NetpathXL—An Excel® Interface to the Program NETPATH

By David L. Parkhurst and Scott R. Charlton

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Abstract

NetpathXL is a revised version of NETPATH that runs under Windows® operating systems. NETPATH (Plummer and others, 1991, 1994) is a computer program that uses inverse geochemical modeling techniques to calculate net geochemical reactions that can account for changes in water composition between initial and final evolutionary waters in hydrologic systems. The inverse models also can account for the isotopic composition of waters and can be used to estimate radiocarbon ages of dissolved carbon in ground water. NETPATH relies on an auxiliary program, DB, to enter the chemical analyses and to perform speciation calculations that define total concentrations of elements, charge balance, and redox state of aqueous solutions that are then used in inverse modeling. NetpathXL relies on Microsoft Excel® to enter the chemical analyses (instead of DB). The speciation calculation formerly included in DB is implemented within the program NetpathXL. A program DBXL can be used to translate files from the old DB format (*.lon* files) to NetpathXL spreadsheets, or to create new NetpathXL spreadsheets. Once users have a NetpathXL spreadsheet with the proper format, DBXL is not needed; new spreadsheets can be generated by copying or saving NetpathXL spreadsheets. NetpathXL can open NetpathXL spreadsheets, NETPATH-format path files (*.pat* files), and NetpathXL-format path files (*.pat* files). Once the speciation calculations have been performed on a spreadsheet file

or a *.pat* file has been opened, NetpathXL performs almost identically to the original NETPATH. Development of models and viewing results in NetpathXL rely on keyboard entry as in NETPATH.

Introduction

NETPATH (Plummer and others, 1991, 1994) is an interactive Fortran 77 computer program used to interpret net geochemical mass-balance reactions between initial (or multiple initial waters that mix) and final waters along real or hypothetical flow paths in aquifers or other hydrologic systems. The program uses inverse geochemical modeling techniques (Plummer and others, 1983; Plummer 1985; Parkhurst and Plummer, 1993; Glynn and Brown, 1996; Nordstrom, 2007) to construct geochemical reaction models by using chemical and isotopic data for waters from the hydrochemical system. The inverse model is a set of mixing fractions and mole transfers that exactly account for the changes in concentration of elements in the waters. Inverse models between selected evolutionary waters are found for every possible combination of the plausible phases that can account for the composition of a selected set of chemical and isotopic constraints in the system. The processes of dissolution, precipitation, ion exchange, oxidation/reduction, degradation of organic compounds, incongruent reaction, gas exchange, mixing, evaporation, and dilution are included. It also is possible to account for changes in isotopic compositions of five elements: hydrogen and oxygen isotopic evolution is accounted for by mixing of waters (no fractionation or mineral mass transfer); carbon, sulfur, nitrogen, and strontium isotopic evolution is accounted for by mixing, mineral mass transfer, isotopic fractionation, and isotopic exchange. Finally, the inverse models can be used to adjust radiocarbon data for geochemical reaction effects and refine estimates of radiocarbon age. The NETPATH software includes a data-base program, DB, for storing and editing chemical and isotopic data for use in NETPATH.

NETPATH has been a used to investigate geochemical and isotopic reactions in a large number of hydrologic systems for more than 15 years (see for example-- Plummer and others, 1990; Aravena

and others, 1995; Plummer and Sprinkle, 2001). 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 (Plummer and Back, 1980; Plummer and others, 1983; Plummer, 1992; Glynn and Plummer, 2005; Parkhurst, 1997) and software contributions (Plummer and others, 1975; Parkhurst, 1982; Plummer and others, 1991, 1992, 1994).

