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Sandia National Laboratories Environmental Fluid Dynamics Code: pH Effects User Manual

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Abstract

This document describes the implementation level changes in the source code and input files of Sandia National Laboratories Environmental Fluid Dynamics Code (SNL-EFDC) that are necessary for including pH effects into algae-growth dynamics. The document also gives a brief introduction to how pH effects are modeled into the algae-growth model. The document assumes that the reader is aware of the existing algae-growth model in SNL-EFDC. The existing model is described by James, Jarardhanam [1] and more theoretical considerations behind modeling pH effects are presented therein. This document should be used in conjunction with the original EFDC manual [2, 3] and the original water-quality manual [4].

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NOMENCLATURE

pH	Potential Hydrogen
CE-QUAL	Water-Quality Code
DOE	Department of Energy
EFDC	Environmental Fluid Dynamics Code
SNL-EFDC	Sandia National Laboratories Environmental Fluid Dynamics Code
SNL	Sandia National Laboratories

1. INTRODUCTION

The algae-growth model in SNL-EFDC is described using the governing equation in CE-QUAL [4, Eqn. 3.1]

$$\frac{\partial B}{\partial t} = \left(P - B_{\mathrm{M}} - P_{\mathrm{R}}\right)B + \frac{\partial}{\partial z}\left(w_{\mathrm{s}}B\right) + \frac{B_{\mathrm{L}}}{V}, \tag{1}$$

where B (g/m^3) is the biomass, t (days) is time, P (day^{-1}) is the production (growth) rate, B_{M} (day^{-1}) is the basal metabolic rate, P_{R} (day^{-1}) is the predation rate, w_{s} (m/day) is the settling velocity, z (m) is the vertical coordinate, B_{L} (g/day) represent the external loads such as deposition or sources, and V (m^3) is the model cell volume.

The model already includes decoupled multiplicative effects of nutrient limitation, $f(\nu)$, light limitation, $g(I)$, and temperature limitation, $h(T)$, that limit biomass production rate under non-optimal conditions, as shown in (2),

$$P = P_{\mathrm{M}}\, f(\nu)\, g(I)\, h(T) \tag{2}$$

where $0 \leq f(\nu) \leq 1$, $0 \leq g(I) \leq 1$, $0 \leq h(T) \leq 1$ and P_{M} (day^{-1}) is the maximum production rate under optimal conditions.

Decoupled effects of non-optimal pH, i(pH), is added to the model through a new multiplicative term in (3) as

$$P = P_{\mathrm{M}}\, f(\nu)\, g(I)\, h(T)\, i(\mathrm{pH}) \tag{3}$$

where $0 \leq i(\mathrm{pH}) \leq 1$. More background on the theory behind the addition of pH limitation in SNL-EFDC is available [5, Section 2.4].

Section 2 describes the various EFDC input files that need to be changed to enable the pH limitation feature and Section 3 describes the relevant source code changes.

2. INPUT FILE CHANGES

pH limitation is enabled when water-quality variable 22, corresponding to CO_2 is enabled (set to 1) in card C02A in `wq3dwc.inp` input file. Card C02A in `wq3dwc.inp` file with pH enabled is shown in Figure 1. pH of the growth media is calculated within SNL-EFDC using CO_2 concentrations following the theory described by [5, Section 2.4] and hence needs CO_2 water-quality variable enabled in `wq3dwc.inp`.

```
C-----------------------------------------------------------------------
C02A KINETIC BYPASS FLAGS
C      ONLY USED IF IWQLVL=1   (ISTRWQ(NV),NV=1,NWQV)
C      ISTRWQ = 0 - Skip Kinetics
C           1 - Compute Kinetics
C        !  1) CHC - cyanobacteria
C        !  2) CHD - diatom algae
C        !  3) CHG - green algae
C        !  4) ROC - refractory particulate organic carbon
C        !  5) LOC - labile particulate organic carbon
C        !  6) DOC - dissolved organic carbon
C        !  7) ROP - refractory particulate organic phosphorus
C        !  8) LOP - labile particulate organic phosphorus
C        !  9) DOP - dissolved organic phosphorus
C        ! 10) P4D - total phosphate
C        ! 11) RON - refractory particulate organic nitrogen
C        ! 12) LON - labile particulate organic nitrogen
C        ! 13) DON - dissolved organic nitrogen
C        ! 14) NHX - ammonia nitrogen
C        ! 15) NOX - nitrate nitrogen
C        ! 16) SUU - particulate biogenic silica
C        ! 17) SAA - dissolved available silica
C        ! 18) COD - chemical oxygen demand
C        ! 19) DOX - dissolved oxygen
C        ! 20) TAM - total active metal
C        ! 21) FCB - fecal coliform bacteria
C        ! 22) CO2 - carbon dioxide ! Enable for pH limitation.
C        ! 22) MAC - macroalgae
C02A   1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
       0  0  1  0  0  0  0  0  0  1  0  0  0  1  1  0  0  0  1  0  0  1  0
C-----------------------------------------------------------------------
```

