

**A Geochemical Model of Redox Reactions in a Tropical Rain Forest  
Stream Riparian Zone:**

**DOC Oxidation, Respiration and Denitrification**

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## **DEDICATION**

To my late grandfather, Diego Jiménez Torres, Mayor of Fajardo, Puerto Rico  
from 1944 to 1960

To my parents, Jose Antonio Jiménez-Estrada and Miriam Rodriguez-Samalot de  
Jiménez

To the Blessed Virgin Mary

## ACKNOWLEDGEMENT

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# TABLE OF CONTENTS

DEDICATION.....	ii
ACKNOWLEDGEMENT.....	iii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	vii
INTRODUCTION.....	1
Redox Chemistry, DOC and Riparian Zones.....	1
Modeling Respiration, Denitrification and DOC Oxidation.....	4
Objectives.....	7
STUDY AREA.....	9
METHODS AND MATERIALS.....	11
Equilibrium Model.....	11
RESULTS.....	15
Geochemical Modeling Simulations.....	16
Products of Aerobic Respiration and Denitrification.....	18
DISCUSSION.....	23
Aerobic Respiration, Denitrification and DOC Oxidation.....	24
PH.....	26
Products of Aerobic Respiration and Denitrification.....	27
Patterns of Electron Donors and Acceptors.....	29
CONCLUSION.....	31
REFERENCES.....	36

## LIST OF TABLES

Table 1. Existing Well Data from Icacos Well Field (1988-1991).....	12
Table 2. Model Values for Initial Solution at Oxidic Zone (Wells I-23 and I-9).....	13
Table 3. Model Runs Loading Observed Mean Carbon to Equilibrium Solution only Accounting for Respiration .....	15
Table 4. Model Runs Loading Observed Mean Carbon and Nitrate to Equilibrium Solution .....	16
Table 5. Progression of Carbon Loads and Corresponding Oxygen Depletion Predicted by PHREEQC Compared to Mean Field Results.....	17
Table 6. Progression of Carbon Loads and Corresponding Nitrate and Oxygen Depletion Predicted by PHREEQC Compared to Mean Field Results.....	19, 20
Table 7. Interval of Carbon Oxidation with Pronounced C, N and O Activity. CH <sub>2</sub> O is Reacted in 30 Total Reaction Steps; 6.66 E-04 mol/L, 20mg/L; Each Step 2.22 E-05 mol/L, 0.67 mg/L.....	21
Table 8. Comparison of Reported Mean C Values and C Reacted in PHREEQC in Order to Reach Mean Field Oxygen and Nitrate Concentrations at Oxidic, Transitional and Anoxic zones.....	30

## LIST OF FIGURES

Figures 1. (a) Soil Profile of Well Field Transect with Well Locations and Depths. (b) Water Table Topography.....	10
Figure 2. PHREEQC Input file.....	14
Figures 3. Simulated pH (a) and pE (b) Values with respect to Reacted CH <sub>2</sub> O.....	22
Figure 4. Conceptual Model for N Processing in the Rio Icacos Basin.....	23
Figures 5. Simulated DO (a) and NO <sub>3</sub> (b) Values with respect to Reacted CH <sub>2</sub> O.....	33
Figures 6. Simulated N <sub>2</sub> (a), HCO <sub>3</sub> (b) and CO <sub>2</sub> (c) Values with respect to Reacted CH <sub>2</sub> O.....	34
Figure 7. Simulated Products of Respiration and Denitrification with respect to Reacted CH <sub>2</sub> O .....	35

## ABSTRACT

### **A Geochemical Model of Redox Reactions in a Tropical Rain Forest Stream Riparian Zone: DOC Oxidation, Respiration and Denitrification**

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A geochemical equilibrium model was used to quantify Dissolved Organic Carbon (DOC) electron donors during aerobic respiration and denitrification in a tropical stream riparian zone of the Luquillo Experimental Forest, Puerto Rico. DOC electron donors were measured across three general redox zones (Oxic: slope, Transitional: slope-riparian interface and Anoxic: riparian-floodplain) of the Icacos watershed. Model results suggest that nitrate and oxygen are completely reduced after approximately 10.1 mg/L of DOC have reacted with an initial ground water solution. In order to reach the observed mean oxygen concentration of 3.79 mg/L in the Oxic zone from the modeled equilibrium oxygen concentration of 9.46 mg/L, approximately 5.33 mg/L of DOC need to be oxidized. Additionally, 2.06 mg/L of DOC are oxidized in order to reach the observed mean oxygen concentration of 1.6 mg/L in the Transitional zone. In order to reach the observed mean Anoxic zone oxygen concentration of 1.27 mg/L from the observed mean Transitional zone oxygen concentration, an additional 0.309 mg/L of DOC are oxidized. From modeled equilibrium concentrations of oxygen (9.46 mg/L), approximately 8.8 mg/L of DOC are oxidized by oxygen before nitrate becomes more thermodynamically favorable as the electron acceptor and begins decreasing in concentration. Model simulations suggest that 1.19 mg/L of DOC reduce the observed mean nitrate concentration of 0.47 mg/L found in the Oxic zone to the lowest observed mean nitrate

concentration of 0.01mg/L found in the Transitional zone. Differences between the observed DOC concentrations in the field and the modeled DOC concentrations needed to reach zone levels of oxygen and nitrate suggest that field reported values for DOC electron donors could represent residual or unused electron donors. Results also indicate that between 8.68 mg/L and 10.7 mg/L of DOC oxidation, 0.42 mg/L of dissolved N<sub>2</sub> are produced, HCO<sub>3</sub> increases from 0.33 mg/L to 2.64 mg/L and CO<sub>2</sub> concentrations decrease from 13.8 mg/L to 13.7 mg/L before continuing to increase. This pronounced interval of DOC oxidation at which denitrification occurs and beyond which CO<sub>2</sub> continues increasing suggests a specific range at which denitrifiers metabolize versus a larger range at which a general heterotrophic population metabolizes.

