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September 1991

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U.S. Army Corps of Engineers
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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS

PREFACE

This report was prepared by Dr. Giles M. Marion, Research Physical Scientist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by DA Project 4A161102AT24, *Research in Snow, Ice and Frozen Ground*; Task SS; Work Unit 020, *Transport of Chemical Species in Soils*.

The author thanks Dean Pidgeon for his assistance in developing the MS-DOS version of the IONPAIR program. Technical review was provided by Dr. C.M. Reynolds, D.C. Leggett and Dr. I.K. Iskandar, all of CRREL.

Anyone wishing either a Macintosh or MS-DOS version of this program on disk should contact Dr Marion by writing to him at CECRL-RC, 72 Lyme Road, Hanover New Hampshire 03755-1290, or by phoning him at 603-646-4676.

IONPAIR: A Chemical Speciation Program for Calcareous and Gypsiferous Soil Solutions

GILES M. MARION

INTRODUCTION

Calcareous and gypsiferous soils are common along many river floodplains in the subarctic and arctic regions of Alaska (Marion et al., in press b) as well as in more arid regions such as deserts and grasslands (Schlesinger 1985; Marion et al. 1990; Marion et al., in press a; Reddy et al. 1990; Suarez et al. 1990). The IONPAIR program was designed to speciate the chemical composition of calcareous and gypsiferous aqueous solutions. There are a number of commercially available chemical speciation programs. However, some programs such as WATEQ4F (Ball and Nordstrom 1987) do not allow P_{CO_2} (the partial pressure of CO_2 [g]) as an input, while other programs such as GEOCHEM handle P_{CO_2} in an inconvenient fashion requiring a trial-and-error approach to solution (Sposito and Mattigod 1979, Suarez 1990). Since P_{CO_2} is an easily controlled variable in laboratory studies, a chemical speciation program that allows one to specify P_{CO_2} would be highly useful, especially in laboratory studies of calcareous soils. In contrast to most existing chemical speciation programs, IONPAIR was developed as a "stand-alone" program, which means that one does not need a programming software package such as BASIC or FORTRAN in order to run the program. Also, in contrast to most other programs, IONPAIR was developed in both Macintosh and MS-DOS (IBM-compatible) versions.

The objective of this report is to document the IONPAIR program. Important features of the IONPAIR program are variable inputs, accuracy, portability and easy utilization.

PROGRAM DESCRIPTION

Chemical speciation programs partition the total (measured) concentration of aqueous-phase constituents into the concentrations of individual chemical species (the unknowns). For every unknown aqueous-phase constituent, an independent equation is needed. In the IONPAIR program, there are either 17 or 19 unknowns (or equations).

The program calculates aqueous-phase concentrations by successive approximations using the Newton–Raphson algorithm to solve a set of non-linear equations (Korn and Korn 1968). The requisite set of equations consists of mass balance equations for the major constituents (Ca, Mg, K, Na, SO_4 and alkalinity), which are defined in terms of concentrations, for example

$$Ca_T = [Ca^{++}] + [CaHCO_3^{+}] + [CaCO_3^{0}] + [CaSO_4^{0}] \qquad (1)$$

and stability relations for the ion-pairs and carbonic acid (Table 1), which are defined in terms of activities, for example

$$(Ca^{++})\,(SO_4^{--})/(CaSO_4^{0}) = K \qquad (2)$$

where brackets refer to concentrations and parentheses refer to activities.

In order to solve the non-linear equations, one must estimate the activity coefficients (γ_i) that are related to concentrations (m_i) and activities (a_i) by

$$a_i = \gamma_i\, m_i \qquad (3)$$

where the subscript i refers to the i^{th} constituent in solution.

The activity coefficients of monovalent and divalent constituents are estimated with the Davies equation

$$\log(\gamma_i) = -A\, z_i^2 \left\{ \left[\sqrt{I}/(1.0 + \sqrt{I}) \right] - 0.3\, I \right\} \qquad (4)$$

Table 1. The *pK* values at 25°C for the solution phase complexes between cation (C) and anion (A), where *pK* = –log (C × A/CA complex). The equilibrium constants were calculated from standard free energy data (Lindsay 1979). In addition to the above constants, the program also uses the Henry's Law constant for CO_2 equilibrium between the aqueous and solution phases (*pK* = 1.464).