More recently, inverse geochemical modeling has been incorporated into the geochemical model PHREEQC (Parkhurst and Appelo, 1999) and its graphical user interface PhreeqcI (Charlton and Parkhurst, 2002) and into a spreadsheet program, SpreadBal (Bowser and Jones, 2002a, 2002b). Advantages and limitations of the NETPATH and PhreeqcI inverse modeling capabilities are discussed in Glynn and Brown (1996) and Glynn and Plummer (2005). NETPATH, PHREEQC (and PhreeqcI), and SpreadBal are all capable of performing basic inverse modeling. The strengths of each program are as follows: NETPATH allows for isotope fractionation, radiocarbon dating, isotope mole balance, and redox processes. SpreadBal is especially designed for aluminosilicate and clay reactions, with special emphasis on the variable compositions of these minerals. PHREEQC considers uncertainties in analytical data for elements and isotopes and allows for redox processes and isotope mole balance (but not isotope fractionation or radiocarbon dating).

The data entry program for NETPATH—DB—requires editing data one piece at a time, whereas spreadsheets give simple and rapid access to all data. DB saves data in two formats: the *.lon* file contains the raw concentration data and the *.pat* file contains selected results from speciation calculations performed by DB (total concentrations of elements, redox state, and isotopic compositions). NETPATH reads the *.pat* file to obtain the data needed for inverse modeling.

Since the original publication of NETPATH, advances in computer technology permit replacement of the DB data-entry style with the universally familiar spreadsheet. NetpathXL is a revised

version of NETPATH that can read an Excel spreadsheet that contains the raw concentration data. The speciation calculation, formerly in the program DB, has been moved to the program NetpathXL. Each time NetpathXL reads a NetpathXL spreadsheet, speciation calculations are performed and a *.pat* file is written; however, the format of a *.pat* file written by NetpathXL differs from one written by DB. NetpathXL can read data from a *.pat* file created by either DB or NetpathXL.

The NetpathXL spreadsheet has a fixed set of columns and header rows (see appendix 2). The program DBXL generates a spreadsheet of the proper format, into which, raw concentration and isotopic data can be entered. DBXL also can translate a *.lon* file (written by NETPATH) to a NetpathXL spreadsheet. It is expected that DBXL will be used initially to translate *.lon* files or to generate a NetpathXL spreadsheet. After this initial use, DBXL will not be needed. Additional NetpathXL spreadsheets can be generated by copying old spreadsheets and clearing the concentration data. New chemical and isotopic data can be entered cell-by-cell or copied and pasted from other spreadsheets or files into NetpathXL spreadsheets.

Installing NetpathXL and DBXL

NetpathXL and DBXL use Microsoft Excel to store and retrieve data. Excel must be accessible on the computer on which NetpathXL and DBXL are installed.

Download the latest version from *http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/netpath*. The file will have the extension *.msi*, and can be installed using the Windows Installer, which is available in Windows XP and higher. As administrator, simply double click on the downloaded file. The programs will be installed in the *C:\Program Files* directory by default. It is possible to install as a non-administrator if a different directory is selected. Once installed, the programs can be run through the Start Menu at the bottom left corner of the screen.

The programs normally are installed in the directory *c:\Program Files\USGS\NetpathXL*. Within this directory are subdirectories: *bin*, which contains the executables for NetpathXL and DBXL; *database*, which contains the database for the speciation model, *db.dat*, and the database of mineral stoichiometries, *netpath.dat*; *doc*, which contains PDF versions of this report and the documentation for NETPATH (Plummer and others, 1994); and *examples*, which contains the data and model files for the examples described in the NETPATH documentation.

Using DBXL

DBXL can be executed from the Windows Start menu at the bottom left of your screen or by browsing for the executable file (*c:\Program Files\USGS\NetpathXL\bin\dbxl.exe*) and double clicking. The user may want to add a desktop icon by right clicking on the executable file (Send To->Desktop). When the program starts, a screen (fig. 1) appears that has four options: (1) create a spreadsheet from the data in a *.lon* file that has been written by DB, (2) open a NetpathXL spreadsheet (*.xls* suffix), (3) create an empty NetpathXL spreadsheet, or (4) exit DBXL. Options are selected by entering 1, 2, 3, or 4 from the keyboard followed by a return. Selecting options 1, 2, or 3 will start the standard Windows file browser to select the file to be read or to specify the name of the new NetpathXL spreadsheet (fig. 2). After a file has been selected, an Excel session will be started with the selected file and DBXL will close. Other functionality of DB, including “Check” charge balance, and “Print” data reports was not retained in DBXL.