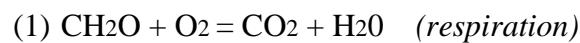
## INTRODUCTION

Despite the efforts of scientists in understanding dynamics of forest riparian denitrification, the accurate quantifying of electron donors and acceptors has proven to be a complicated and arduous task (Davidson and Seitzinger 2006, Groffman et al. 2006, Groffman et al. 2009, Inamdar 2006). One of the critical regulators of respiration and denitrification in the riparian zone that has been targeted in research is organic carbon. Along with anaerobic conditions and heterotrophic bacteria, the availability and concentration of this carbon electron donor are limiting factors in the attenuation of nitrate. Quantifying the products and reactants of organic carbon oxidation during respiration and denitrification in the slope-riparian zone is a ground water and biogeochemical modeling subject that still needs further exploration (Groffman et al. 2009, Rivett et al. 2008).

### *Redox Chemistry, DOC and Riparian Zones*

During respiration, aerobic bacteria utilize free oxygen, the optimum source of energy at the initial stages of the thermodynamic sequence of electron acceptors in order to oxidize organic material (Equation 1). Below the general threshold of 1-2 mg/L of dissolved oxygen, nitrate is then found to be thermodynamically favorable as the primary electron acceptor that heterotrophic bacteria use for carbon oxidation (Equation 2) (Rivett et al. 2008). At this stage, nitrate becomes reduced after accepting the electron from the carbon electron donor. Depending on the redox condition, nitrogen species with different

oxidation states (+ "x") emerge as products from the reaction. Denitrification occurs as nitrogen species move from a higher oxidation state in the form of NO<sub>3</sub><sup>-</sup> (+5) ultimately to inert N<sub>2</sub> gas (0). Intermediate species are NO<sub>2</sub><sup>-</sup> (+3), NO (+2) and N<sub>2</sub>O (+1). Other products formed from this process are bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbon dioxide (CO<sub>2</sub>) and sulphate SO<sub>4</sub><sup>2-</sup> ions. The fate of nitrate can also lead to ammonium NH<sub>4</sub><sup>+</sup> (-3 oxidation state) or microbial biomass, the former being known as dissimilatory nitrate reduction to ammonium (DNRA) (Korom 1992, Rivett et al. 2008). Sources of carbon during respiration and decay reactions include soil or geologic organic matter, plant residues, root exudates, manures and organic contaminants (Rivett et al. 2008). Once the organic matter has been broken down and is available to denitrifiers, nitrate can be reduced. According to Rivett, "subsurface environments with high concentrations of labile organic matter and reducing conditions are likely to be particularly significant zones for denitrification" (Rivett et al. 2008)



An abundance of DOC and organic material used during respiration and denitrification can be found in forest riparian zones (Cirmo and McDonnell 1997). Riparian zones in general are regions in the landscape that are bounded on one side by a freshwater surface body and a sloping terrain on the opposing side. They are where terrestrial and aquatic environments combine to form a complex biogeochemical

community (Groffman et al. 2009, Hill 1996). The topographic change into this transitional land-water area can be associated with sudden dramatic changes vertically and horizontally in hydrology, moisture conditions, soil profile, porosity, texture, hydraulic conductivity, organic matter content, redox potential (pE), pH, microbiological behavior and vegetation characteristics (Cirimo and McDonnell 1997). This type of setting fosters the necessary redox conditions, flow paths, bioavailability of carbon electron donors, vegetation uptake, and presence of heterotrophic behavior for denitrification to take place. The presence of reducing conditions also dissolves iron and aluminum oxides. In an oxic environment, the mineral surfaces of these metal oxides serve as sorption sites for DOC (Jacinthe et al. 2003). With fewer mineral surfaces for sorption sites under the reduced conditions of a poorly drained riparian environment, DOC becomes available to microbes for decay reactions. A study of organic carbon dynamics in a riparian aquifer of Rhode Island found that poorly drained soils with reducing conditions demonstrated more biological activity, nitrate reduction and CO<sub>2</sub> production than moderately well drained soils (Jacinthe et al. 2003).

Researchers have carried out studies and literature reviews on the specific behavior of organic carbon electron donor in riparian processes relative to its specific limiting capacity on denitrification, bio-availability, carbon dynamics, slope-riparian distribution patterns in relation to electron acceptors, soil horizon location, role in microbial behavior and thermodynamics (Boyer and Groffman 1996, Chestnut and McDowell 2000, Flite et al. 2001, Gold et al. 1998, Hedin et al. 1998, Hill 1996, Hill and Cardaci 2004, Kalbitz et al. 2003, Marschner and Kalbitz 2003, Rivett et al. 2008, Robertson and Schiff 2008). Field experiments have also identified hydrologic flow paths as a key factor controlling

electron donor and acceptor dynamics in riparian zone denitrification (Cirimo and McDonnell 1997, Devito et al. 2000, Hill 1990, McDowell et al. 1992, Vidon and Hill 2004). Studies have also observed denitrification in patches of organic material from a riparian forest aquifer in Rhode Island, USA and in hotspots at depths of only a few mm in a soil column study of river marginal wetlands in test sites at SW England (Flynn et al. 1999, Gold et al. 1998, Jacinthe et al. 1998). A study of soil core from a no-till continuous corn field plot containing Beltsville silt loam at the University of Maryland Plant Research Farm found that 0.08 g of plant detritus housed 85% of denitrification activity in the first 5cm of a 15cm core in (Parkin 1987). This study also found that soil denitrification microsites were dispersed in a patchy manner. Trudell found that denitrifiers in a shallow unconfined sand aquifer of the Rodney, Ontario test site could be found between the depths of 1.2 and 1.8 meters (Trudell et al. 1986).