	Cation				
Anion	*Ca*	*Mg*	*K*	*Na*	*H*
SO_4	2.309	2.229	0.850	0.696	
HCO_3	1.129	1.070	-0.249*	-0.249	6.364
CO_3	3.152	3.240	1.268*	1.268	10.330

* Assumed to be the same as the Na analogues.

where *A* is a constant (= 0.5116 at 25°C), z_i is the valence of the i^{th} ion, and *I* is the ionic strength

$$I = 0.5 \sum m_i z_i^2 \qquad (5)$$

(Davies 1962). Neutrally charged constituents (e.g., $CaSO_4^0$) are assumed to have activity coefficients of 1.00. For the justification of this assumption, see the discussion in the *Limitations* section.

In eq 1, Ca_T is the measured total Ca concentration and the constituents on the right are the unknown concentrations. The activities in eq 2 must also be expressed in terms of concentrations by using the relation in eq 3, for example

$$[Ca^{++}][SO_4^{--}]/[CaSO_4^0] = K/\gamma_{Ca}\cdot\gamma_{SO_4} = K' \, . \qquad (6)$$

Initially, the concentrations (m_i), ionic strength (*I*) and activity coefficients (γ_i) are unknown. Rough estimates of the unknown concentrations are made that allow one to estimate the ionic strength (eq 5) and the activity coefficients (eq 4). Then, the initial estimates of the unknown concentrations are refined using the Newton–Raphson algorithm. The new estimates of the concentrations are then used to re-estimate the ionic strength and activity coefficients, which in turn are used to re-estimate the concentrations with the Newton–Raphson algorithm. This interactive process continues until consecutive estimates of every unknown concentration agree to within ± 0.1 %.

The computer program (Appendix A) has three input options requiring a specification of 1) pH and alkalinity, 2) P_{CO_2} and alkalinity, or 3) P_{CO_2} and pH. Given any one of these options, plus measurements of total dissolved Ca, Mg, K, Na, Cl and SO_4, the program calculates the true ionic concentrations in the solution phase. Ion-pairs are considered between the cations, Ca^{++}, Mg^{++}, K^+ and Na^+, and the anions, HCO_3^-, CO_3^{--} and SO_4^{--}. Ion-pairs with Cl^- are ignored because they only form weak complexes (Lindsay 1979).

Input to the program (Appendix B) is via keyboard from computer screen queries. First, a "Title" for the data set is requested; this can be any alphanumeric statement up to 80 characters. Next, you must choose the input option (see previous paragraph). Then, total chemical concentrations of each constituent are requested. Except for pH (no units), alkalinity ($mol_c\ L^{-1}$; where mol_c = equivalents), and P_{CO_2} (atm), the input concentration units are mol L^{-1}. The latter are most conveniently input in "e-format" (i.e., 0.0107 mol L^{-1} = 1.07e–2, Appendix B).

Output from the program (Appendix B) includes a charge balance, the concentrations and activities of the individual chemical species, the ionic strength, and pIAP[*]($CaCO_3$) and pIAP($CaSO_4$) where

$$pIAP(CaCO_3) = -\log\{(Ca^{++})(CO_3^{--})\} \, . \qquad (7)$$

Calculated pIAP($CaCO_3$) and pIAP($CaSO_4$) can be compared to the solubility products for calcite (pK_{sp} = 8.48) and gypsum (pK_{sp} = 4.64) respectively.

The computer program is written in TrueBASIC for both Macintosh and MS-DOS computers; there are two versions for each operating system.[†] One version requires the TrueBASIC software package to open and run; given the latter software, this version can be changed by the user (e.g., input and output formats, stability constants, temperature adjustments, etc.). The second version is a "stand-alone" (or executable file) program that does not require the TrueBASIC software package; however, this version can not be user-modified.

This program was initially written in Fortran in 1970 and has been tested with many data sets over the years (Marion and Babcock 1977; Schlesinger 1985; Marion et al. 1990; Marion et al., in press a,b). However, the author accepts no responsibility for the accuracy of these calculations and urges users to verify accuracy for themselves. Moreover, there is no assurance that the Newton–Raphson algorithm will always converge. If problems develop with non-converging data sets, then program lines 1590–1860 may need to be modified. For problems with the program, you can phone the author.

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[*] Ion activity product.

[†] If you want a copy of the IONPAIR program on disk, please contact Dr. Giles Marion, USACECRL-RC, 72 Lyme Road, Hanover New Hampshire 03755 and specify if you need a Macintosh version or an MS-DOS version, or call Dr. Marion at 603-646-4676.

The current Macintosh version has run on the Macintosh Plus, SE, Classic and II computers with both ImageWriter and LaserWriter printers. The MS-DOS version has also been tested on a wide range of MS-DOS computers.