Figure 1. Enable water-quality variable 22 (CO_2) in `wq3dwc.inp` to enable pH limitation.

If pH of the growth medium is available as a measured value, then SNL-EFDC can get those pH values through the atmospheric series input file, `aser.inp`. In such a case, `aser.inp` will have 9 columns instead of the usual 8 columns, and the last column contains the measured pH values. A section of `aser.inp` with pH values added as the 9th column is shown in Figure 2. SNL-EFDC reads pH values from `aser.inp` only when all half-saturation constants for CO_2, KHCO2*x*, in card C08 in wq3dwc.inp are set to negative values, as shown in Figure 3. For actual use of half-saturation constants of CO_2 in SNL-EFDC, such as in nutrient limitation calculations, the absolute value of KHCO2x is used. If KHCO2*x* is set as a positive number, then SNL-EFDC reads only 8 columns from aser.inp and pH would be calculated using CO_2 concentrations found in the growth medium.

```
C ** MASER TCASER    TAASER    IRELH    RAINCVT  EVAPCVT  SOLRCVT   CLDCVT
C ** IASWRAD REVC    RCHC      SWRATNF  SWRATNS   FSWRATF  DABEDT    TBEDIT
HTBED1  HTBED2
C ** TASER(M)  PATM(M)  TDRY(M)  TWET(M)  RAIN(M)  EVAP(M)  SOLSWR(M)
CLOUD(M)  PH(M)
1825 86400.000 0.000  1  1.1574E-05  1.1574E-05    1.000    1.000
0 1.5 0 1.4 .052 .3 2 19.6 0 .3
0.000 1000  10.09 0.9   0.0   0.0   0.00  0.0   7.96
0.010 1000  9.84  0.9   0.0   0.0   0.00  0.0   7.97
0.021 1000  9.58  0.9   0.0   0.0   0.00  0.0   7.97
0.031 1000  9.31  0.9   0.0   0.0   0.00  0.0   7.97
0.042 1000  9.09  0.9   0.0   0.0   0.00  0.0   7.98
0.052 1000  8.90  0.9   0.0   0.0   0.00  0.0   7.98
0.063 1000  8.74  0.9   0.0   0.0   0.00  0.0   7.98
0.073 1000  8.59  0.9   0.0   0.0   0.00  0.0   7.98
0.083 1000  8.47  0.9   0.0   0.0   0.00  0.0   7.98
0.094 1000  8.35  0.9   0.0   0.0   0.00  0.0   7.99
0.104 1000  8.25  0.9   0.0   0.0   0.00  0.0   7.99
0.115 1000  8.14  0.9   0.0   0.0   0.00  0.0   7.99
0.125 1000  8.05  0.9   0.0   0.0   0.00  0.0   7.99
0.135 1000  7.96  0.9   0.0   0.0   0.00  0.0   7.98
0.146 1000  7.88  0.9   0.0   0.0   0.00  0.0   7.98
0.156 1000  7.82  0.9   0.0   0.0   0.00  0.0   7.98
                                               └──> pH values
```