### ***Modeling Respiration, Denitrification and DOC Oxidation***

Previous studies have modeled denitrification in both land and water environments at field, watershed and regional ecosystem scales utilizing mechanistic and process based models, including DAYCENT, DNDC, EPIC, GLEAMS, SWAT, CREAMS, SWRRB, QUAL2E, ANIMO, DRAIMOND, RHYESSys and INCA (Band et al. 2001, Boyer et al. 2006). Modelers have also carried out ground water nitrate transport and denitrification studies in agricultural riparian zones and forest stream hyporheic zones at field and catchment scales utilizing ground water modeling programs such as MODFLOW and MT3DMS (Schilling et al. 2007, Schilling et al. 2006, Shibata et al.

2004, Wriedt et al. 2007). Remote sensing techniques and GIS have been utilized to analyze denitrification and trace gas fluxes at plot, reach, basin, landscape and regional modeling scales (Madden 2004, Rassam et al. 2008, Wang et al. 2009, Wang et al. 2010). While these various modeling techniques have merit and have contributed to the denitrification and nutrient cycling knowledge base, denitrification research could benefit from finer scale rigorous modeling techniques at the column, plot and field scales. (Boyer et al. 2006, Groffman et al. 2009).

Higher resolution modeling techniques have addressed carbon oxidation, respiration and denitrification processes in the riparian zone. Utilizing numerical reactive transport models and coupled geochemical and transport models, studies have explored the role of electron donors and acceptors in ground water aquifers and in riparian zones with respect to hydrologic flow paths. (Chen and MacQuarrie 2004, Kinzelbach et al. 1991, Miotlinski 2008). In order to study nitrates and related changes in agricultural practices involving a glacial outwash aquifer of west-central Minnesota, Puckett and Cowdery examined denitrification and the role of carbon electron donor in redox processes along flow paths utilizing the biogeochemical model NETPATH and hydrologic models MODFLOW and MODPATH. The NETPATH model utilizes a “reverse-reaction process that predicts the net amount of various minerals or gas phases that must enter or leave solution to explain the observed changes in water chemistry between two points on a flow path”(Puckett and Cowdery 2002). Approximately 66.5% of the net increase in C was found to be the product of nitrate and oxygen reduction by the oxidation of organic material. Nitrate and oxygen reduction accounted for 92% and 8% respectively of organic C oxidation (Puckett and Cowdery 2002). O<sub>2</sub> reduction took

place in the first 3 to 4m of the saturated zone. Denitrification took place in the next 3 to 4 m thick zone below the area of respiration. In a study of an agricultural region of Southeastern Wisconsin, redox reactions involving nitrate along shallow groundwater flowpaths were modeled utilizing a forward modeling technique of the geochemical model PHREEQC. In this model, a closed aqueous phase system reacts to equilibrium (no gas or mineral phase equilibria) after incremental additions of CH<sub>2</sub>O leading to N<sub>2</sub> production. The study found that after reacting 0.17 mmol and later 0.34 mmol of CH<sub>2</sub>O, the system had depleted oxygen and nitrate respectively (Saad et al. 1998). A seminal geochemical modeling study of denitrification in a shallow unconfined sand aquifer was conducted by solving a system of equations using the Newton-Raphson numerical method (Trudell et al. 1986). This study confirmed in-situ field injection results of HCO<sub>3</sub><sup>-</sup>-bicarbonate and demonstrated that for every mmole of nitrate denitrified, 2.59 mmole HCO<sub>3</sub><sup>-</sup> were produced. This value corresponded with the theoretical value of 2.645 mmole HCO<sub>3</sub><sup>-</sup> for every mmole of nitrate denitrified. Another study in a forested area of Jutland, Denmark modeled nitrate reduction in a shallow unconfined sandy aquifer utilizing an equilibrium approach available in PHREEQE. Electron transfers in the redoxcline were modeled by adding ground water with electron acceptors (beginning with O<sub>2</sub> and then O<sub>2</sub> and nitrate) to sediment with pyrite, the most important electron donor in the study. The model consisted of a two-layer modeling column with “an oxidized layer of 20 cells in equilibrium with goethite and a reduced layer of 20 cells in equilibrium with both pyrite and goethite”(Postma et al. 1991). Kedziorek, Geoffriau and Bourg were able to identify the specific type of carbon electron donor involved in the oxidation of organic material during infiltration of the Lot riverbank in Aveyron, France

by clever usage of the MIX function in PHREEQC (Kedziorek et al. 2008). The researchers were able to identify the amounts of biodegraded organic material or corresponding electron acceptors consumed by subtracting the observed redox species values along the flow path from the theoretical MIX calculated (non-reacted) values of the same species. They were able to deduce that the quantity of DOC degraded was not enough to be solely from river infiltration and concluded that some of the carbon electron donor came from a secondary source in the form of SOC that had gone through hydrolysis. In 2004, Skubinna identified carbon as a primary electron donor in the evaluation of denitrification in North Dakota's ELK Valley Aquifer through an effective use of several PHREEQC keyword functions. They included a MIX function which addresses the dilution of solutions, an EXCHANGE function that accounts for cation exchange capacity and EQUILIBRIUM PHASES which relates to saturation index and the amount of moles of that phase which are to react with a solution (Skubinna 2004). The study used preexisting data from in-situ mesocosm studies in order to simulate the mixing and reaction of control and research solutions containing bromide and bromide-nitrate solutions respectively, which in turn would reveal if the nitrate was being lost to bromide dilution or if nitrate was in fact attenuating as a result of reaction with a preexisting equilibrium phase such as organic carbon.

### ***Objectives***

Utilizing field data results of research carried out by William H. McDowell, William B. Bowden and Clyde E. Asbury from 1988-1991 (Mcdowell et al. 1992) at the

Icacos site, the objectives of the equilibrium geochemical model presented here are to (1) quantify the amount of carbon electron donor needed to reduce observed mean nitrate and oxygen values across three general redox zones of the Icacos watershed (Oxic: slope, Transitional: slope-riparian interface and Anoxic: riparian-floodplain) and (2) quantify specific products of these reactions ( $\text{N}_2$ ,  $\text{HCO}_3$  and  $\text{CO}_2$ ).