LIMITATIONS

This program requires a specification of all constituents; you can not enter a "zero" concentration. The latter will cause program failure. If a constituent is not present in measurable amounts, then an arbitrary low concentration must be assigned. For example, if the major constituents are present at the 10^{-3} mol L^{-1} range and Na was not detectable, enter an arbitrary low concentration for Na (e.g., 10^{-8} mol L^{-1}); at these low concentrations, Na will not have a significant impact on either the ionic strength or ion-pairing.

If there are constituents not explicitly included in the program that are present in significant concentrations (e.g., NH_4 or NO_3), these constituents can sometimes be lumped with explicitly recognized constituents as input (e.g., NH_4 with K [or Na] and NO_3 with Cl). Otherwise, the program will have to be modified to explicitly recognize the additional constituents.

The program was written to analyze laboratory experiments at 25°C. As a consequence, the stability constants are only defined for 25°C; significant departures from this temperature will require program modification. For example, the solubility of CO_2 in aqueous solution is about 15% greater at 20°C than at 25°C. This solubility difference is substantial and would require program modification if you wanted to use the program at 20°C.

The range of validity of the IONPAIR program with respect to ionic strength (I) is $I \leq 0.1$ M. Monovalent and divalent activity coefficients are estimated using the Davies equation (eq 4), which is considered valid for all valency types up to $I = 0.1$ M, with an error not exceeding 2% (Davies 1962). Generally, activity coefficients of neutral molecules deviate from 1.00 by less than 2–3% at $I \leq 0.1$ M (Harned and Owen 1958); furthermore, these deviations may be both greater than or less than 1.00. Given the small magnitude of this effect on neutrally charged constituents, the assumption is made in the IONPAIR program that activity equals concentration (i.e., activity coefficient = 1.00) for neutral molecules.

At present, the computer program in options 1 and 2 assumes that measured total alkalinity is equivalent to inorganic carbon alkalinity, and therefore partitions the alkalinity amongst the inorganic carbon species. If this assumption is incorrect, then the program will overestimate the true inorganic carbon concentrations and, as a consequence, overestimate the true ion activity products for $CaCO_3$. However, given measurements of P_{CO_2} and pH (option 3), the computer program will calculate the true concentrations of inorganic carbon species, which can then be compared to the measured total alkalinity. Recent work suggests that generally total alkalinity equals inorganic carbon alkalinity in soils (Suarez 1990; Marion et al., in press a); but, there are apparently exceptions to this generality when total alkalinity does not equal inorganic carbon alkalinity (Amrhein and Suarez 1987, Takkar et al. 1987, Reddy et al. 1990).

TESTING CHEMICAL SPECIATION MODELS

The validity of aqueous-phase chemical speciation models can be examined by "overdetermining" the state of these aqueous systems. For example, given any two of the following three measurements—pH, alkalinity and P_{CO_2}—the third can be calculated. For IONPAIR's option 1 (pH + alkalinity), P_{CO_2} can be calculated from the output by

$$P_{CO_2} = (H^+)(HCO_3^-)/K_1 K_H$$

$$= (H^+)(HCO_3^-)/1.49 \times 10^{-8} \qquad (8)$$

where parentheses refer to activities. From the data in Appendix B (option 1), the calculated P_{CO_2} (9.02×10^{-3} atm) agrees very well with the measured P_{CO_2} (8.96×10^{-3} atm). For option 2 (alkalinity and P_{CO_2}), the calculated pH is given by

$$pH = -\log [(P_{CO_2})\ 1.49 \times 10^{-8}/(HCO_3^-)]\ . \qquad (9)$$

In this case, the calculated pH (7.29) and measured pH (7.29) agree exactly (Appendix B). And last, the inorganic carbon alkalinity can be estimated from option 3 (pH and P_{CO_2}) by summing up the equivalent concentrations of the inorganic carbon species. In this case, the calculated inorganic carbon alkalinity (3.35×10^{-3} mol_c L^{-1}) is in agreement with the measured total alkalinity (3.38×10^{-3} mol_c L^{-1}) (Appendix B).

In this particular example, the calculated and measured quantities (pH, P_{CO_2} and alkalinity) were in excellent agreement as were the charge balances (± 0.6 %, Appendix B). Over-determining the state of aqueous solutions allows one to check the internal consistency of experimental measurements, equilibrium constants and model assumptions.