Figure 2. pH values in last column of aser.inp is read by SNL-EFDC when KHCO2*x* is set negative in wq3dwc.inp.

```
C-----------------------------------------------------------------------------
C08 ONE TITLE CARD FOLLOWS:
$$ C08 constant parameters for ALGAE (see Table 3-1) $$
C
C    KHNc = nitrogen half-saturation for cyanobacteria (mg/L)
C    KHNd = nitrogen half-saturation for algae diatoms (mg/L)
C    KHNg = nitrogen half-saturation for algae greens algae (mg/L)
C    KHNm = nitrogen half-saturation for macroalgae (mg/L)
C    KHPc = phosphorus half-saturation for cyanobacteria (mg/L)
C    KHPd = phosphorus half-saturation for algae diatoms (mg/L)
C    KHPg = phosphorus half-saturation for algae greens algae (mg/L)
C    KHPm = phosphorus half-saturation for macroalgae (mg/L)
C     KHS = silica half-saturation for algae diatoms (mg/L)
C    STOX = salinity at which microsystis growth is halved for cyanobacteria
C  KHCO2c = CO2 half-saturation for cyanobacteria (mg/L)
C  KHCO2d = CO2 half-saturation for algae diatoms (mg/L)
C  KHCO2g = CO2 half-saturation for algae greens algae (mg/L)
C  KHCO2m = CO2 half-saturation for macroalgae (mg/L)
C
C08   KHNc     KHNd     KHNg     KHNm     KHPc     KHPd     KHPg     KHPm     KHS
STOX  KHCO2c KHCO2d KHCO2g KHCO2m
      .01      .01      .01      .01     .001     .001     .002     .001     .05
1 -0.02772 -0.02772 -0.02772 -0.05
C-----------------------------------------------------------------------------
```

Figure 3. Set all half-saturation constants for CO_2, `KHCO2`*x*, to negative values in `wq3dwc.inp` to read measured pH values provided in `aser.inp`.

3. SOURCE CODE CHANGES

The code snippet from `WQSKE1.f90` in Figure 4 shows the calculation of pH limitation value and actual production rate. The global variables `WQPHDC`, `WQPHDD`, and `WQPHDG` store the pH limitation value that ranges between 0 and 1, for cyanobacteria, diatoms and green algae respectively. If water-quality variable 22 is not enabled (equal to 0) in `wq3dwc.inp`, then `WQPHDC`, `WQPHDD`, and `WQPHDG` are set to 1.0 and as a result pH limitation is not enabled. `WQPC`, `WQPD`, and `WQPG` store the actual production rates and they are calculated as the product of maximum production rate under optimal conditions (`WQPM`*x*), and nutrient limitation (`WQF1N`*x*), light limitation (`WQF2I`*x*), temperature limitation (`WQTDG`*x*) and pH limitation (`WQPHD`*x*) values.

The functional form of pH limitation values `WQPHD`*x* depends on hydrogen ion concentration (`WQPHHCONC`), and rate constants (`WQPHKH` and `WQPHKOH`) and is based on the function form of Mayo [6] as described elsewhere [1, Section 2.4]. The rate constants are themselves functions of instantaneous temperature (`TWQ`) in the growth medium.

```
IF(ISTRWQ(22)  >  0)THEN
  WQPHHCONC = 10.0**(-WQGPH(L,K)) ! Hydrogen ion concentration as function of pH
  WQPHKH = 1E-7*( -5.*(TWQ(L)**3) + 300.*(TWQ(L)**2) - 5000.*TWQ(L) + 3E4 ) !K_H as function of temp
  WQPHKOH = 1E-13*( 8.*(TWQ(L)**2) - 500.*TWQ(L) + 8000) ! K_OH as function of temp

  IF(WQKHCO2G<0.0)THEN
      WQPHHCONC = 10.0**(-CPH)
  ENDIF

  WQPHDC = WQPHHCONC / ( WQPHHCONC + WQPHKOH + ((WQPHHCONC**2)/WQPHKH) )
  WQPHDD = WQPHHCONC / ( WQPHHCONC + WQPHKOH + ((WQPHHCONC**2)/WQPHKH) )
  WQPHDG = WQPHHCONC / ( WQPHHCONC + WQPHKOH + ((WQPHHCONC**2)/WQPHKH) )
ELSE
  WQPHDC = 1.0
  WQPHDD = 1.0
  WQPHDG = 1.0
ENDIF

! *** Compute the Growth Rate based on Maximums & Limiting Factors
IF(IWQSTOX == 1)THEN
  WQF4SC = WQSTOX / (WQSTOX + SWQ(L)*SWQ(L)+1.E-12)
  WQPC(L)=WQPMC(IMWQZT(L))*WQF1NC*WQF2IC*WQTDGC(IWQT(L))*WQF4SC*WQPHDC
ELSE
  WQPC(L) = WQPMC(IMWQZT(L))*WQF1NC*WQF2IC*WQTDGC(IWQT(L))*WQPHDC
ENDIF
WQPD(L) = WQPMD(IMWQZT(L))*WQF1ND*WQF2ID*WQTDGD(IWQT(L))*WQPHDD
WQPG(L) = WQPMG(IMWQZT(L))*WQF1NG*WQF2IG*WQTDGG(IWQT(L))*WQPHDG
```