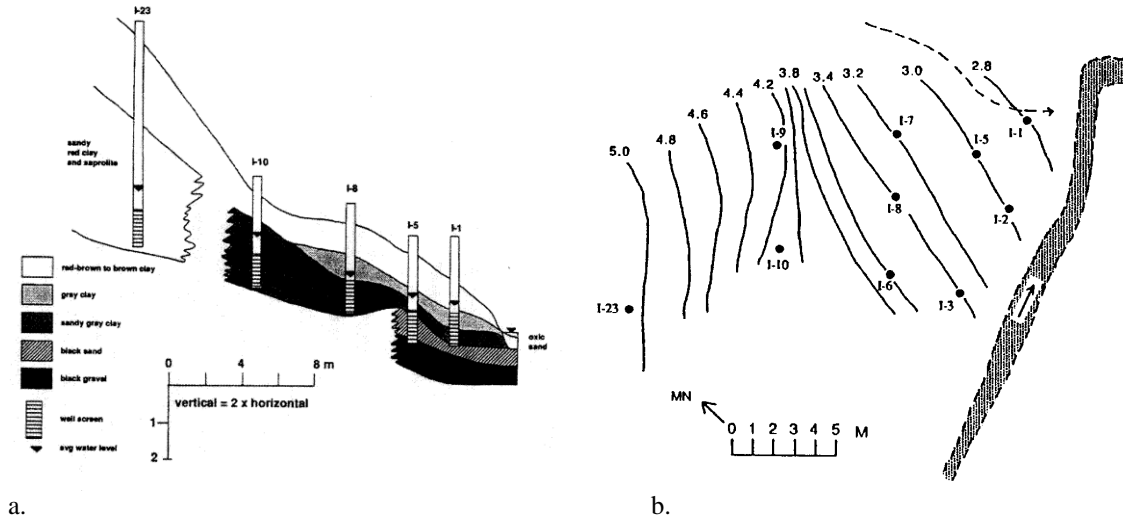
## STUDY AREA

Field data were taken from a well field located on a small floodplain of a tributary connecting to the Rio Icacos of the Luquillo Experimental Forest, Puerto Rico. The well field stands at an elevation of 620 m above MSL and is 12.4 ha. (Figure 1) The Luquillo Experimental Forest, ranging in elevation from 200 to 1000m, is categorized within the Holdridge Life Zone System as subtropical moist, wet, lower montane wet and lower montane rain. The vegetation at the Icacos well field site consists of palms (*Prestoea Montana*) in the floodplain and in the higher upslope topographic regions, vegetation consisting of *Cyrilla racemiflora*. At least 10 hand augered wells (augered with a 3.7 cm bucket auger) have been installed at stream bank, floodplain and upslope (along the flanking ridge) positions to depths of 180 cm and 210 cm forming the Icacos well field.

While stream channel substrate consists of sand with intermittent boulders, the Rio Icacos drainage basin is underlain by quartz diorite bedrock. Utuado clays (Inceptisols) make up the soils at the Icacos site (McDowell et al. 1992). According to McDowell, these soils can be characterized as having

“ strong vertical zonation in texture and redox status in the floodplain. Oxidized clays at the surface graded to reduced clays and very reduced sands and gravel at depths of 1.8-2.1m below the surface. In upslope sites, surface soils were oxidized (red and yellow) clays, grading to red sand and saprolite at depths greater than 2.5 m. In both floodplain and upslope soils, earthworm tubes were commonly observed at depths of 30 cm or more....saturated hydraulic conductivities near the wells were about  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  cm/sec...conductivity of stream side wells tend to be higher than conductivity at upslope wells” (McDowell et al. 1992).

Figures 1. a. Soil profile of well field transect with well locations and depths. b. Water table topography. (Mcdowell et al. 1992)



In the past 25 years, researchers have carried out carbon and nitrogen studies in the slope-riparian and hyporheic zones of the Icacos watershed basin. Specific topics include characterization of subsurface solute patterns, nitrate reduction, N<sub>2</sub>O gas fluxes, the particular behavior of NH<sub>4</sub><sup>+</sup>, hydrologic and geomorphic controls on related fluxes and estimation of these fluxes at various scales (Bowden et al. 1992, Chestnut and McDowell 2000, Madden 2004, Mcdowell et al. 1992, McSwiney et al. 2001).

## METHODS AND MATERIALS

### *Equilibrium Model*

The geochemical model PHREEQC was utilized for this study. PHREEQC stands for “ph-redox-equilibrium-equations”. It is a geochemical model derived from an ion-association aqueous model that is written in the C programming language. It is capable of simulating system geochemical reactions that include: “mixing of waters with different compositions, imposing net irreversible reactions to solution, dissolving and precipitating phases to achieve equilibrium with the aqueous phase, evaluating temperature effects, ion-exchange equilibria, surface-complexation equilibria, fixed pressure gas-phase equilibria, advective transport, kinetically controlled reactions with user-defined rate expressions, solid-solution equilibria, variation of the number of exchange or surface sites in response to the dissolution or precipitation of a mineral or kinetic reactant, 1D diffusive or dispersive transport, speciation and saturation-index calculations, 1D solute transport and batch reactions” (Mastrolo 2009, Parkhurst et al. 1999).

As discussed earlier in this paper, there are critical areas of denitrification that can occur at organic patches in riparian soil horizons through which the path of water flows. (Gold et al. 1998, Jacinthe et al. 1998, Parkin 1987). Conceptually, PHREEQC is being utilized to specifically model the oxidation of organic carbon in a scenario where the DOC of these patchy zones or hotspots reacts with the path of water flowing across three redox zones of the Iacos watershed. The redox zones consist of an Oxic zone found in the slope region of the topo-sequence, a Transitional zone, where the slope breaks in the

topography to form the slope-riparian interface and an Anoxic zone consisting of a riparian or floodplain zone that ultimately ends at the stream bank (Figure 1 and Table 1).