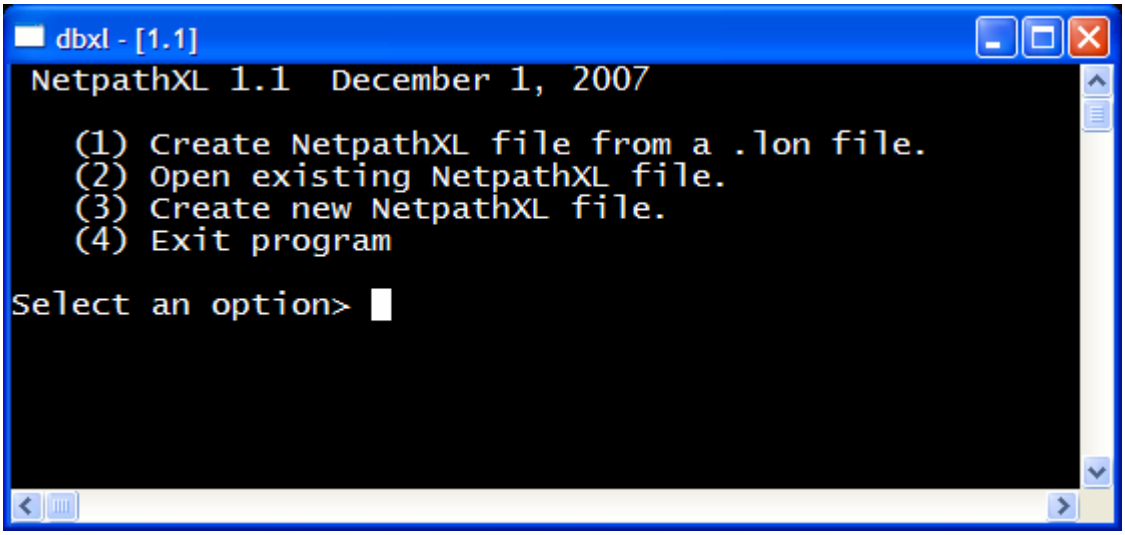

Figure 1. Options screen for DBXL.