Figure 4: pH limitation code change in `WQSKE1.F90`.

The variable `WQGPH` stores the local pH of the growth medium and is computed from the $[CO_2]$ concentration in the medium using the relation

$$\mathrm{pH} = -\frac{1}{2}\log_{10}\left(k_w + k_1 k_h [\mathrm{CO}_2]\right). \tag{4}$$

The relation between pH and CO_2 concentration is derived in detail elsewhere [5, Section 2.4]. In Figure 5, if water-quality variable 22 corresponding to CO_2 is enabled, then pH (`WQGPH`) is calculated as a function of $[CO_2]$ concentrations (`WQV (L, K, 22)`).

```
!  Calculate local pH as function of CO2
IF(ISTRWQ(22)  >  0)THEN
WQGPH(L,K) = -0.5*LOG10(1.008E-14 + (1.7E-3*4.45E-7*WQV(L,K,22)))
XLIMPHC(L,K) = XLIMPHC(L,K) + WQGPH(L,K)
XLIMPHD(L,K) = XLIMPHD(L,K) + WQGPH(L,K)
XLIMPHG(L,K) = XLIMPHG(L,K) + WQGPH(L,K)
ENDIF
```

Figure 5: Calculation of pH as a function of CO2 concentration in `WQSKE1.F90`

If pH values of the growth medium are measured and available through `aser.inp` as described in Section 2, then SNL-EFDC reads pH values from the last column of `aser.inp`. When measured pH values are available, then half-saturation constant of CO_2 should be set to a negative value, and hence variable `WQKHCO2G` should be negative. If `WQKHCO2G` would be negative in the code snippet shown in Figure 4, then hydrogen ion concentration is calculated using `CPH`, which is in turn computed from measured pH values.

Computation of instantaneous pH values (`CPH`) from measured pH values available in `aser.inp` is done using a simple linear interpolation in time using the code snippet shown in Figure 6. pH value at current time (`CPH`) is calculated by doing a linear interpolation between the two pH values (`PHVAL(CPOS-1,1)` and `PHVAL(CPOS,1)`) that are closest in time to the current time (`CTIME`).

```
!  Calculate pH from aser.inp if WQKHCO2C is negative. Find current time,
!  look into TASER array and find the two times between which current time falls.
!  Then do a linear interpolation using the pH values at the above two times and
!  calculate the pH at the current time.
   ! Current time is calculated from global variable NITERAT couting the number
   ! of iterations.
    CTIME = NITERAT*dt/86400.
    CPOS = 0                     ! Index
    CPH = 0.0                    ! Interpolated pH
   ! Iterating through the 1st time column in aser.inp and finding the position
   ! where current simulation time lies.
    DO CITER=1,MASER(NASER)
      IF (TASER(CITER,NASER) > CTIME)THEN
         CPOS = CITER
         EXIT
      ENDIF
    ENDDO

   ! Linear interpolation (PHVAL read from aser.inp)
    CPH = PHVAL(CPOS-1,1) + (PHVAL(CPOS,1) - PHVAL(CPOS-1,1)) / (TASER(CPOS,1) - TASER(CPOS-1,1)) * (CTIME - TASER(CPOS-1,1))
```

Figure 6: Interpolation of measured pH values to get instantaneous pH values in `WQSKE1.F90`

The measured pH values are read from `aser.inp` and they are stored in the array PHVAL. The time when pH measurements were measured are read into the array TASER. The two pH values that are closest in time to the current time are obtained by iterating through the time values stored in TASER and stopping when current time becomes smaller than the time values obtained from TASER.