**Table 1. Existing Geochemical Data from Icacos Well field (1988-1991): Means by Redox Zones**

<b>Zone</b>	<b>Wells</b>	<b>C (mg/L)</b>	<b>C (mol/L)</b>	<b>O<sub>2</sub> (mg/L)</b>	<b>O<sub>2</sub>(mol/L)</b>	<b>NO<sub>3</sub> (mg/L)</b>	<b>NO<sub>3</sub> (mol/L)</b>	<b>pH</b>
<b>Oxic (Slope)</b>	<b>I-23, I-9</b>	<b>.48</b>	<b>1.6 E-05</b>	<b>3.79</b>	<b>1.2 E-04</b>	<b>.47</b>	<b>3.4 E-04</b>	<b>4.80</b>
<b>Transitional (Break)</b>	<b>I-10</b>	<b>.75</b>	<b>2.5 E-05</b>	<b>1.60</b>	<b>5.0 E-05</b>	<b>.01</b>	<b>7.0 E-07</b>	<b>4.96</b>
<b>Anoxic (Floodplain/ Bank)</b>	<b>I-8- I-1</b>	<b>2.68</b>	<b>8.92 E- 05</b>	<b>1.27</b>	<b>4.0 E-05</b>	<b>.02</b>	<b>1.0 E-06</b>	<b>5.68</b>

Icacos well field data collected between 1988 and 1991 were averaged and organized into these three redox zones. An average concentration for each zone was then calculated based on the average field values at each well within each zone. This data was then inputted into the geochemical model PHREEQC. Utilizing mean values of cations along with oxygen and nitrate (depending on the simulation run), an initial solution was created with corresponding values for pH, pE, temperature, water density and mass found in the upslope wells of the watershed in the Oxidic zone. Atmospheric oxygen at 0.209 atmospheres was established as being in equilibrium with dissolved oxygen (Figure 2 and Table 2). PE values were calculated using PHREEQC based on the mean Oxidic zone data for the NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> redox couple. In order to initiate a forward model involving carbon oxidation, the REACTION keyword was used to specify the addition of incremental amounts of carbon to this initial solution. The approximation of the oxidized carbon

source (CH<sub>2</sub>O) was executed using the Redfield stoichiometry for the average content of algae.

**Table 2. Model Values for Initial Solution at Oxidic zone (Wells I-23 and I-9)**

<b>Variable</b>	<b>Value</b>	<b>Reference</b>
<b>Temperature (Celsius)</b>	<b>19.4</b>	(United States Department of Agriculture and National Resources Conservation Service 2002)
<b>PH</b>	<b>4.8</b>	(Mcdowell et al. 1992)
<b>PE</b>	<b>9.38</b>	“
<b>Density</b>	<b>1 (g/cm<sup>3</sup>)</b>	(Parkhurst et al. 1999)
<b>Units</b>	<b>mg/L</b>	
<b>Cl</b>	<b>8.41</b>	(Mcdowell et al. 1992)
<b>SO<sub>4</sub><sup>2-</sup></b>	<b>0.39</b>	“
<b>Na</b>	<b>3.87</b>	“
<b>K</b>	<b>0.43</b>	“
<b>Mg</b>	<b>1.14</b>	“
<b>Ca</b>	<b>0.27</b>	“
<b>O(0)</b>	<b>1E-010 O<sub>2</sub> (g)</b> <b>-0.68</b>	<b>Input for equilibrium conditions</b>
<b>Water</b>	<b>1 #kg</b>	(Parkhurst et al. 1999)

After identifying the chemical species to be analyzed using the SELECTED OUTPUT keyword, the model simulations were run. The first simulation was run in order to establish the value of dissolved oxygen at equilibrium conditions. We identified this value as 9.46 mg O<sub>2</sub>/L. The next simulations consisted of modeling redox reactions of DO under equilibrium conditions without nitrate in order to isolate how much of the carbon source was being utilized to reduce the dissolved oxygen at each zone. The initial carbon amounts added at each zone reflect the mean carbon concentrations measured at each zone. Subsequent model runs were made with oxygen and nitrate in order to isolate the amount of carbon needed to reduce the nitrate. 4 sets of simulations were ultimately run. A simulation was run for each redox zone within each set. The focus of this

geochemical model was to identify the quantity of carbon electron donor needed to reduce oxygen and nitrate across these three general redox zones of the Icacos well field transect. In addition to quantifying carbon electron donors, we were also following the predicted product quantities of respiration and denitrification across these three zones.

Figure 2. PHREEQC Input File

```

SOLUTION 1
  temp  19.4
  pH    4.8
  pe    9.38
  redox pe
  units mg/l
  density 1
  Cl    8.41
  S(6)  0.39
  Na    3.87
  K     0.43
  Mg    1.14
  Ca    0.27
  O(0)  1e-010 O2(g)  -0.68
  N(5)  0.47
  -water 1 # kg
SOLUTION_MASTER_SPECIES
  C(0)   CH2O      0  30.03
SOLUTION_SPECIES
CO2 + 4H+ + 4e- = CH2O + H2O
  log_k  -4.8
REACTION 1
  CH2O   1
  0.000666 moles in 30 steps
SELECTED_OUTPUT
  -file      F:\Final Capstone Work II (3 zones)\PHREEQC
Runs\Nitrate_Carbon_10_30_step>Loading II.xls
  -totals    O(0) N(5) N(0) N(3) N(-3) C(0) C(4)
             C(-4)
END

```

## RESULTS

### *Geochemical Modeling Simulations*

In the first set of modeling runs, field values of mean carbon concentrations from each of the three zones were reacted with an initial solution separately in order to identify the amount of carbon needed to reduce oxygen from its modeled equilibrium concentration (9.46 mg/L) to field values at each zone (Table 1.) After running the first set of simulations, oxygen decreased however not to levels found in the field. Resulting DO levels from these initial simulations were 8.9 mg/L (Oxic zone), 8.7 mg/L (Transitional zone) and 6.6 mg/L (Anoxic zone). Ph levels decreased from 4.8 in the initial solution to 4.75 after reacting the 2.68 mg/L of C observed in the Anoxic zone (Table 3).

