock reactions, such as usually occur in shallow recharge areas of carbonate aquifers, but, depending on choice of model, can be applied to radiocarbon dating of DIC in groundwater systems undergoing carbonate-mineral dissolution, gypsum dissolution, Ca/Na ion exchange, CO₂ gas dissolution, and isotope exchange between soil CO₂, calcite, and DIC during recharge. In general, many more geochemical reactions can occur in groundwater systems that are often overlooked. Some of the more important reactions that are not accounted for in traditional adjustment models include degradation of organic matter accompanying

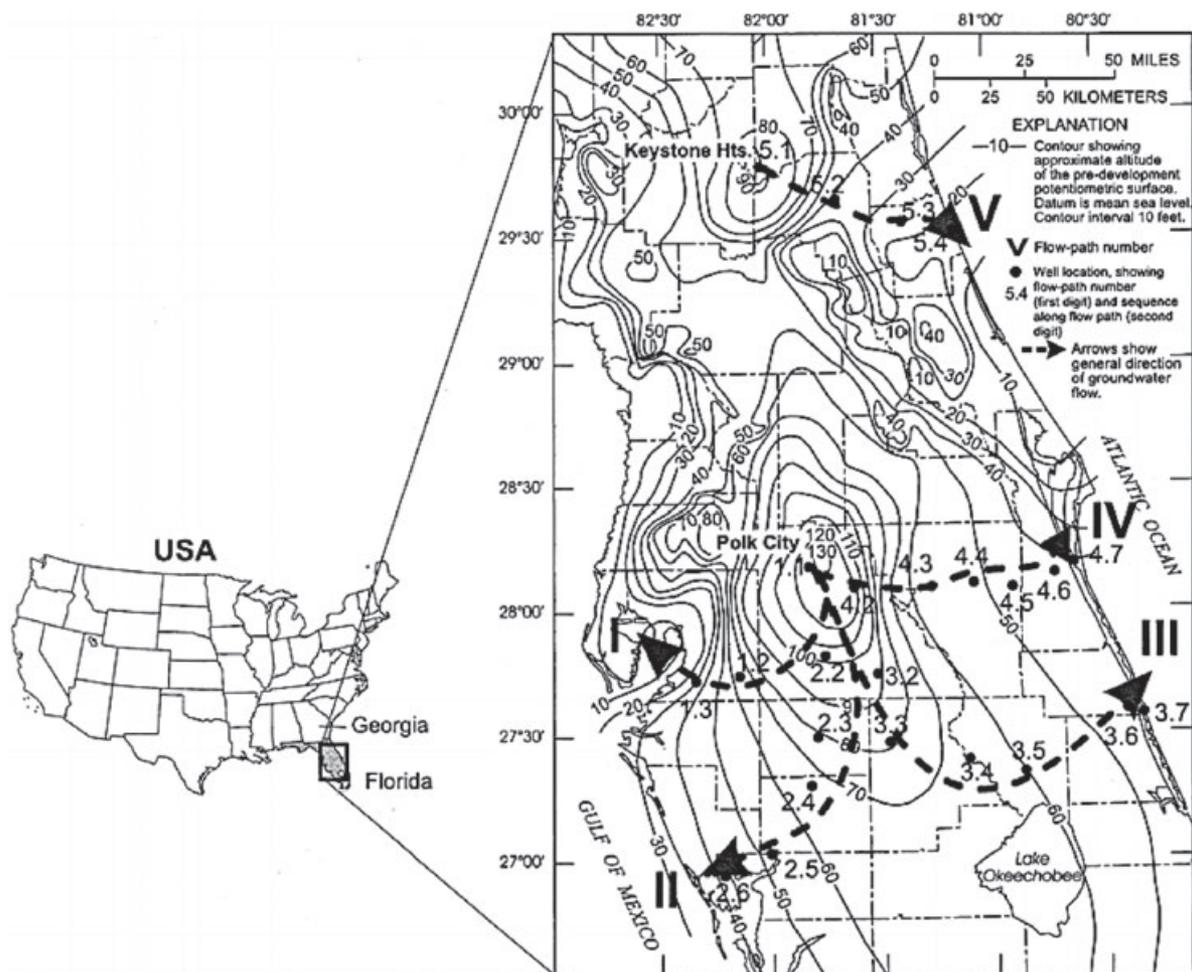


Figure 3. Location of wells sampled and flow paths I to V in relation to altitude of the predevelopment potentiometric surface of the Upper Floridan aquifer. Contours in feet (1 foot = 0.3048 m; Plummer and Sprinkle 2001).

various redox reactions, such as in iron reduction, sulfate reduction, methanogenesis, degradation of DOC, isotopic fractionation in precipitation of carbonate phases, and recrystallization of carbonate minerals. Adjusted radiocarbon ages will likely be overestimated if calculated from traditional adjustment models in systems undergoing more complex geochemical reactions. More complete geochemical calculations can be made using the DOS version of NETPATH (Plummer et al. 1994), the adaptation to the DOS version, NetpathXL, that uses Microsoft Excel® (Parkhurst and Charlton 2008), or using the code described here, NETPATH-WIN, that has been constructed to migrate NETPATH and NetpathXL applications into the Microsoft WINDOWS® environment.

Software Availability

NETPATH-WIN is maintained by the Isotope Hydrology Section of the International Atomic Energy Agency and can be downloaded free of charge from URL <http://www-naweb.iaea.org/napc/ih/index.html>, or from the U.S. Geological Survey at http://www.brr.cr.usgs.gov/projects/GWC_coupled/netpath/.

Summary