The reading of pH values from `aser.inp` is done in `input.for` using the code snippet shown in Figure 7. If the half-saturation constants for CO_2 are positive, then `aser.inp` has only 8 columns of data and a standard read is done. If the half-saturation constants for CO_2 are negative, then `aser.inp` has 9 columns of data and pH values are read from the 9^{th} column.

```
IF(MAX(WQKHCO2C,WQKHCO2D,WQKHCO2G,WQKHCO2M)<0.0)THEN !SCJ read in pH values from aser.inp last column
          DO M=1,MASER(N)
            READ(1,*,IOSTAT=ISO)TASER(M,N),PATM(M,N),TDRY(M,N),
     &        TWET(M,N),RAIN(M,N),EVAP(M,N),SOLSWR(M,N),CLOUD(M,N),
     &        PHVAL(M,N)
            IF(ISO.GT.0) GOTO 940
          ENDDO
        ELSE !SCJ standard read
          DO M=1,MASER(N)
            READ(1,*,IOSTAT=ISO)TASER(M,N),PATM(M,N),TDRY(M,N),
     &        TWET(M,N),RAIN(M,N),EVAP(M,N),SOLSWR(M,N),CLOUD(M,N)
            IF(ISO.GT.0) GOTO 940
          ENDDO
        ENDIF
```

Figure 7: In `input.for` measured pH values are read from 9th column in `aser.inp`, when all half-saturation constants for CO_2 are negative. If the half-saturation constants are positive, a standard read of `aser.inp` is done.

Table 1. Variable dictionary relevant to source code changes.

Variable Name	Description
`WQPHD`*x*	Global variables that store the actual pH limitation value ranging between 0 and 1 (*x* = C, D, G refers to Cyanobacteria, Diatoms, and Green algae, respectively).
`WQP`*x*	Actual production rate ranging between 0 and 1.
`WQPM`*x*	Maximum production rate under optimal conditions i.e., when all limitation factors are 1.
`WQF1N`*x*	Nutrient limitation factor ranging between 0 and 1.
`WQF2I`*x*	Light limitation factor ranging between 0 and 1.
`WQTDG`*x*	Temperature limitation factor ranging between 0 and 1.
`WQPHHCONC`	Hydrogen ion concentration calculated from local pH.
`WQPHKH`	Protonation rate constant.
`WQPHKOH`	Deprotonation rate constant.
`TWQ`	Local temperature of the medium.
`WQKHCO2`*x*	Half-saturation constant for CO_2 limited growth.
`WQGPH`	Local pH of the medium.
`WQV`	Water-quality variable and variable 22 contains the CO_2 concentrations in the medium.
`CPH`	pH found at current time, which is calculated by interpolating measured pH values obtained from atmospheric series file.
`PHVAL`	pH values read from atmospheric series input file.
`CPOS`	Position variable used while iterating through measured pH values, which identifies the two closest measured pH values that should be used in linear interpolation to get pH at current time.
`CTIME`	Variables that stores the current time during the simulation period.
`TASER`	Time information from atmospheric series input file.

4. CONCLUSION

The changes in source code (`wqske1.f90`, `input.for`) and input files (`wq3dwc.inp`, `aser.inp`) that are needed to include the effects of pH limitation into the algae-growth model have been described in this document. The reader of this document should incorporate the source code changes and build new binaries for testing pH limitation effects. The input files also should be changed so that pH limitation can be switched on. The reader can check the effects of pH limitations by running the model with and without pH limitations and looking into the difference in output variables of interest, like algae biomass.

5. REFERENCES

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