**Table 3. Model Runs Loading Observed Mean Carbon to Equilibrium Solution only Accounting for Respiration**

<b>Carbon Loading Zone Runs</b>	<b>C (mg/L)</b>	<b>C (mol/L)</b>	<b>Resulting O2 from equilibrium 9.46(mg/L)</b>	<b>Resulting O2 from equilibrium 2.96 E-04(mol/L)</b>	<b>Resulting pH from 4.8</b>
<b>Oxic (Slope)</b>	<b>0.48</b>	<b>1.6 E-05</b>	<b>8.9</b>	<b>2.80 E-04</b>	<b>4.79</b>
<b>Transitional (Break)</b>	<b>0.75</b>	<b>2.5 E-05</b>	<b>8.7</b>	<b>2.71 E-04</b>	<b>4.78</b>
<b>Anoxic (Floodplain/Bank)</b>	<b>2.68</b>	<b>8.92 E-05</b>	<b>6.6</b>	<b>2.07 E-04</b>	<b>4.75</b>

(Note: active concentrations are reported for input and output values of oxygen and nitrate found in Tables 3-8.)

The following set of simulations were run with mean zone DO and nitrate field values in order to determine if nitrate concentrations decreased as a result of the reaction with the same amount of carbon utilized for the initial oxygen runs (Table 4). Nitrate exhibited no change while oxygen and pH demonstrated changes identical to the first set of runs. This result corresponds with basic thermodynamics of redox reactions, as oxygen must be depleted first (respiration), before heterotrophic bacteria begin depleting nitrate (denitrification).

**Table 4. Model Runs Loading Observed Mean Carbon and Nitrate to Equilibrium Solution**

<b>Carbon and Nitrate Loading Zone Runs</b>	<b>C (mg/L)</b>	<b>C (mol/L)</b>	<b>NO3 (mg/L)</b>	<b>NO3 (mol/L)</b>	<b>Simulated Results of O2 from equilibrium 9.46(mg/L)</b>	<b>Simulated Results of O2 from equilibrium 2.96 E-04(mol/L)</b>	<b>Simulated Results of NO3 (mg/L)</b>	<b>Simulated Results of NO3 (mol/L)</b>
<b>Oxic (Slope)</b>	<b>0.48</b>	<b>1.6 E-05</b>	<b>0.47</b>	<b>3.4 E-05</b>	<b>8.9</b>	<b>2.80 E -04</b>	<b>No Change Observed</b>	<b>No Change Observed</b>
<b>Transitional (Break)</b>	<b>0.75</b>	<b>2.5 E-05</b>	<b>0.01</b>	<b>7.0 E-07</b>	<b>8.7</b>	<b>2.71 E -04</b>	<b>“</b>	<b>“</b>
<b>Anoxic (Floodplain/Bank)</b>	<b>2.68</b>	<b>8.92 E-05</b>	<b>0.02</b>	<b>1.0 E-06</b>	<b>6.6</b>	<b>2.07 E -04</b>	<b>“</b>	<b>“</b>

A third set of simulations were run in order to identify the amount of carbon needed to reduce oxygen to the mean field result levels at each zone (Table 5). From the equilibrium oxygen concentration of 9.46 mg/L, 5.33 mg/L of DOC were added to the initial solution in order to reach the Oxic zone concentration of oxygen. 7.39 mg/L of DOC were added to the initial solution in order to reach oxygen levels in the Transitional zone from equilibrium conditions. In order to reach Anoxic zone levels of oxygen from

equilibrium conditions, 7.7 mg/L of DOC were added to the initial solution. The simulated values for O<sub>2</sub> correspond accurately with field values. PH levels decreased from 4.8 in the initial solution to 4.68 in the anoxic zone after adding a total of 7.7 mg/L to the initial solution.

**Table 5. Progression of Carbon Loads and Corresponding Oxygen Depletion Predicted by PHREEQC Compared to Mean Field Results**

<b>Carbon Loading Zone Runs</b>	<b>C (mg/L) added at each zone in order to reach field O<sub>2</sub></b>	<b>C (mol/L)</b>	<b>Field Results of O<sub>2</sub> at each zone (mg/L)</b>	<b>Simulated Results of O<sub>2</sub> at each zone from equilibrium (9.46 mg/L)</b>	<b>Field Results of O<sub>2</sub> at each zone (mol/L)</b>	<b>Simulated Results of O<sub>2</sub> at each zone from equilibrium (2.96 E-04 mol/L)</b>	<b>Simulated Results of pH from 4.8</b>
<b>Oxic (Slope)</b>	<b>5.33 from Equilib.</b>	<b>1.77 E-04</b>	<b>3.79</b>	<b>3.78</b>	<b>1.2 E-04</b>	<b>1.18 E-04</b>	<b>4.71</b>
<b>Transitional (Break)</b>	<b>2.06 from Oxic</b>	<b>6.86 E-05</b>	<b>1.60</b>	<b>1.58</b>	<b>5.0 E-05</b>	<b>4.94 E-05</b>	<b>4.69</b>
	<b>7.39 from Equilib.</b>	<b>2.46 E-04</b>					
<b>Anoxic (Floodplain/Bank)</b>	<b>.309 from Transitional</b>	<b>1.03 E -05</b>	<b>1.27</b>	<b>1.25</b>	<b>4.0 E-05</b>	<b>3.90 E-05</b>	<b>4.68</b>
	<b>7.7 from Equilib.</b>	<b>2.56 E-04</b>					