NETPATH employs hydrochemical data in constructing quantitative models of chemical evolution of waters along real or hypothetical flow paths in hydrologic systems. These models provide important constraints on numerical groundwater flow models. However, the program use, in its DOS version, is hampered by difficulties in setting up data needed for simulations. This note documents NETPATH-WIN, a Microsoft WINDOWS® version, that simplifies data preparation and results analysis, while preserving all of the capabilities of the original DOS version. The note includes examples illustrating features of NETPATH-WIN as applied to adjustment of radiocarbon data for geochemical reactions in groundwater systems. It is recommended that a future update of NETPATH-WIN include an option to export model results to a spreadsheet that would be beneficial particularly if many models are run for multiple chemical analyses.

Acknowledgments

We thank D.L. Parkhurst (USGS, Lakewood, CO), D.L. Nelms (USGS, Richmond, VA), Peter McMahon

(USGS, Lakewood, CO), and two anonymous reviewers for their constructive reviews of the manuscript. Kayo Fujiwara, a graduate student, University of Hawaii, contributed to programming. The software was programmed with Fortran 90 of Lahey Computer Systems, Inc., and Winteracter of Interactive Software Service Ltd. Any use of trade, product, or firm names in this article is for descriptive purposes only and does not imply endorsement by the U.S. government.

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Supplementary material detailing the example described above, including captured screens, is provided with the online version. The material also can be downloaded from the web sites listed above.

Figure S1. The opening screen of DB-WIN showing various options. Steps start by selecting “Open LON file...” followed by other selections including manipulating the well data, running the thermodynamic speciation code, WATEQF, and examining the WATEQF results. A specific well to edit is chosen from the pull-down menu, which is well 3.5 in this screen.

Figure S2. Example showing the Edit well screen from DB-WIN. The pull-down menus allow editing of specific information pertaining to the well (location, aquifer, date/time sampled, well depth, amount of casing, and land-surface elevation), concentration data for the sample, and Flags that set units of concentration, activity coefficient option used in WATEQF, concentration unit of inorganic carbon, and choice of redox option.