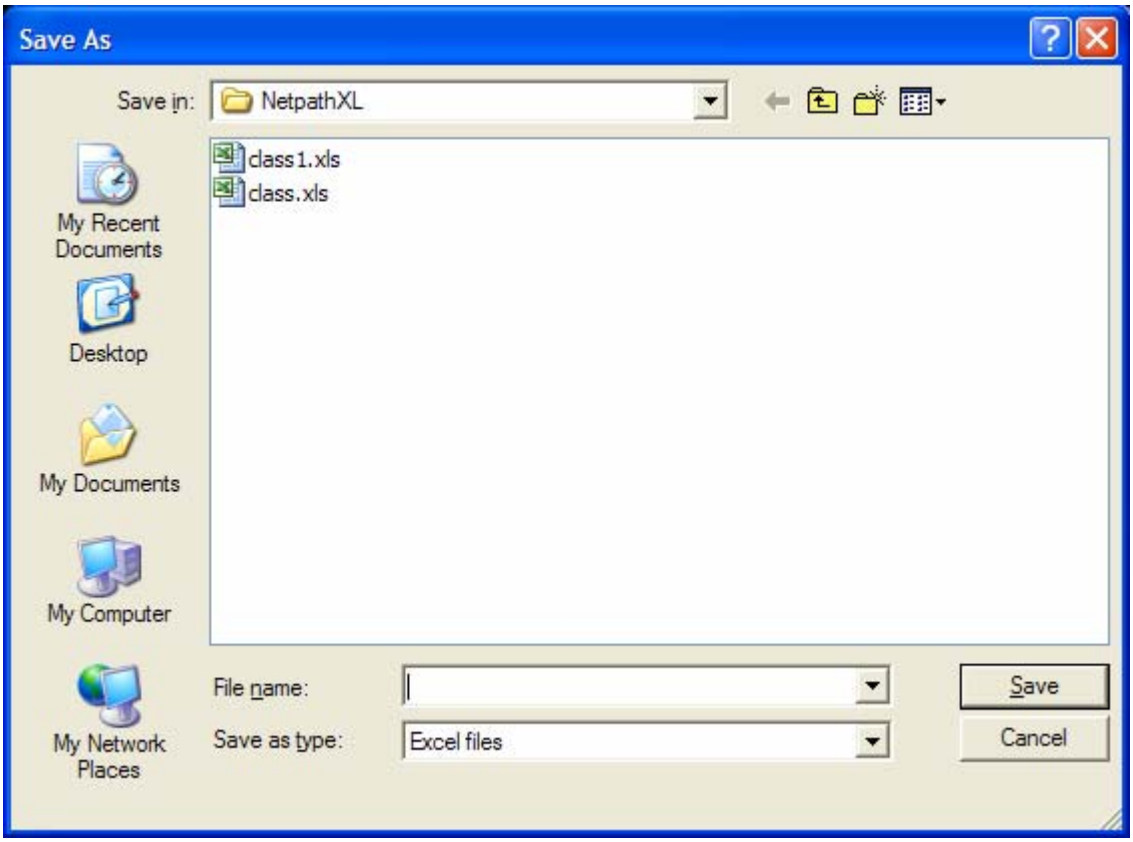

Figure 2. File browser using DBXL option 3.

Using NetpathXL

NetpathXL can be executed from the Windows Start menu at the bottom left of your screen or by browsing for the executable file (*c:\Program Files\USGS\NetpathXL\bin\netpathxl.exe*) and double clicking. The user may want to add a desktop icon by right clicking on the executable file (Send To->Desktop). When the program starts, a screen (fig. 3) appears that has three options: (1) open an existing NetpathXL spreadsheet (*.xls* suffix), (2) open a *.pat* file created by DB or NetpathXL, or (3) exit NetpathXL. Options are selected by entering 1, 2, or 3 from the keyboard followed by a return. Once option 1 or 2 is selected, the standard Windows file browser is used to select a file. After a file has been selected, execution will be the same as the program NETPATH; all options and data entry are by keystrokes and the mouse is not functional except to give focus to the NetpathXL window. The working directory will be the directory that contains the selected file.