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APPENDIX A: PROGRAM LISTING

```
1000 !
1010 ! THIS PROGRAM CALCULATES SOLUTION IONIC CONCENTRATIONS
1020 ! WITH CORRECTIONS FOR ION-PAIRS.
1030 !
1040 OPTION NOLET
1050 DIM K(15), X(20), ACT (20), A(19,19)
1060 DIM B(19), AC(20), C(19), AINV(19,19)
1070 !
1080 ! SET UP SCREEN AND PRINTER
1090 !
1100 PAGE = 0.0
1110 OPEN #1: SCREEN 0,1,0,1
1120 OPEN #2: PRINTER
1130 PRINT #2
1140 !
1150 ! DEFINE THE STABILITY CONSTANTS
1160 !
1170 DATA  7.43E-2, 7.04E-4, 4.90E-3, 8.50E-2, 5.75E-4
1180 DATA  5.91E-3, 1.78, 5.39E-2, 1.41E-1, 1.78
1190 DATA  5.39E-2, 2.01E-1, 4.68E-11, 4.33E-7, 3.43E-2
1200 MAT READ K
1210 !
1220 ! INPUT DATA
1230 !
1240 LINE INPUT PROMPT "TITLE:    ": TITLE$
1250 PRINT "CHOOSE INPUT OPTION"
1260 PRINT "OPTION 1 = HCO3T + PH"
1270 PRINT "OPTION 2 = HCO3T + CO2"
1280 PRINT "OPTION 3 = PH + CO2"
1290 INPUT PROMPT "ENTER NUMERIC VALUE OF OPTION  ": OPT
1300 INPUT PROMPT "ENTER CA CONC (MOL/L)  ": CALT
1310 INPUT PROMPT "ENTER MG CONC (MOL/L)  ": MGT
1320 INPUT PROMPT "ENTER K CONC (MOL/L)  ": KT
1330 INPUT PROMPT "ENTER NA CONC (MOL/L)  ": NAT
1340 INPUT PROMPT "ENTER SO4 CONC (MOL/L)  ": SO4T
1350 INPUT PROMPT "ENTER CL CONC (MOL/L)  ": CL
1360 X(20) = CL
1370 SELECT CASE OPT
1380   CASE 1
1390     ND=19
1400      INPUT PROMPT "ENTER PH  ": PH
1410      H=EXP(-2.3026*PH)
1420      INPUT PROMPT "ENTER ALKALINITY (EQ/L)  ": HCO3T
1430   CASE 2
1440     ND=19
1450      INPUT PROMPT "ENTER ALKALINITY (EQ/L)  ": HCO3T
1460      INPUT PROMPT "ENTER CO2 (ATM)  ": CO2
1470   CASE 3
1480     ND=17
1490      INPUT PROMPT "ENTER PH  ": PH
1500      H=EXP(-2.3026*PH)
1510      INPUT PROMPT "ENTER CO2 (ATM)  ": CO2
1520 END SELECT
1530 MAT REDIM A(ND,ND), B(ND), C(ND), AINV(ND,ND)
1540 MAT A = ZER
1550 MAT AINV = ZER
1560 !
1570 !  ESTIMATE INITIAL IONIC CONCENTRATIONS
1580 !
1590 SELECT CASE OPT
1600   CASE 1
1610       X(18)=HCO3T*0.95
1620       X(19)=X(18)*K(13)/H
1630   CASE 2
1640       X(18)=HCO3T*0.95
1650       X(19)=X(18)^2*K(13)/(K(14)*K(15)*CO2)
```

```
1660   CASE 3
1670        X(18)=K(14)*K(15)*CO2/H
1680        X(19)=K(13)*X(18)/H
1690 END SELECT
1700 X(1)=0.85*CALT
1710 X(2)=X(1)*X(18)/K(1)
1720 X(3)=X(1)*X(19)/K(2)
1730 X(4)=X(1)*SO4T/K(3)
1740 X(5)=0.85*MGT
1750 X(6)=X(5)*X(18)/K(4)
1760 X(7)=X(5)*X(19)/K(5)
1770 X(8)=X(5)*SO4T/K(6)
1780 X(9)=0.97*KT
1790 X(10)=X(9)*X(18)/K(7)