Figure S3. Prior to speciating the LON data set in WATEQF, an option is available to adjust the chemical analyses for charge imbalance, in proportion to their equivalents in the analysis. Selecting “Yes” will alter all the analytical data in creating the PAT file (the original LON file is unaltered). This can be a useful option for testing existing NETPATH-WIN models for uncertainties in analytical data, but is not recommended for initial model construction.

Figure S4. More advanced users may construct their own thermodynamic data files for WATEQF. Here the option is given to select an alternate thermodynamic data file, or to select “Open” to use the data file provided with the distribution package for NETPATH-WIN. The existing thermodynamic data are consistent with the original NETPATH (Plummer et al. 1994).

Figure S5. The water analyses in the FLORIDA.LON file were speciated and the NETPATH-WIN data file, FLORIDA.PAT, was created. DB-WIN then returns to the main screen (Figure S1).

Figure S6. Display of the analytical data in the LON file for the selected well in the main screen of DB-WIN. Close the window to exit this display.

Figure S7. The opening screen of NETPATH-WIN showing various options. Steps start by opening an

existing PAT file (FLORIDA.pat, in this example), followed by opening a selected DAT file (a model file) from the pull-down menu (which can be edited and saved). New models (DAT files) can be created using tabs under the Edit option, and saved using the tabs “Save DAT file” or “Save DAT file as.” Existing DAT files can be deleted using the “Delete selected file” tab. Various actions under the “Edit” heading include the “Well list” (permits selection of wells to be included in the model), “Phases” (selection of phases to consider in the model), “Constraints” (selection of chemical and isotopic constraints in the model), and “Model data” (definition of specific parameters applicable to the model). Options also include examining “Data summary,” “Warnings” (includes identifying missing data), and running NETPATH, “Run NETPATH.”

Figure S8. From the “Well list” tab, the model file (FL well 3.5.dat) for well 3.5 includes two initial waters, water from well 1.1 and a Sea Water analysis (upper panel displaying wells used in the model). The lower panel contains a list that permits changing the wells in the model. The wells in the model are updated by clicking the “Use selected wells” tab. Finally click the “OK” button to return to the main menu of NETPATH-WIN.

Figure S9. The “Phases” menu for the selected model (FL well 3.5.dat). The upper panel allows phases to be removed from the model and the lower panels allows addition of phases to the model (by marking the open boxes on the left of each panel and then clicking the “Remove selected phase” or “Add selected phase” tab). In the upper panel, a phase included in the model can be marked to be included in every model. In cases where multiple models are found in NETPATH-WIN, this option forces NETPATH to display only models that contain the phase or phases selected with a mark in the box “Phase in every model?”. By clicking on the cell for “Transfer (choose from drop-down menu),” a phase can be marked for “dissolution only,” “precipitation only,” “both” (permitting NETPATH to display models in which the phase either dissolves or precipitates), and “isotopic exchange,” where the amount of the phases to be exchanged, in mmols/kg water, is entered in the last column to the right of the upper panel. The case of isotopic exchange in NETPATH includes the option “both” (permitting net dissolution or net precipitation) plus isotopic exchange of the prescribed mass of the phase. Additional phases in the model can be displayed using the list, which includes 74 phases in its default database (only the first 8 are shown here). The list can be edited by running the Phase Editor program in the NETPATH-WIN distribution package.

Figure S10. Example showing the “Constraints” menu which was accessed from the main menu of NETPATH-WIN. The upper panel shows the list of constraints selected in the model (use the side arrows to display all the constraints in the model). The lower panel permits adding or removing constraints in the model. The “Use selected constraints” button updates the list of constraints in the model. Click “OK” to return to the main menu of NETPATH-WIN.

Figure S11. Display of the “Model parameters” window that branches to many chemical and isotopic details of the phases and models.

Figure S12. Example of the “Geochemical parameters” menu. In this example, the model includes two initial waters that are allowed to mix, evaporation or dilution is not permitted, simple Ca/Na cation exchange is allowed (i.e., options involving Ca-Mg/Na exchange are not considered), the model will use the original ^{14}C data as defined in the LON file, and no data for the fraction of CO_2 in a $\text{CO}_2\text{-CH}_4$ gas mixture is permitted because the phase was not included in the model and the fraction of Ca in Ca/Mg exchange is not allowed because the “Variable CaMg” option was not selected under the “Ion Exchange” panel.