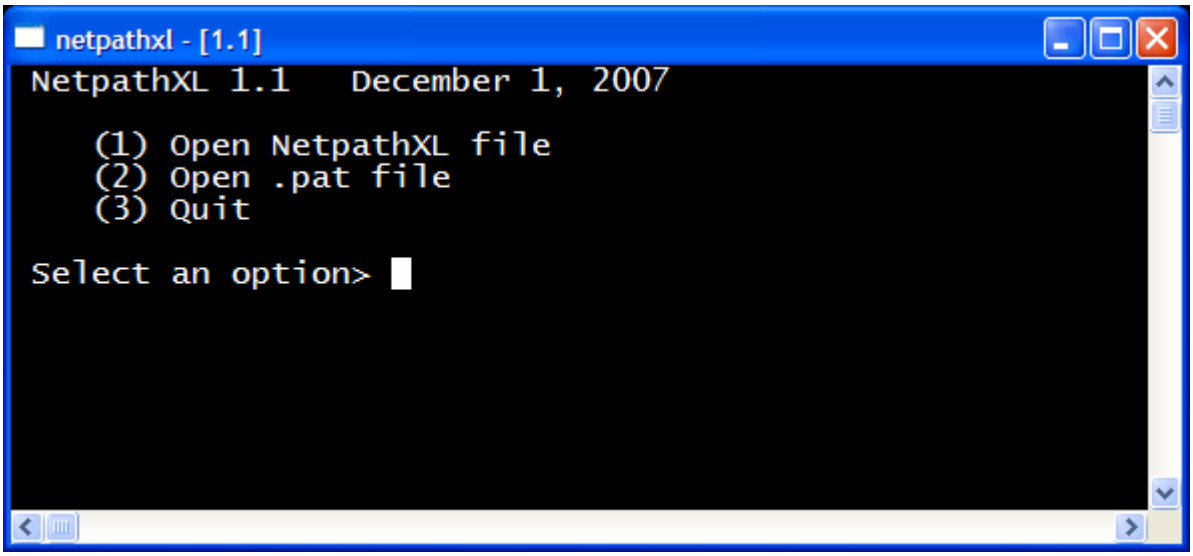

Figure 3. Options screen for NetpathXL.

If a NetpathXL spreadsheet is selected (option 1), a speciation calculation will be performed. A database file is required for this speciation calculation. The default database file is found in the *database* subdirectory of the installation directory (*c:\Program Files\USGS\NetpathXL\database*).

Another file, *netpath.dat*, contains mineral stoichiometry and isotopic composition, which are needed for inverse modeling calculations. NetpathXL will look for this file in the working directory (the directory containing the file read at startup). If it is not found in the working directory, the file will be copied from the database subdirectory of the installation directory (*c:\Program Files\USGS\NetpathXL\database*).

If a NetpathXL spreadsheet is read, one additional option is added to the edit screen that was not in the original NETPATH program. The first option of the edit screen is now “1) Reread Excel file” (fig. 4), which is not available in NETPATH. (The edit screen is invoked by typing “E” on the main screen of NetpathXL, fig. 5.) This option will reread the last NetpathXL spreadsheet and perform speciation calculations by using the same options (charge balance option and database file) that were used when the NetpathXL spreadsheet was originally read. (If you want to reread the Excel file, but use different options, select the option “Well file”, which will query for each option.) The current inverse model—wells, phases, constraints, and other options—is retained when the NetpathXL spreadsheet is reread. By using the reread option, concentration or isotopic data can be revised in the NetpathXL spreadsheet and then quickly imported into NetpathXL. Typically, the Excel spreadsheet will be left open and the reread option will be used whenever changes are made to the spreadsheet. Note that the changes to the spreadsheet must be saved (File->Save within Excel) before the spreadsheet is reread. The capability to view Excel while running NetpathXL replaces the <V>iew option of the main screen of NETPATH.

