

MEMO : EN/INPA/DH-08
SUBJECT: A NEW VERSION OF WQ-ARM (OXY)
TO : PPA-ELE TRONORTE
FROM : JOHANNES SMITS
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1. INTRODUCTION

OXY HAS BEEN RENAMED, BECAUSE THE OLD NAME DOES NOT COVER ITS CAPACITIES ANY LONGER. WQ-ARM HAS BEEN CHOSEN AS A NEW NAME (PROVISIONALLY), WHICH IS SHORT FOR WATER QUALITY - ANALYSIS FOR RESERVOIR MANAGEMENT.

AT PRESENT WQ-ARM HAS TWO VERSIONS, THE STANDARD VERSION (WQARM) FOR OXYGEN, ORGANIC MATTER, NUTRIENTS AND PHYTOPLANKTON AND AN EXTENDED VERSION (WQARMEX) COMPRISING THESE PARAMETERS, METHANE, SULFIDE AND SULFATE. THE STANDARD VERSION HAS BEEN CALIBRATED ON TUCURUI RESERVOIR. THE EXTENDED VERSION HAS PASSED ITS FIRST PHASE OF DEVELOPMENT, FUNCTIONS CORRECTLY, BUT LACKS CALIBRATION AND NEEDS FURTHER ELABORATION.

THIS MEMO DESCRIBES THE ADDITIONAL FORMULATIONS OF THE EXTENDED VERSION. IN OTHER WORDS, IT DEALS WITH THE FORMULATIONS FOR METHANE, SULFATE AND SULFIDE. ONLY THE 'REACTIONS' ARE CONSIDERED. MASS TRANSPORT IS BEING CALCULATED ACCORDING TO THE SAME EQUATIONS AS USED FOR ALL THE OTHER PARAMETERS.

2. METHANE

THREE DIFFERENT PROCESSES ARE RELEVANT WITH RESPECT TO METHANE: 1) METHANOGENESIS, 2) METHANE OXYDATION, AND 3) VOLATILIZATION.

METHANOGENESIS OCCURS DURING THE DEGRADATION OF ORGANIC MATTER UNDER STRONG AND STEADY ANAEROBIC CONDITIONS. THE PRODUCTION OF METHANE IS POSSIBLE ONLY WHEN NO OXYGEN, NO NITRATE AND SMALL QUANTITIES OF SULFATE ARE PRESENT. METHANOGENESIS IS THEREFORE USUALLY RESTRICTED TO A BOTTOM ENVIRONMENT. THE FORMULATION USED IN THE MODEL IS:

$$DCM/DT = FM * RSOD * SOD * AB / V \quad (2.1)$$

IN WHICH,

CM = CONCENTRATION OF METHANE (IN OXYGEN EQUIV. MG O₂/L)
FM = MULTIPLIER (=1 IF O₂<0, NO₃<0.001 AND SO₄<0.001, =0 OTHERWISE)
RSOD = DEGRADATION RATE CONSTANT (1/D)
SOD = QUANTITY OF ORGANIC MATTER AT THE BOTTOM (G O₂/M²)
AB = BOTTOM SURFACE AREA OF A WATER LAYER (M²)
V = VOLUME OF A WATER LAYER (M³)

NOTICE THAT METHANOGENESIS ONLY OCCURS WHEN FM IS EQUAL TO 1. ACCORDINGLY, OXYGEN CONSUMPTION IN THE DEGRADATION OF ORGANIC MATTER AT THE BOTTOM ONLY TAKES PLACE WHEN FM IS EQUAL TO 0. TO ACHIEVE THIS, THE OXYGEN CONSUMPTION IS MULTIPLIED WITH (1-FM).

METHANE OXYDATION IS CONSIDERED TO BE A FIRST ORDER PROCES WITH RESPECT TO THE METHANE CONCENTRATION:

$$DCM/DT = -FO * RMOX * CM \quad (2.2)$$

IN WHICH,

RMOX = OXYDATION RATE CONSTANT (1/D)
FO = MULTIPLIER (=1 IF O₂>0 AND =0 OTHERWISE)

THE RATE CONSTANT IS A FUNCTION OF TEMPERATURE (SEE MEMO EN/INPA/DHL-4). INDICATIONS CAN BE FOUND IN LITERATURE, THAT THE RATE IS ALSO A FUNCTION OF THE OXYGEN CONCENTRATION. HIGH OXYGEN CONCENTRATIONS MAY INHIBIT THE OXYDATION OF METHANE SUBSTANTIALLY. THE BACTERIA INVOLVED IN THE OXYDATION SEEM TO BE MICRO-AEROPHILE, WHICH IMPLIES THAT THEY FUNCTION OPTIMALLY IN THE PRESENCE OF LOW (1 PPM) OXYGEN CONCENTRATIONS. HOWEVER, INHIBITION BY HIGH OXYGEN CONCENTRATIONS WILL BE IGNORED FOR THE TIME BEING. THIS ASPECT DESERVES ATTENTION IN FUTURE MODEL DEVELOPMENTS.

