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A BASIC Computer Program for Speciation of Total and Ion Copper in Toxicological Bioassays

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Metals exist both as free metal ions and combined chemical forms in natural waters. Copper is of special interest to aquatic biologist because there may be only small differences between the concentrations required for growth and those having an adverse effect (Harrison 1986). Copper ion has been considered as the toxic form, although one or more of the hydroxides may also be toxic (Alabaster and Lloyd 1980). Recent reports seem also to demonstrate the toxicity of copper-amino acid complexes (Borgmann and Ralph 1983; 1984).

The use of models for heavy metals speciation is difficult for toxicologists not familiar with computer models. Many computer models have hardware requirements that are not usual in personal computers (i.e. the US EPA's MINTEQ model needs a 8087 mathematical coprocesor). General speciation models are required in natural waters, because factors like absortion and humic acid complexes must also be considered. But in bioassays for experimental toxicity purposes, speciation may be accomplished by handling only homogeneous equilibria in solution (Chakoumakos et al. 1979).

This paper is an attempt to provide a simple computer program for both total and ion copper speciation, with low hardware requeriments. This program can be used and expanded by users without any knowledge about water quality modelling.

MATERIAL AND METHODS

The program was developed as an interative one and was written in "generic" BASIC. The model calculates the chemical equilibria for carbonate, then for copper, calcium and magnesium. The adequacy of the result is tested comparing the total concentrations with the sum of the concentrations of each specie (copper ion, three copper hydroxides and three copper carbonates). The

user selects the maximum error that the program can accept. Equilibria equations appear in the model as algebraic equations where the variables are the molar concentrations. The model uses the equations and constants described by Chakoumakos et al. (1979), but both can be easily changed.

The adequacy of the model has been tested comparing the results described by Chakoumakos et al. (1979) with the results obtained using this model with a selected error of 0.5 %.

RESULTS AND DISCUSSION

Copper speciation is calculated from values of alkalinity (total carbonates), pH, calcium, magnesium and total dissolved copper. Both molar or ppm concentrations can be used. Data can be entered manually or stored in a DATA file.

Results obtained with this program were similar to those described by Chakoumakos et al. (1979) (Table I). These results are also useful as a sample output in order to test the installation of the program.

The source listing of the program appears in Table 2. It is easy to make changes in this source listing in order to change the equilibria constants or to include other equations. Table 3 shows an example of the changes that are needed to include a copper-amino acid complex.

At times it is important to make the inversed calculations (i.e. copper speciation when copper ion concentrations are available), that is not posible to make in other speciation programs. Table 4 shows the changes that are needed in the program for copper ion speciation.