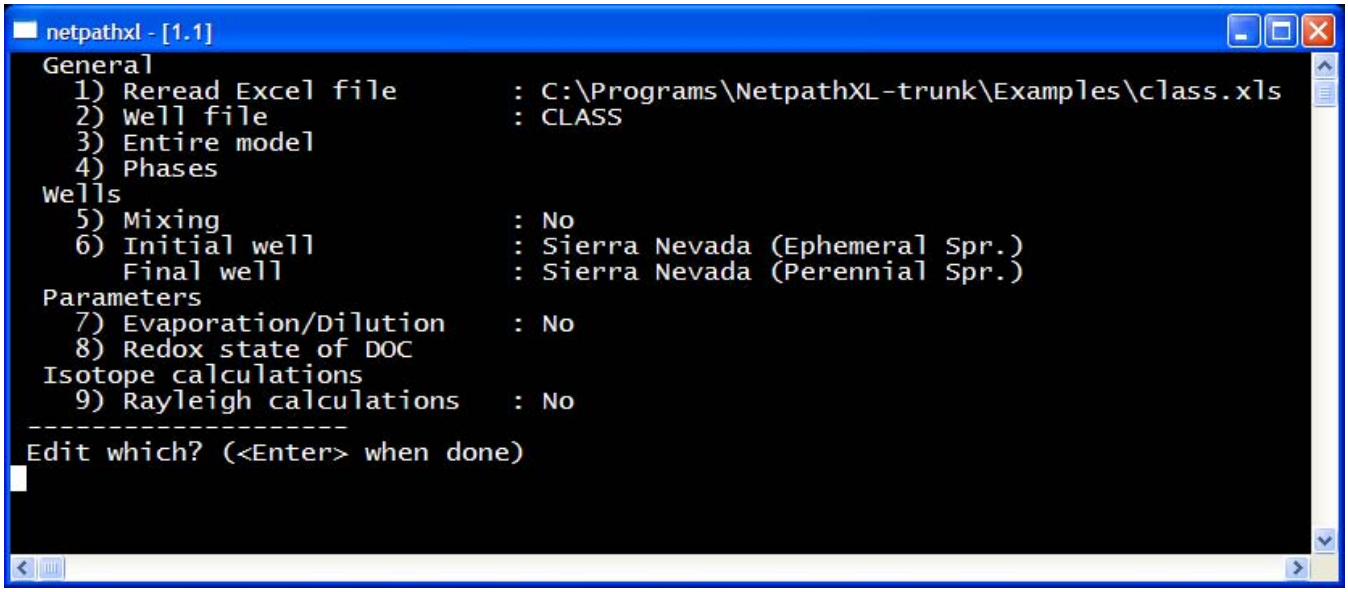

Figure 4. Edit screen for NetpathXL.

One additional option (<F>ont) has been added to the main screen (fig. 5). Typing “F” at the main screen prompt will result in a query for a font size. The default font size is 16; specifying a larger or smaller number will correspondingly increase or decrease the font size used for painting the screens in NetpathXL.

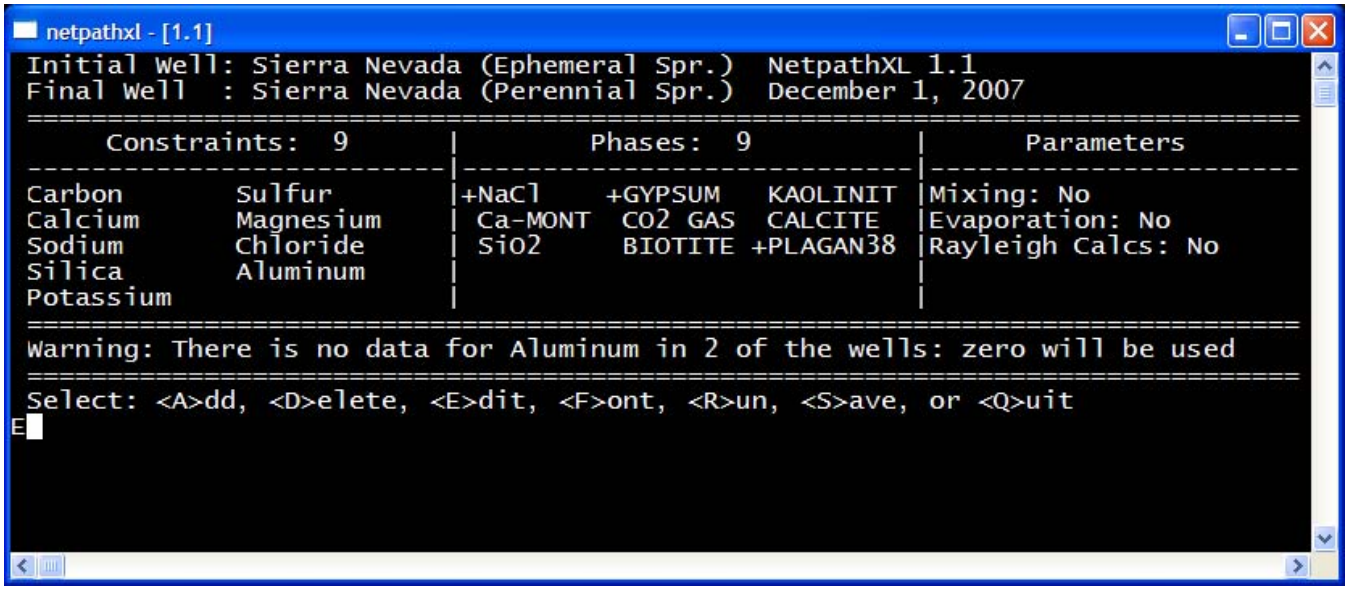

Figure 5. Selecting the edit screen from the main screen of NetpathXL.