The final set of simulations involved identifying specifically how much carbon was needed to reduce nitrate to mean field concentrations found at each zone once DO had been depleted (Table 6a). Once we had identified that approximately 10 mg/L of C would deplete both oxygen and nitrate, a linear step reaction modeling technique was employed in order to identify the concentration at which nitrate begins decreasing as well as identify carbon concentrations needed to reach mean field nitrate concentrations at each zone. After reacting 20 mg/L of the carbon source in 20,000 steps, simulations reveal that nitrate begins to attenuate after 8.8 mg/L of CH<sub>2</sub>O has been reacted with the initial solution. In order to reach the nitrate field concentration of 0.01 mg/L in the Transitional zone from the nitrate field concentration of 0.47 mg/L in the Oxidic zone, model simulations suggest that 1.19 mg/L of carbon need to be oxidized. In order to reach the nitrate field concentration of 0.02 mg/L in the Anoxic zone from the Oxidic zone nitrate field concentration of 0.47 mg/L, approximately 1.18 mg/L of carbon need to be oxidized. The small carbon amounts accounting for the DO depletion while nitrate attenuates are accounted for in Table 6a PH increased from 4.8 in the initial solution to 5.22 in the Anoxic Zone (Table 6b).

### ***Products of Aerobic Respiration and Denitrification***

Results of this geochemical analysis suggest that there is a narrow range of carbon oxidation (8.68-10.7 mg/L of reacted CH<sub>2</sub>O) where there are pronounced increases and decreases of chemical species (see Table 7). From 8.68 to 10.00 mg/L of oxidized C, the

**Table 6a. Progression of Carbon Loads and Corresponding Nitrate and Oxygen Depletion Predicted by PHREEQC Compared to Mean Field Results  
(\* from amount of carbon reacted which initiates nitrate depletion (8.80 mg/L C))**

<b>Carbon Loading Zone Runs</b>	<b>C (mg/L) added at each zone in order to reach field NO3</b>	<b>C (mol/L)</b>	<b>Field Results of NO3 at each zone (mg/L)</b>	<b>Simulated Results of NO3 at each zone from O2 equilibrium (9.46 mg/L)</b>	<b>Field Results of NO3 at each zone (mol/L)</b>	<b>Simulated Results of NO3 at each zone from O2 equilibrium (2.96 E-04 mol/L)</b>	<b>Simulated Results of O2 at each zone from equilibrium (9.46 mg/L)</b>	<b>Simulated Results of O2 at each zone from equilibrium (2.96 E-04 mol/L)</b>	<b>Approximate Amount of Carbon used to reduce Oxygen (mg/L)</b>
<b>Oxic (Slope)</b>	<b>* .02</b>	<b>6.66 E-07</b>	<b>.47</b>	<b>.46</b>	<b>3.4 E-05</b>	<b>3.29 E-05</b>	<b>4.6 E-04</b>	<b>1.43 E-08</b>	<b>-----</b>
	<b>8.82 from Equilib.</b>	<b>2.94 E-04</b>							
<b>Transitional (Break)</b>	<b>1.19 from Slope</b>	<b>3.96 E-05</b>	<b>.01</b>	<b>.01</b>	<b>7.0 E-07</b>	<b>7.02 E-07</b>	<b>1.6 E-06</b>	<b>5.12 E-11</b>	<b>4.29 E-04</b>
	<b>10.01 from Equilib.</b>	<b>3.34 E-04</b>							
<b>Anoxic (Floodplain/Bank)</b>	<b>1.18 from Slope</b>	<b>3.93 E-05</b>	<b>.02</b>	<b>.02</b>	<b>1.0 E-07</b>	<b>1.4 E-06</b>	<b>2.9 E-06</b>	<b>9.12 E-11</b>	<b>4.28 E-04</b>
	<b>10.00 from Equilib.</b>	<b>3.33 E-04</b>							

**Table 6b. Progression of Carbon Loads and Corresponding pH Predicted by PHREEQC Compared to Mean Field Results (\* from amount of carbon reacted which initiates nitrate depletion (8.80 mg/L C))**

Carbon Loading Zone Runs	C (mg/L) added at each zone in order to reach field $\mu$ NO <sub>3</sub>	C (mol/L)	pH (Field)	pH (Sim.)
Oxic (Slope)	* 0.02	6.66 E-07	4.80	4.68
	8.82 from Equilibrium	2.94 E-04		
Transitional (Break)	1.19 from Slope	3.96 E-05	4.96	5.23
	10.01 from Equilibrium	3.34 E-04		
Anoxic (Floodplain/Bank)	1.18 from Slope	3.93 E-05	5.68	5.22
	10.00 from Equilibrium	3.33 E-04		

PE has decreased from 16.03 to 14.31 representing the transition to a more reducing environment. Figures 3b, 6 and 7 illustrate the decreasing pE values and the products of respiration and denitrification that emerge as the pE values decrease. Once approximately 10.7 mg/L of DOC have been oxidized, the PE has reached -1.39. As much as 0.42 mg/L of dissolved di-nitrogen are produced from the oxidation of approximately 10 mg/L of DOC. Both CO<sub>2</sub> and HCO<sub>3</sub>, products of respiration and denitrification, display a steady increase throughout most of the carbon oxidation. However, corresponding with the changes in N<sub>2</sub> and related carbon oxidation previously mentioned, the concentration of HCO<sub>3</sub> increases from 0.33 mg/L to 2.64 mg/L between 8.68 mg/L and 10.7 mg/L of carbon oxidation while CO<sub>2</sub> continues a steady increase up to 13.8 mg/L and then