Table 2. Source listing for total copper speciation.

```
2 CLS
5 REM PROGRAM FOR TOTAL COPPER SPECIATION
6 REM THIS PROGRAM CALCULATES THE DISSOLVED COPPER
SPECIATION BASED UPON PHISICO-CHEMICAL PARAMETERS
ENTERED BY THE USER
7 REM PROGRAM AUTOR J.V. TARAZONA
8 REM INSTITUTO NACIONAL DE INVESTIGACIONES AGRARIAS,
SPAIN
9                          CLS:PRINT                    "
**********************************************************
************
                              INSTITUTO    NACIONAL    DE
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Table 1. Results described by Chakoumakos et al. (1979) (C), and obtained by this program (P), for copper speciation in nine different conditions (Concentrations in Moles (x 10^6)/Liter).

	C	P	C	P	C	P	C	P	C	P	C	P	C	P	C	P
Cu_T	578		293		57.9		365		255		116		143		69.9		24.7	
Ca_T	124000		45900		12000		161000		50900		19700		143000		61600		15000	
Mg_T	80700		23900		6170		42400		32100		11100		16500		12800		11500	
Inorganic C	371000		354000		373000		164000		152000		159000		55400		48100		42300	
pH	7.73		8.54		8.07		7.61		7.40		8.32		7.53		7.57		7.64	
CO_3^{2-}	871	871	5510	5513	2000	1995	289	289	162	162	1510	1512	80.7	80.7	78.0	78.0	81.7	81.7
$Ca^{2+}(x10^{-3})$	118	118	41.3	41.3	11.3	11.3	158	158	50.1	50.1	19.0	19.0	142	142	61.3	61.3	14.9	14.9
$CaOH^+$	1.27	1.27	2.86	2.85	.264	.264	1.28	1.28	.251	.251	.792	.790	.961	.961	.454	.454	.130	.130
$CaHCO_3^+$	4110	4107	1400	1403	409	409	2390	2393	692	692	294	293	724	724	275	275	59.7	59.7
$CaCO_3$	1460	1457	1400	1403	409	409	2390	2393	692	692	294	293	724	724	275	275	59.7	59.7
Mg^{2+}	77800	77767	22300	22263	5890	5888	41700	41739	31700	31668	10800	10803	16400	16413	12700	12740	11500	11450
$MgOH^+$	15.9	15.9	29.4	29.3	2.63	2.63	6.46	6.46	3.02	3.02	8.59	8.58	2.11	2.11	1.80	1.80	1.90	1.90
$MgHCO_3^+$	2400	2404	675	675	191	191	563	564	390	390	149	149	74.5	74.5	51.0	51.0	40.9	40.9
$MgCO_3$	514	514	931	931	89.1	89.1	91.4	91.4	39.0	39.0	124	124	10.0	10.0	7.54	7.54	7.10	7.10
Cu^{2+}	8.78	8.81	.319	.318	.313	.312	13.9	14.0	18.5	18.4	.385	.384	12.1	12.2	5.47	5.44	1.58	1.58
$CuOH^+$	9.41	9.44	2.21	2.20	.733	.731	11.3	11.4	9.26	9.24	1.61	1.60	8.21	8.24	4.05	4.03	1.38	1.38
$Cu(OH)_2$	121	122	183	183	20.6	20.6	111	111	55.8	55.7	80.5	80.2	66.7	67.0	36.1	35.9	14.4	14.4
$Cu_2(OH)_2^{2+}$	.111	.112	.00612	.00610	.000676	.000673	.161	.162	.108	.107	.00324	.00322	.0848	.856	.0207	.0205	.00238	.00239
$CuHCO_3^+$	2.84	2.85	.101	.101	.106	.106	1.97	1.98	2.38	2.38	.0556	.0554	.577	.580	.229	.228	.0590	.0591
$CuCO_3$	430	431	98.8	98.6	35.1	35.0	226	227	169	168	32.8	32.6	55.1	55.4	24.0	23.9	7.26	7.28

INVESTIGACIONES AGRARIAS

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10 PRINT "                    DEPARTMENT  OF  TOXICOLOGY,
MADRID,    SPAIN
11  PRINT:PRINT "WELCOME TO THE TOTAL COPPER SPECIATION
PROGRAM"
12 PRINT:PRINT "THIS  PROGRAM  CALCULATES THE INORGANIC