THE OXYDATION OF METHANE HAS BEEN ADDED TO THE OXYGEN BALANCE, USING EQUATION 2.2, WHICH NEED NOT TO BE ADJUSTED SINCE METHANE IS EXPRESSED IN OXYGEN UNITS.

VOLATILIZATION OF METHANE IMPLIES THE ESCAPE OF METHANE TO THE ATMOSPHERE. PRESENTLY, NO LITERATURE IS AVAILABLE WITH RESPECT TO THIS PROCESS. HOWEVER, IT SEEMS REASONABLE TO ASSUME, THAT THE RATE OF VOLATILIZATION CAN BE FORMULATED ON THE BASIS OF THE (OXYGEN) REAERATION EQUATION. THE SATURATION CONCENTRATION IS EQUAL TO ZERO, SINCE THE CONCENTRATION OF METHANE IN THE ATMOSPHERE IS EXTREMELY SMALL. THE EQUATION FOR VOLATIZATION THEN BECOMES:

$$DCM/DT = -RKL*CM*A/V \quad (2.3)$$

IN WHICH,

RKL = VOLATILIZATION RATE CONSTANT (M/D)
 A = SURFACE AREA OF THE UPPER WATER LAYER (M²)
 V = VOLUME OF THE UPPER WATER LAYER (M³)

THE RATE CONSTANT IS EQUAL TO THE REAERATION RATE CONSTANT AND THEREFORE A FUNCTION OF WINDSPEED AND TEMPERATURE. (SEE DH-REPORT KABA LEBO).

VOLATILIZATION OCCURS AT THE SPILLWAY TO AN EXTENT EQUAL TO THE EXTENT OF REAERATION.

METHANE IS ALSO CONSIDERED IN SUBROUTINE RIVER, DESCRIBING THE WATER QUALITY OF THE DOWN-STREAM RIVER. IT IS ASSUMED THAT THE SAME OXYDATION RATE CAN BE APPLIED HERE. THE VOLATILIZATION IS FORMULATED ACCORDING TO THE REAERATION EQUATION, THIS TIME USING A RATE CONSTANT, WHICH IS A FUNCTION OF THE FLOW VELOCITY. ALL ASSUMPTIONS HAVE TO BE VERIFIED IN FUTURE MODEL DEVELOPMENTS.

3. THE SULFUR BUDGET

SULFATE IS CONSUMED IN SULFATE REDUCTION (COUPLED TO DEGRADATION OF ORGANIC MATTER IN WATER AND BOTTOM) AND PRIMARY PRODUCTION, IT IS PRODUCED BY SULFIDE OXIDATION.

THE REDUCTION OF SULFATE OCCURS IN WATER UNDER ANAEROBIC CONDITIONS IF VERY SMALL QUANTITIES OF NITRATE ARE PRESENT. SINCE THIS PROCESS IS COUPLED DIRECTLY TO THE DEGRADATION (OXYDATION) OF ORGANIC MATTER, ITS FORMULATION IS DERIVED FROM THIS DEGRADATION PROCESS:

$$DC SU/DT = -FR*SR*FA*(ROD1*COD1+ROD2*COD2+RDET*CD) \quad (3.1)$$

IN WHICH,

CSU = CONCENTRATION OF SULFATE (MG S/L)
 COD1 = CONCENTRATION OF ORG. MATTER (LITTER) (MG O₂/L)
 COD2 = CONCENTRATION OF ORG. MATTER (FRESH PHYT) (MG O₂/L)
 CD = CONCENTRATION OF DETRITUS (MG O₂/L)
 FR = MULTIPLIER (=1 IF O₂<0 AND NO₃<0.001, =0 OTHERWISE)
 FA = MULTIPLIER (=1 IF O₂>0, =FAN OTHERWISE)
 SR = STOICHIOMETRIC CONSTANT SULFATE REDUCTION (G S/G O₂)

ROD1 = DEGRADATION RATE CONSTANT FOR COD1 (1/D)
ROD2 = DEGRADATION RATE CONSTANT FOR COD2 (1/D)
RDET = DEGRADATION RATE CONSTANT FOR CD (1/D)

IN ORDER TO PREVENT SIMULTANEOUS CONSUMPTION OF OXYGEN IN THE DEGRADATION OF ORGANIC MATTER, THIS PROCESS HAS BEEN MULTIPLIED WITH (1-FR) IN THE EQUATION FOR THE OXYGEN BALANCE. SULFATE REDUCTION AT THE BOTTOM IS DESCRIBED WITH:

$$DC\ SU/D T = -R\ SRB * C_{SU} * A_B / V \quad (3.2)$$

IN WHICH,
RSRB = SULFATE REDUCTION RATE CONSTANT AT THE BOTTOM (M/D)

THIS SIMPLE FIRST ORDER EQUATION HAS BEEN CHOSEN ON GROUNDS ANALOGOUS TO THOSE FOR DENITRIFICATION AT THE BOTTOM (SEE MEMO EN/INPA/DHL-4). THE RATE CONSTANT IS A FUNCTION OF TEMPERATURE.