Figure S13. Example of the “Isotopic data” menu accessed from the “Geochemical parameters” window (Figure S11). In this example, the upper panel allows definition of the $\delta^{13}\text{C}$, ^{14}C , ^{34}S , ^{87}Sr , and ^{15}N isotopic composition of all carbon-, sulfur-, strontium-, and nitrogen-bearing phases in the model. The middle panel displays calculated default values of the additive fractionation factors (relative to the isotopic composition in solution) which can be redefined in this panel, and the lower panel is used to define the $\delta^{13}\text{C}$ and ^{14}C composition of dissolved organic carbon and dissolved methane in the water analyses.

Figure S14. Example of the “Data for C-14 Ao models” window accessed from the “Geochemical parameters” window (Figure S11). This window permits selection of a radiocarbon adjustment model that is to be applied to the initial water composition to estimate Ao. The pull-down tab displays seven models (options) for defining Ao. Depending on selection of the Ao model, NETPATH-WIN permits definition of other values needed in the model calculations. Using the default values shown, NETPATH-WIN calculates estimates of Ao based on these models.

Figure S15. Pull-down menus that display water samples, constraints, phases, and chemical composition data to be used in the NETPATH-WIN model calculations. The vertical and horizontal arrows permit viewing of all the values.

Figure S16. The Results page from NETPATH-WIN. The upper panel shows the calculated phase transfers for each phase in the model (negative for precipitation, positive for dissolution). The mixing fractions of initial solutions 1 and 2 (well 1.1 and sea water, respectively) are 0.9947 and 0.0053. The lower panel gives computed and observed isotopic data. The modeled radiocarbon age is shown below the lower panel, 22,779 years in this case.

Figure S17. Calculated Rayleigh distillation paths of the isotopic composition of precipitating phases along the flow path.

Figure S18. Display of the adjusted radiocarbon ages of total dissolved carbon at well 3.5 based on application of a range of Ao models to the initial water. In our case, the original data were used to define Ao

corresponding to an adjusted radiocarbon model age of 22,779 years.

Figure S19. From the “Well list” menu under the Edit heading of NETPATH-WIN, the FL well 3.5 DAT file is modified choosing well 3.5 as both the initial and final well and removing seawater as an additional initial water. Other options are described in Figure S8.

Figure S20. Screen showing the “Phases” menu in which calcite was changed to dissolution (only), removing the option of isotopic exchange with calcite. Other features of the “Phases” menu are described in Figure S9.

Figure S21. This screen permits selection of the Ao model to be applied to the initial water, and allows editing of all data used in all the Ao models. Cells that can be edited have white background (active), depending on selected model and/or options. Two optional sets of carbon-isotope fractionation factors are available. It is possible to define an alternative value of the $\delta^{13}\text{C}$ of DIC in the initial water, possibly accounting for paleoclimatic variations in C_3/C_4 plant abundance. Four options are provided for defining the $\delta^{13}\text{C}$ of soil-gas CO_2 .

Figure S22. The first screen that appears after selecting “Run NETPATH” displays the wells in the model. The initial and final wells are identical in the case of application of traditional adjustment models in radiocarbon dating, as in this example. The screen also previews the constraints and compositions of solutions and phases in the model. As the initial and final solutions are defined identically, the calculated mass transfer will be zero.

Figure S23. The “Results” window of NETPATH-WIN showing zero mass transfer of phases in this example applying traditional adjustment models and identical computed and observed isotopic values.

Figure S24. The “Results” screen showing all radiocarbon ages of total dissolved carbon in FL well 3.5 as calculated from all the traditional adjustment models in NETPATH (and NETPATH-WIN).

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