FORMS OF COPPER BASED UPON DATA SUPPLIED BY THE USER"
13 PRINT:PRINT "SIMPLY ANSWER THE QUESTIONS"
14 PRINT:PRINT "IF YOU WANT, YOU CAN ENTER ALL DATA  IN
SUBROUTINE 10000"
15  PRINT:PRINT  "YOU  CAN CHOOSE THE MAXIMUM ERROR YOU
WANT ADMIT"
16 DIM CA(10),C(10),CB(4),CC(4)
17 DIM CD(4),CM(4),CE(7),CU(7)
20 PRINT:PRINT:PRINT  "ARE  DATA  ENTERED IN SUBROUTINE
10000? (Y/N)":INPUT A$
30 IF A$="Y" THEN GOTO 10000
35 PRINT "ENTER MAXIMUM ERROR FOR  DIFFERENCES  BETWEEN
REAL AND CALCULATED CONCENTRATIONS":INPUT E
40  PRINT  "ARE  DATA EXPRESED AS MOLAR CONCENTRATIONS?
(Y/N)": INPUT B$
50 IF B$="Y" THEN GOTO 1000
60 CLS:PRINT "INPUT CONCENTRATIONS (ppm) OF:"
70 PRINT "CALCIUM":INPUT C
80 PRINT "MAGNESIUM":INPUT M
90 PRINT  "ALCALINITY OR CARBONATES+BICARBONATES":INPUT
A
100 PRINT "pH":INPUT P
110 PRINT "TOTAL COPPER":INPUT CU
120 CA=LOG(C/40000!)/LOG(10)
130 MA=LOG(M/24300)/LOG(10)
140 AA=LOG(A/61000!)/LOG(10)
150 CUA=LOG(CU/63540!)/LOG(10)
160 CB=CA:MB=MA:AB=AA:CUB=CUA
170 GOTO 1100
1000 CLS:PRINT"INPUT MOLAR CONCENTRATIONS OF:"
1010 PRINT "CALCIUM":INPUT C
1020 PRINT "MAGNESIUM":INPUT M
1030  PRINT  "ALCALINITY  OR  CARBONATES+BICARBONATES":
INPUT A
1040 PRINT "pH":INPUT P
1050 PRINT "TOTAL COPPER":INPUT CU
1060 CA=LOG(C)/LOG(10):CB=CA
1070 MA=LOG(M)/LOG(10):MB=MA
1080 AA=LOG(A)/LOG(10):AB=AA
1090 CUA=LOG(CU)/LOG(10):CUB=CUA
1095 REM LETTERS ARE  CONCENTRATIONS,  LETTERS  +A  ARE
LOGARITHMES  OF  MOLAR  CONCENTRATIONS,  LETTERS +B ARE
CONTROL COPIES
1100 REM
```

```
1102 AM=10^AB:CM=10^CB:MM=10^MB:CUM=10^CUB
1103 E1=AM*E/100:E2=CM*E/100:E3=MM*E/100:E4=CUM*E/100
1110 CA(1)=AA
1111 PRINT "ESTIMATING VALUES FOR CARBONATE SPECIATION"
1120 CA(2)=CA(1)-10.33+P
1130 CA(3)=CA(2)-2*P+16.68
1140 CA(4)=CA(2)+CA-P+11.33
1150 CA(5)=CA(2)+CA+3.15
1160 CA(6)=CA(2)+MA-P+11.28
1170 CA(7)=CA(2)+MA+2.88
1175 GOTO 6000
1180 CA(8)=CA(2)+CUA-P+12.3
1190 CA(9)=CA(2)+CUA+6.75
1200 CA(10)=2*CA(2)+CUA+9.92
1205 CT=0
1210 FOR I=1 TO 10
1220 C(I)=10^CA(I):CT=CT+C(I)
1230 NEXT I
1235 GOTO 3000
1260 CLS:LPRINT"                          RESULTS"
1270 LPRINT " MOLAR CONCENTRATIONS"
1280 LPRINT "HCO3-    =";C(1);"      Ca++         =";CC(1)
1290 LPRINT "CO3--    =";C(2);"      CaOH+        =";CC(2)
1300 LPRINT "H2CO3    =";C(3);"      Mg++         =";CM(1)
1310 LPRINT "CaHCO3+  =";C(4);"      MgOH+        =";CM(2)
1320 LPRINT "CaCO3    =";C(5);"      CuOH+        =";CU(2)
1330 LPRINT "MgHCO3+  =";C(6);"      Cu(OH)2      =";CU(3)
1340 LPRINT "MgCO3    =";C(7);"      Cu2(OH)2++   =";CU(4)
1350 LPRINT "CuHCO3+  =";C(8);"      Cu(CO3)2--   =";C(10)
1360 LPRINT "CuCO3    =";C(9);"      Cu++         =";CU(1)
1375 IF A$="Y" THEN GOTO 10000
1380 END
3000 REM ESTIMATE CALCIUM SPECIATION
3001 PRINT"ESTIMATING VALUES FOR CALCIUM SPECIATION"
3010  REM   DIMENSIONATED   VARIABLES:  CB=LOGARITHMES,
CC=MOLAR CONCENTRATIONS
3020 CB(1)=CA
3030 CB(2)=CA+P-12.7