1800 X(11)=X(9)*X(19)/K(8)
1810 X(12)=X(9)*X(17)/K(9)
1820 X(13)=0.97*NAT
1830 X(14)=X(13)*X(18)/K(10)
1840 X(15)=X(13)*X(19)/K(11)
1850 X(16)=X(13)*X(17)/K(12)
1860 X(17)=SO4T*0.85
1870 !
1880 !  ESTIMATE THE IONIC STRENGTH AND THE MONO- AND DI-VALENT
1890 !  ACTIVITY COEFFICIENTS USING THE DAVIES EQUATION.
1900 !
1910 IONSTR=0.5*(X(2)+X(6)+X(9)+X(11)+X(12)+X(13)+X(15)+X(16)+X(18)+X(20))
1920 IONSTR=IONSTR + 2.0*(X(1)+X(5)+X(17)+X(19))
1930 FACTOR=SQR(IONSTR)/(1.0+SQR(IONSTR))-0.3*IONSTR
1940 AC1=EXP(-1.1720*FACTOR)
1950 AC2=EXP(-4.6881*FACTOR)
1960 !
1970 !  DEFINE THE ELEMENTS OF THE PARTIAL DERIVATIVE (A) AND THE
1980 !  DIFFERENCE (B) MATRICES FOR THE NEWTON-RAPHSON ALGORITHM
1990 !
2000 A(1,1)=-1.0
2010 A(1,2)=-1.0
2020 A(1,3)=-1.0
2030 A(1,4)=-1.0
2040 A(2,5)=-1.0
2050 A(2,6)=-1.0
2060 A(2,7)=-1.0
2070 A(2,8)=-1.0
2080 A(3,9)=-1.0
2090 A(3,10)=-1.0
2100 A(3,11)=-1.0
2110 A(3,12)=-1.0
2120 A(4,13)=-1.0
2130 A(4,14)=-1.0
2140 A(4,15)=-1.0
2150 A(4,16)=-1.0
2160 A(5,17)=-1.0
2170 A(5,4)=-1.0
2180 A(5,8)=-1.0
2190 A(5,12)=-1.0
2200 A(5,16)=-1.0
2210 AK1=K(1)/AC2
2220 AK2=K(2)/AC2^2
2230 AK3=K(3)/AC2^2
2240 AK4=K(4)/AC2
2250 AK5=K(5)/AC2^2
2260 AK6=K(6)/AC2^2
2270 AK7=K(7)/AC1^2
2280 AK8=K(8)/AC2
2290 AK9=K(9)/AC2
2300 AK10=K(10)/AC1^2
2310 AK11=K(11)/AC2
2320 AK12=K(12)/AC2
2330 A(6,1)=X(18)
2340 A(6,2)=-AK1
2350 A(7,1)=X(19)
```

```
2360 A(7,3)=-AK2
2370 A(8,1)=X(17)
2380 A(8,17)=X(1)
2390 A(8,4)=-AK3
2400 A(9,5)=X(18)
2410 A(9,6)=-AK4
2420 A(10,5)=X(19)
2430 A(10,7)=-AK5
2440 A(11,5)=X(17)
2450 A(11,17)=X(5)
2460 A(11,8)=-AK6
2470 A(12,9)=X(18)
2480 A(12,10)=-AK7
2490 A(13,9)=X(19)
2500 A(13,11)=-AK8
2510 A(14,9)=X(17)
2520 A(14,17)=X(9)
2530 A(14,12)=-AK9
2540 A(15,13)=X(18)
2550 A(15,14)=-AK10
2560 A(16,13)=X(19)
2570 A(16,15)=-AK11
2580 A(17,13)=X(17)
2590 A(17,17)=X(13)
2600 A(17,16)=-AK12
2610 SELECT CASE OPT
2620   CASE 1 TO 2
2630         A(18,18)=-1.0
2640         A(18,2)=-1.0
2650         A(18,6)=-1.0
2660         A(18,10)=-1.0
2670         A(18,14)=-1.0
2680         A(18,19)=-2.0
2690         A(18,3)=-2.0
2700         A(18,7)=-2.0
2710         A(18,11)=-2.0
2720         A(18,15)=-2.0
2730         A(6,18)=X(1)
2740         A(7,19)=X(1)
2750         A(9,18)=X(5)
2760         A(10,19)=X(5)
2770         A(12,18)=X(9)
2780         A(13,19)=X(9)
2790         A(15,18)=X(13)
2800         A(16,19)=X(13)
2810         B(18)=HCO3T-X(18)-2.0*X(19)-X(2)-2.0*X(3)-X(6)-2.0*X(7)-X(10)