Summary and Conclusions

NETPATH is unique in some of the capabilities it provides for geochemical inverse modeling and radiocarbon dating of ground waters. NetpathXL is a partial modernization of the program NETPATH. NetpathXL simplifies data input by using a fixed-format Excel spreadsheet in place of the program DB. File browsing, installation, and concentration data input have the look and feel of current computer programs. The model development process remains essentially unchanged from that of NETPATH and requires keyboard input rather than point and click technology. However, keyboard input is efficient and the model development process is simple and straightforward. The calculation engine in NetpathXL is identical to NETPATH.

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Appendix 1—Coding methods

NetpathXL is written in FORTRAN 90 and compiled with Intel® FORTRAN compiler within the Microsoft Visual Studio® 8.0 programming environment. Originally, NetpathXL and DBXL were written to eliminate the method of screen painting that is used in NETPATH. NETPATH relies on a terminal mode described by *ansi.sys*, which is increasingly difficult to implement in recent Windows® operating systems. NetpathXL replaces the routines that cleared the screen and moved the cursor position (*clpart*, *moverelative*, *cls*, *home*, *poscur*) with new routines that use subroutines available for Intel FORTRAN QuickWin Applications, thereby eliminating the use of *ansi.sys*.

With the use of Intel FORTRAN, it was also possible to implement file browsing with standard Windows system calls, which gives NetpathXL and DBXL more of the look and feel of current programming and simplifies the application of these programs in multiple directories.

Finally, the Excel Component Object Module (COM) interface was accessible through Intel FORTRAN and it was possible to replace the functions of DB with Excel. A fixed format spreadsheet was devised for entering the data that were formerly entered through DB. Data entry is much simpler through a spreadsheet and spreadsheet manipulations are familiar to most users. The use of Excel obviates the need for DB although DBXL is used to generate the fixed format spreadsheet. Once a spreadsheet has been generated, DBXL is not needed.

Appendix 2—NetpathXL Spreadsheet File

NetpathXL requires an Excel file with a specified format. Cell A1 must contain the string "Netpath Spreadsheet 2.14." Cells A7-AU7 must contain the literal headings specified in Table 1. In files generated by DBXL, the cells A1:AU7 are locked so that they can not be edited. The maximum number of analyses is limited to 50, a limitation retained from DB and NETPATH. Only rows 8 through 57 may contain analyses.

If data for an analysis are given in milligrams per liter (mg/L) or parts per million (ppm), then a gram formula weight is used to convert from mass to moles. The default gram formula weights for analytes are given in column 3 of Table 1, and, for the case of alkalinity, in footnote 5 of Table 1. These gram formula weights are specified in the file *db.dat*. The conversion factor from equivalents of $CaCO_3$ to equivalents of HCO_3 (1.2193) is hard coded in the source for NetpathXL.