3040 CB(3)=CA(4)
3050 CB(4)=CA(5)
3060 CBT=0
3070 FOR I=1 TO 4
3080 CC(I)=10^CB(I)
3090 NEXT I
3095 CBT=CC(1)+CC(2)+CC(3)+CC(4)
4000 REM ESTIMATE MAGNESIUM SPECIATION
4001 PRINT"ESTIMATING VALUES FOR MAGNESIUM SPECIATION"
4010  REM   DIMENSIONATED   VARIABLES:   CD=LOGARITHMES
,CM=MOLAR CONCENTRATIONS
4020 CD(1)=MA
4030 CD(2)=MA+P-11.42
4040 CD(3)=CA(6)
4050 CD(4)=CA(7)
```

```
4060 CDT=0
4070 FOR I=1 TO 4
4080 CM(I)=10^CD(I):CDT=CDT+CM(I)
4090 NEXT I
5000 REM TEST THE ADEQUACY OF CO3H-,Ca++ AND Mg++
CONCENTRATIONS
5010 IF ABS(CT-AM)<E1 AND ABS(CBT-CM)<E2 AND
ABS(CDT-MM)<E3 AND ABS(CUT-CUM)<E4 THEN GOTO 1260
5025 IF CUT>CUM THEN CUA=LOG(CU(1)-CU(1)*.1)/LOG(10)
5030 IF CUT<CUM THEN CUA=LOG(CU(1)+CU(1)*.1)/LOG(10)
5035 CA=LOG(10^CB+CC(1)-CBT)/LOG(10)
5045 MA=LOG(10^MB+CM(1)-CDT)/LOG(10)
5050 AA=LOG(10^AB+C(1)-CT)/LOG(10)
5055 GOTO 1110
6000 REM ESTIMATE COPPER SPECIATION
6001 PRINT "ESTIMATING VALUES FOR COPPER SPECIATION"
6010 CE(1)=CUA
6020 CE(2)=CUA+P-7.7
6030 CE(3)=CUA+2*P-14.32
6040 CE(4)=2*CUA+2*P-10.3
6050 CE(5)=CA(2)+CUA-P+12.3
6060 CE(6)=CA(2)+CUA+6.75
6070 CE(7)=CA(2)*2+CUA+9.92
6075 CUT=0
6080 FOR I=1 TO 7
6090 CU(I)=10^CE(I):CUT=CUT+CU(I)
6100 NEXT I
6110 IF CUM-CUT>CUM*.9 THEN CUA=CUA+1:GOTO 6000
6120 IF CUM-CUT>CUM*.5 THEN CUA=LOG(CU(1)+CU(1)*.1)/LOG
(10):GOTO 6000
6130 IF CUM-CUT>CUM*.2 THEN CUA=LOG(CU(1)+CU(1)*.01)/LO
G(10):GOTO 6000
6140 IF CUT-CUM>CUM*.9 THEN CUA=LOG(CU(1)-CU(1)*.5)/LOG
(10):GOTO 6000
6150 IF CUT-CUM>CUM*.5 THEN CUA=LOG(CU(1)-CU(1)*.05)/LO
G(10):GOTO 6000
6160 IF CUT-CUM>CUM*.2 THEN CUA=LOG(CU(1)-CU(1)*.005)/L
OG(10):GOTO 6000
6170 IF CUM+CU(1)<CUT THEN CU(1)=CU(1)-CU(1)*.01: CUA=L
OG(CU(1))/LOG(10):GOTO 1110
6175 GOTO 1180
10000 REM ENTER concentration (M=molar;P=ppm),calcium,
magnesium, alkalinity, pH, total dissolved copper,
maximum error (per cent)
10010 READ C$,C,M,A,P,CU,E
10020 IF C$="M" THEN GOTO 1060
10030 IF C$="P" THEN GOTO 120
10035 IF C$="FIN" THEN END
10040 PRINT "CONCENTRATION NOT ALLOWED, ABORTING....."
10050 END
10100 DATA M,.00124,.000807,.00371,7.73,.00000578,.5
10110 DATA M,.000459,.000239,.00354,8.54,.00000293,.5
10120 DATA FIN,0,0,0,0,0,0,0,0,0,0,0,0
```

Table 3. Source listing changes for including a copper-alanine complex in copper speciation.

```
17 DIM CD(4), CM(4), CE(8), CU(8)
1100 PRINT "ENTER  ALANINE  MOLAR CONCENTRATION": INPUT
ALANINE
1101 LALA = LOG (ALANINE)/LOG (10)
1365 LPRINT "ALA-Cu"          =";CU(8)
6072 CE(8) = CUA + LALA + 8.5
6080 fOR I=1 TO 8
```

Table 4. Source listing changes for copper ion speciation.

```
110 PRINT "COPPER ION": INPUT CU
1050 PRINT "COPPER ION": INPUT CU
1175 REM
1360 LPRINT "CuCO3     =" C(9);"  TOTAL COPPER    = ";CUT
4100 GOTO 6000
5010  IF  ABS (CT-AM) < E1 AND ABS (CBT-CM) <E2 AND ABS
(CDT-MM) <E3 THEN GOTO 1260
5025 REM
5030 REM
6105 GOTO 5000
```

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