2820         B(18)=B(18)-2.0*X(11)-X(14)-2.0*X(15)
2830       SELECT CASE OPT
2840         CASE 1
2850              AK13=K(13)*AC1/(AC2*H)
2860              A(19,19)=1.0
2870              A(19,18)=-AK13
2880              B(19)=X(19)-AK13*X(18)
2890         CASE 2
2900              AK14=K(14)*K(15)*CO2*AC2/(K(13)*AC1^2)
2910              A(19,18)=2.0*X(18)
2920              A(19,19)=-AK14
2930              B(19)=X(18)^2-AK14*X(19)
2940       END SELECT
2950   CASE 3
2960         X(18)=K(14)*CO2*K(15)/(H*AC1)
2970         X(19)=K(13)*X(18)*AC1/(H*AC2)
2980 END SELECT
2990 B(1)=CALT-X(1)-X(2)-X(3)-X(4)
3000 B(2)=MGT-X(5)-X(6)-X(7)-X(8)
3010 B(3)=KT-X(9)-X(10)-X(11)-X(12)
3020 B(4)=NAT-X(13)-X(14)-X(15)-X(16)
3030 B(5)=SO4T-X(17)-X(4)-X(8)-X(12)-X(16)
3040 B(6)=X(1)*X(18)-AK1*X(2)
3050 B(7)=X(1)*X(19)-AK2*X(3)
```

```
3060 B(8)=X(1)*X(17)-AK3*X(4)
3070 B(9)=X(5)*X(18)-AK4*X(6)
3080 B(10)=X(5)*X(19)-AK5*X(7)
3090 B(11)=X(5)*X(17)-AK6*X(8)
3100 B(12)=X(9)*X(18)-AK7*X(10)
3110 B(13)=X(9)*X(19)-AK8*X(11)
3120 B(14)=X(9)*X(17)-AK9*X(12)
3130 B(15)=X(13)*X(18)-AK10*X(14)
3140 B(16)=X(13)*X(19)-AK11*X(15)
3150 B(17)=X(17)*X(13)-AK12*X(16)
3160 FOR I=1 TO ND
3170      B(I)=-1.0*B(I)
3180 NEXT I
3190 !
3200 !  SOLVE THE SET OF LINEAR EQUATIONS (C=B/A)
3210 !
3220 MAT AINV = INV(A)
3230 MAT C = AINV*B
3240 !
3250 !  CHECK FOR SOLUTION CONVERGENCE
3260 !
3270 FOR I=1 TO ND
3280      X(I)=X(I)+C(I)
3290 NEXT I
3300 FOR I=1 TO ND
3310      PCEN=(C(I)/X(I))*100.0
3320      PCEN=ABS(PCEN)
3330      IF PCEN>0.1 THEN GO TO 1910
3340 NEXT I
3350 !
3360 !  PRINT RESULTS
3370 !
3380 PRINT #2
3390 PRINT #2
3400 PRINT #2: TAB(7); "INPUT"
3410 PRINT #2: TAB(8); TITLE$
3420 PRINT #2, USING "        CAT=#.##^^^^  MGT=#.##^^^^  KT=#.##^^^^  NAT=#.##^^^^": CALT,MGT,KT,NAT
3430 SELECT CASE OPT
3440   CASE 1
3450      PRINT #2, USING "        SO4T=#.##^^^^  CL=#.##^^^^  ALK=#.##^^^^  PH=#.###": SO4T,CL,HCO3T,PH
3460   CASE 2
3470      PRINT #2, USING "        SO4T=#.##^^^^  CL=#.##^^^^  ALK=#.##^^^^  CO2=#.##^^^^": SO4T,CL,HCO3T,CO2
3480   CASE 3
3490      PRINT #2, USING "        SO4T=#.##^^^^  CL=#.##^^^^  PH=#.###  CO2=#.##^^^^": SO4T,CL,PH,CO2
3500       HCO3T=X(2)+2*X(3)+X(6)+2*X(7)+X(10)+2*X(11)+X(14)+2*X(15)
3510       HCO3T=HCO3T+X(18)+2.0*X(19)
3520 END SELECT
3530 CATION=2.0*(CALT+MGT)+KT+NAT
3540 ANION=2.0*SO4T+CL+HCO3T
3550 PERCENT=((CATION-ANION)/CATION)*100.0