Cell number	Required heading	Default gram formula weight in db.dat grams per mole	Meaning of data values	Footnote
A7	Number		Well identification number	
B7	Well name (required)		Well identifier (character string)	
C7	Units Flag		Options for concentration units	1
D7	Eh Flag		Options for interpretation of Eh	2
E7	Alk/ TDIC Flag		Flag for interpretation of carbon data	3
F7	Act Coef Flag		Flag for activity coefficient selection	4
G7	Temp		Temperature, Celcius	
H7	pH		pH, standard units	
I7	Eh		Eh, in volts	
J7	Ca	40.08	Calcium concentration	
K7	Mg	24.312	Magnesium concentration	
L7	Na	22.9898	Sodium concentration	
M7	K	39.102	Potassium concentration	
N7	Cl	35.453	Chloride concentration	
O7	SO4 as SO4	96.0616	Sulfate concentration	
P7	Alk/TDIC	61.0173 or 50.04289	Alkalinity or total dissolved inorganic carbon concentration	5
Q7	Fe	55.847	Iron concentration	
R7	Mn	54.938	Manganese concentration	
S7	Al	26.9815	Aluminum concentration	
T7	F	18.9984	Fluoride concentration	
U7	Si as SiO2	60.0848	Silica concentration	
V7	Br	79.904	Bromide concentration	
W7	B	10.81	Boron concentration	
X7	Ba	137.34	Barium concentration	
Y7	Li	6.939	Lithium concentration	
Z7	Sr	87.62	Strontium concentration	
AA7	NO3 as N	14.0067	Nitrate concentration	
AB 7	NH4 as N	14.0067	Ammonium concentration	
AC7	P	30.9738	Phosphorus concentration	
AD7	O2(aq) as O2	31.9988	Dissolved oxygen concentration	
AE7	H2S(aq) as S	32.06	Dissolved sulfide concentration	
AF7	N2(aq) as N	14.0067	Dissolved nitrogen concentration	
AG7	CH4(aq) as CH4	16.0428	Dissolved methane concentration	
AH7	DOC as C	12.011	Dissolved organic carbon concentration	
AI7	RS of DOC		Redox state of dissolved organic carbon	
AJ7	C-13 TDIC		Carbon-13 ratio, permil	
AK7	C-14 TDIC		Carbon-14 concentration, percent modern carbon	
AL7	S-34 SO4		Sulfur-34 ratio of sulfate, permil	
AM7	S-34 H2S		Sulfur-34 ratio of sulfide, permil	
AN7	H-2		Hydrogen-2 ratio, permil	
AO7	H-3		Tritium concentration, tritium units	

AP7	O-18	Oxygen-18 ratio, permil
AQ7	Sr-87	Strontium -87 ratio
AR7	N-15 N2(aq)	Nitrogen-15 ratio of dissolved nitrogen, permil
AS7	N-15 NO3	Nitrogen-15 ratio of nitrate, permil
AT7	N-15 NH4	Nitrogen-15 ratio of ammonium, permil
AU7	Density	Density, grams per centimeter cubed

[1] Options for concentration units: 0 millimoles per liter; 1 milliequivalents per liter; 2 milligrams per liter; 3 parts per million; and 4 millimoles per kilogram water.

[2] Options for calculating the Eh used to speciate redox elements (Fe and Mn): 0 redox is ignored; 1 specified Eh is used; 2 dissolved oxygen is used to calculate Eh; 3 the Sato relation is used to calculate Eh from dissolved oxygen concentration; and 4 sulfate and sulfide concentrations are used to calculate Eh.

[3] Options for alkalinity and total dissolved inorganic carbon (Alk/TDIC) data: 0 field alkalinity is entered as HCO3; 1 carbonate alkalinity (exclusive of all other alkalinity species) is entered as HCO3; 2 total dissolved inorganic carbon (TDIC) is entered as HCO3; and 3 field alkalinity is entered as CaCO3. Note that the gram equivalent weights for the formulas HCO3 and CaCO3 are needed only for converting mass concentration units—mg/L (milligrams per liter) and ppm (parts per million)—to moles or equivalents per kilogram water.

[4] Options for activity coefficients: 0 use the extended Debye-Hückel formula; and 1 use the Davies formula.

[5] Gram formula or equivalent weights for carbon and alkalinity: for TDIC, the gram formula weight used to convert mg/L and ppm to mol/kg water is 61.0173; for alkalinity, the gram equivalent weights used to convert mg/L and ppm to equivalents per kilogram of water are 61.0173 for HCO3 and 50.04289 for CaCO3.