THE CONSUMPTION OF SULFATE IN PRIMARY PRODUCTION IS PROPORTIONAL TO THE NET PRIMARY PRODUCTION:

$$DC\ SU/D T = -SS_3 * (PG - R) * CP \quad (3.3)$$

IN WHICH,
CP = PHYTOPLANKTON CONCENTRATION (MG O₂/L)
PG = GROSS PRIMARY PRODUCTION RATE CONSTANT (1/D)
R = RESPIRATION RATE CONSTANT (1/D)
SS₃ = STOICHIOMETRIC CONSTANT FOR SULFUR IN PHYTOPLANKTON (MG S/MG O₂)

MORE INFORMATION ABOUT THE PRIMARY PRODUCTION CAN BE ENCOUNTERED IN MEMO EN/INPA/DHL-4.

THE ONLY PRODUCTION PROCESS FOR SULFATE IS THE OXYDATION OF SULFIDE, WHICH IS USUALLY MAINLY A CHEMICAL PROCESS, ALTHOUGH BACTERIA MAY PLAY AN IMPORTANT PART. THE CHEMICAL OXIDATION IS VERY FAST. WITHIN A FEW HOURS ALL SULFIDE MAY HAVE DISAPPEARED FROM AN AEROBIC ENVIRONMENT. THE FORMULATION CHOSEN IN THE MODEL CORRESPONDS WITH THIS MORE OR LESS INSTANTANEOUS OXYDATION:

$$DC\ SU/D T = FO * C_{SI} * 0.5 / \Delta T_C \quad (3.4)$$

IN WHICH,
C_{SI} = SULFIDE CONCENTRATION (MG S/L)
FO = MULTIPLIER (=1 IF O₂>0, =0 OTHERWISE)
ΔT_C = TIMESTEP FOR PROCESSES (D)

THE OXYDATION OF SULFIDE IS TAKEN INTO ACCOUNT IN THE OXYGEN BALANCE WITH THE SAME EQUATION, DIVIDED BY A STOICHIOMETRIC CONSTANT SR.

SULFIDE IS PRODUCED IN SULFATE REDUCTION AND DEGRADATION OF ORGANIC MATTER. WITH RESPECT TO SULFIDE CONSUMPTION, OXYDATION IS CONSIDERED TO BE THE ONLY RELEVANT PROCESS FROM A

QUANTITATIVE POINT OF VIEW. THE OTHER IMPORTANT REMOVAL PROCESS IS SEDIMENTATION OF PRECIPITATED SULFIDES, MAINLY IRON(II) SULFIDE.

IT IS LOGICAL THAT THE SULFIDE PRODUCTION FROM THE REDUCTION OF SULFATE IS DESCRIBED WITH THE POSITIVE VERSION OF EQUATION 3.1:

$$DC\ SI/DT = FR*SR*FA*(ROD1*COD1+ROD2*COD2+RDET*CD) \quad (3.5)$$

THE PRODUCTION OF SULFIDE FROM ORGANIC MATTER IN WATER AND BOTTOM HAS BEEN FORMULATED IN THE FOLLOWING WAY:

$$DC\ SI/DT = SS1*ROD1*COD1+SS2*ROD2*COD2+SS3*RDET*CD+SSS*(RSOD+RREF)*SOD*AB/V \quad (3.6)$$

IN WHICH,

SS1 = STOICHIOMETRIC CONST. FOR SULFUR IN COD1 (G S/G O2)
 SS2 = STOICHIOMETRIC CONST. FOR SULFUR IN COD2 (G S/G O2)
 SSS = STOICHIOMETRIC CONST. FOR SULFUR IN SOD (G S/G O2)
 RREF = FRACTION OF REFRACTORY ORGANIC MATTER, PRODUCED IN THE DEGRADATION.