3560 PRINT #2
3570 PRINT #2: TAB(7); "OUTPUT"
3580 PRINT #2, USING "      TOTAL CATIONS #.##^^^^  TOTAL ANIONS=#.##^^^^": CATION,ANION;
3590 PRINT #2, USING "  PERCENT DIFF= +###.##": PERCENT
3600 AC(1)=AC2
3610 AC(2)=AC1
3620 AC(3)=1.0
3630 AC(4)=1.0
3640 AC(5)=AC2
3650 AC(6)=AC1
3660 AC(7)=1.0
3670 AC(8)=1.0
3680 AC(9)=AC1
3690 AC(10)=1.0
3700 AC(11)=AC1
3710 AC(12)=AC1
3720 AC(13)=AC1
3730 AC(14)=1.0
3740 AC(15)=AC1
3750 AC(16)=AC1
```

```
3760 AC(17)=AC2
3770 AC(18)=AC1
3780 AC(19)=AC2
3790 AC(20)=AC1
3800 FOR I=1 TO 20
3810      ACT(I)=X(I)*AC(I)
3820 NEXT I
3830 PRINT #2: "       SPECIES  CONC.    ACT.       SPECIES  CONC.    ACT."
3840 PRINT #2, USING "           CA=    #.##^^^^  #.##^^^^     CAHCO3=#.##^^^^  #.##^^^^": X(1),ACT(1),X(2),ACT(2)
3850 PRINT #2, USING "           CACO3=#.##^^^^  #.##^^^^     CASO4= #.##^^^^  #.##^^^^": X(3),ACT(3),X(4),ACT(4)
3860 PRINT #2, USING "           MG=    #.##^^^^  #.##^^^^     MGHCO3=#.##^^^^  #.##^^^^": X(5),ACT(5),X(6),ACT(6)
3870 PRINT #2, USING "           MGCO3=#.##^^^^  #.##^^^^     MGSO4= #.##^^^^  #.##^^^^": X(7),ACT(7),X(8),ACT(8)
3880 PRINT #2, USING "           K=     #.##^^^^  #.##^^^^     KHCO3= #.##^^^^  #.##^^^^": X(9),ACT(9),X(10),ACT(10)
3890 PRINT #2, USING "           KCO3= #.##^^^^  #.##^^^^     KSO4=   #.##^^^^  #.##^^^^": X(11),ACT(11),X(12),ACT(12)
3900 PRINT #2, USING "           NA=    #.##^^^^  #.##^^^^     NAHCO3=#.##^^^^  #.##^^^^": X(13),ACT(13),X(14),ACT(14)
3910 PRINT #2, USING "           NACO3=#.##^^^^  #.##^^^^     NASO4= #.##^^^^  #.##^^^^": X(15),ACT(15),X(16),ACT(16)
3920 PRINT #2, USING "           SO4=  #.##^^^^  #.##^^^^     HCO3=   #.##^^^^  #.##^^^^": X(17),ACT(17),X(18),ACT(18)
3930 PRINT #2, USING "           CO3=  #.##^^^^  #.##^^^^     CL=     #.##^^^^  #.##^^^^": X(19),ACT(19),X(20),ACT(20)
3940 CAS=ACT(1)*ACT(17)
3950 CAS=-LOG10(CAS)
3960 ACTPROD=ACT(1)*ACT(19)
3970 PIAP=-LOG10(ACTPROD)
3980 PRINT #2, USING "      IONIC STRENGTH=#.##^^^^   PIAP(CACO3)=##.###": IONSTR,PIAP;
3990 PRINT #2, USING "   PIAP(CASO4)=##.###": CAS
4000 PAGE=PAGE+1.0
4010 IF PAGE=2.0 THEN
4020    PRINT #2: CHR$(12)
4030    PAGE=0.0
4040 ELSE
4050    PRINT #2
4060 END IF
4070 !
4080 !  CHECK FOR MORE DATA
4090 !
4100 INPUT PROMPT "IS THERE MORE DATA (Y(1) OR N(0))?": MORE
4110 IF MORE = 1 THEN GO TO 1240
4120 IF PAGE=0 THEN GO TO 4140
4130 PRINT #2: CHR$(12)
4140 END
```

APPENDIX B: SAMPLE INPUT AND OUTPUT

```
INPUT
 ALTAMONT - 41 DAYS - OPTION 1
   CAT=1.07e-02  MGT=3.52e-03  KT=1.13e-04  NAT=6.09e-04
   SO4T=1.28e-02  CL=5.08e-05  ALK=3.38e-03  PH=7.290

OUTPUT
 TOTAL CATIONS=2.92e-02  TOTAL ANIONS=2.90e-02  PERCENT DIFF= +    .45
  SPECIES  CONC.     ACT.        SPECIES  CONC.     ACT.
    CA=    7.41e-03  3.60e-03     CAHCO3=1.52e-04  1.27e-04
    CACO3=1.22e-05  1.22e-05      CASO4= 3.13e-03  3.13e-03
    MG=    2.57e-03  1.25e-03     MGHCO3=4.61e-05  3.85e-05
    MGCO3=5.19e-06  5.19e-06      MGSO4= 8.99e-04  8.99e-04
    K=     1.10e-04  9.15e-05     KHCO3= 1.35e-07  1.35e-07
    KCO3= 4.86e-09  4.05e-09      KSO4=  3.31e-06  2.76e-06
    NA=    5.96e-04  4.97e-04     NAHCO3=7.31e-07  7.31e-07
    NACO3=2.64e-08  2.20e-08      NASO4= 1.26e-05  1.05e-05
    SO4=   8.76e-03  4.26e-03     HCO3=  3.14e-03  2.62e-03
    CO3=   4.92e-06  2.39e-06     CL=    5.08e-05  4.24e-05
 IONIC STRENGTH=3.95e-02    PIAP(CACO3)= 8.065    PIAP(CASO4)= 4.815
```

```
INPUT
 ALTAMONT - 41 DAYS - OPTION 2
   CAT=1.07e-02  MGT=3.52e-03  KT=1.13e-04  NAT=6.09e-04
   SO4T=1.28e-02  CL=5.08e-05  ALK=3.38e-03  CO2=8.96e-03

OUTPUT
 TOTAL CATIONS=2.92e-02  TOTAL ANIONS=2.90e-02  PERCENT DIFF= +    .45
  SPECIES  CONC.     ACT.        SPECIES  CONC.     ACT.
    CA=    7.41e-03  3.60e-03     CAHCO3=1.52e-04  1.27e-04
    CACO3=1.23e-05  1.23e-05      CASO4= 3.13e-03  3.13e-03
    MG=    2.57e-03  1.25e-03     MGHCO3=4.61e-05  3.85e-05
    MGCO3=5.23e-06  5.23e-06      MGSO4= 8.99e-04  8.99e-04
    K=     1.10e-04  9.15e-05     KHCO3= 1.35e-07  1.35e-07
    KCO3= 4.90e-09  4.09e-09      KSO4=  3.31e-06  2.76e-06
    NA=    5.96e-04  4.97e-04     NAHCO3=7.31e-07  7.31e-07
    NACO3=2.66e-08  2.22e-08      NASO4= 1.26e-05  1.05e-05
    SO4=   8.76e-03  4.26e-03     HCO3=  3.14e-03  2.62e-03
    CO3=   4.96e-06  2.41e-06     CL=    5.08e-05  4.24e-05
 IONIC STRENGTH=3.95e-02    PIAP(CACO3)= 8.062    PIAP(CASO4)= 4.815
```

```
INPUT
 ALTAMONT - 41 DAYS - OPTION 3
   CAT=1.07e-02  MGT=3.52e-03  KT=1.13e-04  NAT=6.09e-04
   SO4T=1.28e-02  CL=5.08e-05  PH=7.290   CO2=8.96e-03

OUTPUT
 TOTAL CATIONS=2.92e-02  TOTAL ANIONS=2.90e-02  PERCENT DIFF= +    .55
  SPECIES  CONC.      ACT.        SPECIES  CONC.      ACT.
    CA=    7.41e-03  3.60e-03     CAHCO3=1.51e-04  1.26e-04
    CACO3=1.21e-05  1.21e-05     CASO4= 3.13e-03  3.13e-03
    MG=    2.57e-03  1.25e-03     MGHCO3=4.57e-05  3.81e-05
    MGCO3=5.14e-06  5.14e-06     MGSO4= 8.99e-04  8.99e-04
    K=     1.10e-04  9.15e-05     KHCO3= 1.33e-07  1.33e-07
    KCO3= 4.81e-09  4.02e-09     KSO4=  3.31e-06  2.76e-06
    NA=    5.96e-04  4.97e-04     NAHCO3=7.25e-07  7.25e-07
    NACO3=2.62e-08  2.18e-08     NASO4= 1.26e-05  1.05e-05
    SO4=   8.76e-03  4.26e-03     HCO3=  3.11e-03  2.59e-03
    CO3=   4.87e-06  2.37e-06     CL=    5.08e-05  4.24e-05
  IONIC STRENGTH=3.95e-02   PIAP(CACO3)= 8.069   PIAP(CASO4)= 4.815
```

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The IONPAIR program was designed to speciate the chemical composition of calcareous and gypsiferous soil solutions. The program uses the Newton–Raphson algorithm to solve by successive approximations a set of non-linear equations relating ionic concentrations and activities. This program allows the user to specify as input any two of the following three variables: pH, alkalinity and P_{CO_2}. This flexibility allows one to check the internal consistency of experimental measurements, equilibrium constants and model assumptions. For example, is total alkalinity equal to inorganic carbon alkalinity? IONPAIR was designed as a "stand-alone" program, which means that it is easily usable and is available in both Macintosh and MS-DOS versions.

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