THE STOICHIOMETRIC CONSTANT SSS IS A FUNCTION OF TIME AND DEPTH. AN EXPLANATION HAS BEEN GIVEN IN MEMC EN/INPA/DHL-4. THE RELEASE OF SULFIDE BY DEGRADATION OF ORGANIC MATTER AT THE BOTTOM HAS BEEN FORMULATED VERY SIMPLY. IN REALITY THE RELEASE IS A FUNCTION OF THE PRESENCE OF OXYGEN ON THE ONE HAND AND THE IRON CONCENTRATION AND PH ON THE OTHER. THE PRESENCE OF OXYGEN NEAR THE BOTTOM CAUSES OXYDATION OF ANY SULFIDE RELEASED TO THE WATER. THE MODEL TAKES CARE OF THIS. THE PRESENCE OF LARGE QUANTITIES OF IRON AND A RELATIVELY HIGH PH WILL PREVENT THE RELEASE OF SULFIDE BY MEANS OF IRON(II)SULFIDE PRECIPITATION. THE SMALLER THE QUANTITY OF IRON AND THE LOWER THE PH THE MORE SULFIDE MAY ESCAPE TO THE OVERLYING WATER. THIS RELEASE LIMITING EFFECT IS NOT CONSIDERED IN THE PRESENT MODEL. ALTHOUGH THE RELEASE UNDER ANAEROBIC CONDITIONS IS COUNTERBALANCED BY SEDIMENTATION AND REMOVAL OF PRECIPITATED SULFIDE, THESE PROCESSES SHOULD BE CONSIDERED MORE CAREFULLY IN FUTURE MODEL DEVELOPMENTS.

THE OXIDATION OF SULFIDE IS DESCRIBED WITH THE NEGATIVE VERSION OF EQUATION 3.4:

$$DC\ SI/DT = -FO*CSI*0.5/DETC \quad (3.7)$$

THE MOST COMPLICATED PROCESS IS PRECIPITATION/SEDIMENTATION OF METAL SULFIDES, MAINLY IRON(II)SULFIDE. IT HAS BEEN AVOIDED TO INCORPORATE IRON INTO THE MODEL, BECAUSE IT IS SUBJECT TO COMPLICATED AND ONLY PARTIALLY UNDERSTOOD PROCESSES. HOWEVER, IT IS EVIDENT THAT THE PROCESS OF SEDIMENTATION CAN NOT BE IGNORED. A PROVISIONAL AND PARTIAL SOLUTION HAS BEEN FOUND IN THE FOLLOWING. ASSUME THAT: 1) THE MAXIMAL DISSOLVED SULFIDE CONCENTRATION CAN BE ESTIMATED ON THE BASIS OF AN AVERAGE IRON CONCENTRATION AND A KNOWN PH, AND 2) THE CHEMICAL CONDITIONS IN

THE HYPOLIMNION ARE RELATIVELY CONSTANT OVER DEPTH. UNDER THESE ASSUMPTIONS THE PRECIPITATION/SEDIMENTATION CAN BE DESCRIBED WITH:

$$DC\ SI /DT = -RSS*(CSIS2-CSIS1)*A \quad (3.8)$$

$$CSIS1 = CSI(I)-CSID \quad (3.9)$$

$$CSIS2 = CSI(I+1)-CSID \quad (3.10)$$

$$\text{IF } CSIS1 < 0, CSIS1 = 0.0 \quad (3.11)$$

$$\text{IF } CSIS2 < 0, CSIS2 = 0.0 \quad (3.12)$$

IN WHICH,

CSIS1 = PRECIPITATED SULFIDE CCNC. IN LAYER I (MG S/L)

CSIS2 = PRECIPITATED SULFIDE CCNC. IN LAYER I+1 (MG S/L)

CSID = DISSOLVED SULFIDE CONCENTRATION (MG S/L)

RSS = SEDIMENTATION RATE FOR PRECIPITATED SULFIDE (M/D)

A = UPPER SURFACE AREA OF LAYER I (M²)

CSID IS A (CONSTANT) INPUT PARAMETER AND SHOULD BE QUANTIFIED USING ESTIMATED IRON CONCENTRATION, PH, CONDITIONAL SOLUBILITY CONSTANTS, ETC. A MORE ACCURATE FORMULATION, TAKING INTO ACCOUNT THE SPACIAL AND TEMPORAL VARIABILITY OF THE SOLUBILITY OF IRON(II)SULFIDE, HAS TO BE PURSUED IN THE FUTURE.

THE SULFIDE CONCENTRATION IS NOT TAKEN INTO ACCOUNT AS SUCH IN THE DOWN-STREAM RIVER. THE CONCENTRATION IS DIVIDED BY STOICHIOMETRIC CONSTANT SR AND SUBTRACTED FROM THE OXYGEN CONCENTRATION IN THE OUTFLOW OF THE RESERVOIR. THEREFORE, IN THE RIVER SULFIDE IS CONSIDERED AS A NEGATIVE OXYGEN EQUIVALENT, WHICH AGREES WITH THE STANDARD VERSION OF THE MODEL.