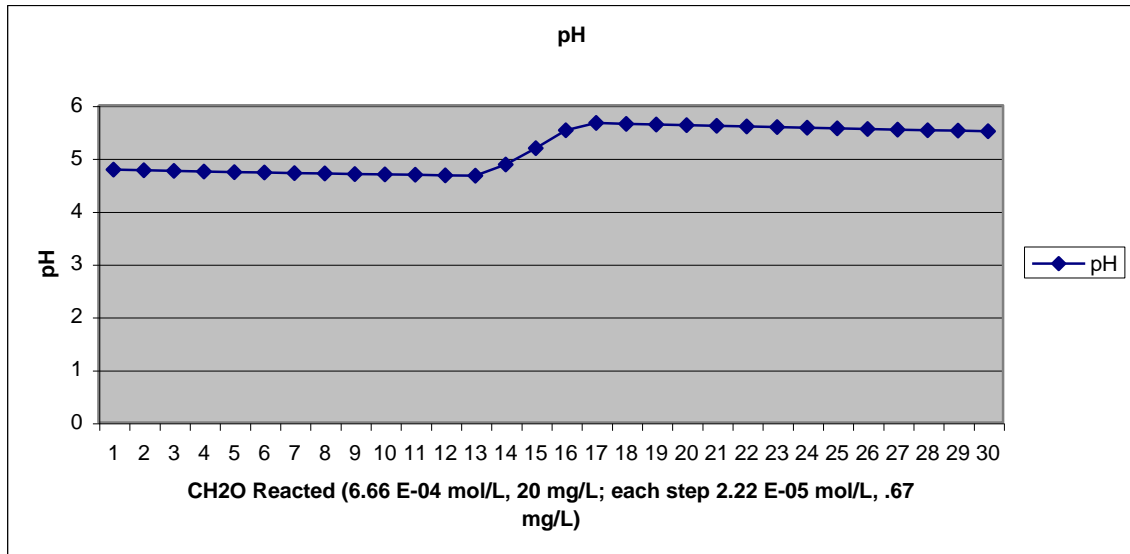
slightly decreases to 13.7 mg/L before increasing again as more carbon is reacted. In the same range of carbon oxidation, nitrate decreased from 0.47 to 0.0 mg/L. PH increased from 4.67 to 5.53.

**Table 7. Interval of Carbon Oxidation with pronounced C, N and O activity. CH<sub>2</sub>O is Reacted in 30 Total Reaction Steps; 6.66 E-04 mol/L, 20mg/L; each step 2.22 E-05 mol/L, 0.67 mg/L.**

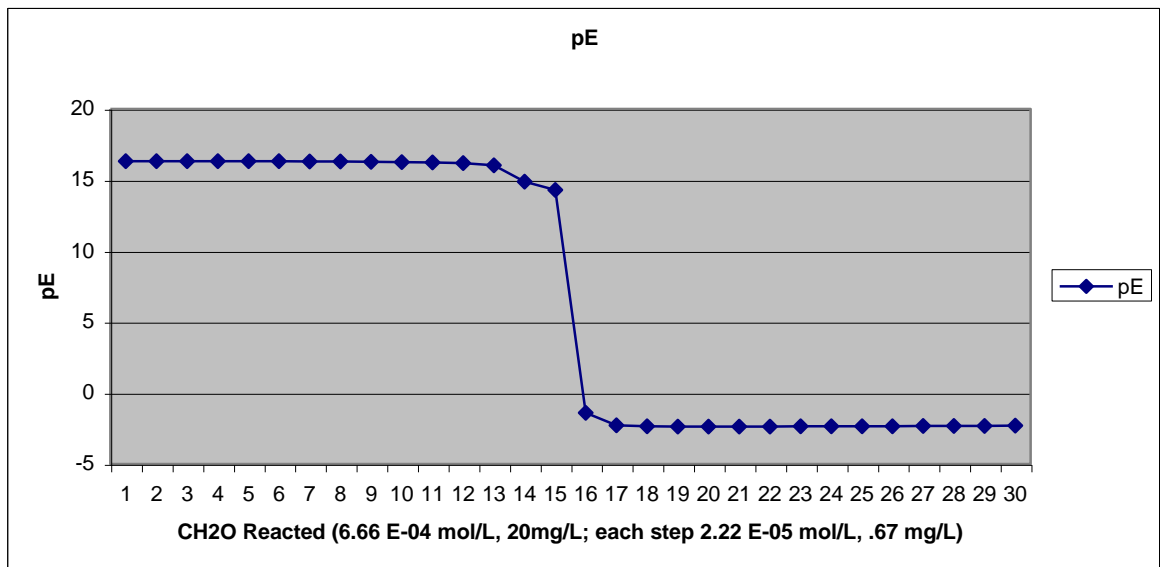
<b>Carbon Reaction Step</b>	<b>CH<sub>2</sub>O reacted (mg/L)</b>	<b>NO<sub>3</sub> (N mg/L)</b>	<b>O<sub>2</sub> (mg/L)</b>	<b>N<sub>2</sub> (N mg/L)</b>	<b>CO<sub>2</sub> (mg/L)</b>	<b>HCO<sub>3</sub> (mg/L)</b>	<b>pE</b>	<b>pH</b>
<b>13</b>	<b>8.68</b>	<b>0.47</b>	<b>0.44</b>	<b>3.82 E-10</b>	<b>12.5</b>	<b>0.33</b>	<b>16.03</b>	<b>4.67</b>
<b>14</b>	<b>9.34</b>	<b>0.3</b>	<b>7.1 E-5</b>	<b>0.17</b>	<b>13.3</b>	<b>0.57</b>	<b>14.88</b>	<b>4.88</b>
<b>15</b>	<b>10</b>	<b>0.05</b>	<b>6.7 E-6</b>	<b>0.42</b>	<b>13.8</b>	<b>1.22</b>	<b>14.31</b>	<b>5.19</b>
<b>16</b>	<b>10.7</b>	<b>0</b>	<b>0</b>	<b>0.14</b>	<b>13.7</b>	<b>2.64</b>	<b>-1.39</b>	<b>5.53</b>

Figures 3 a. and b. Simulated pH and pE values with respect to CH2O reacted.

a.



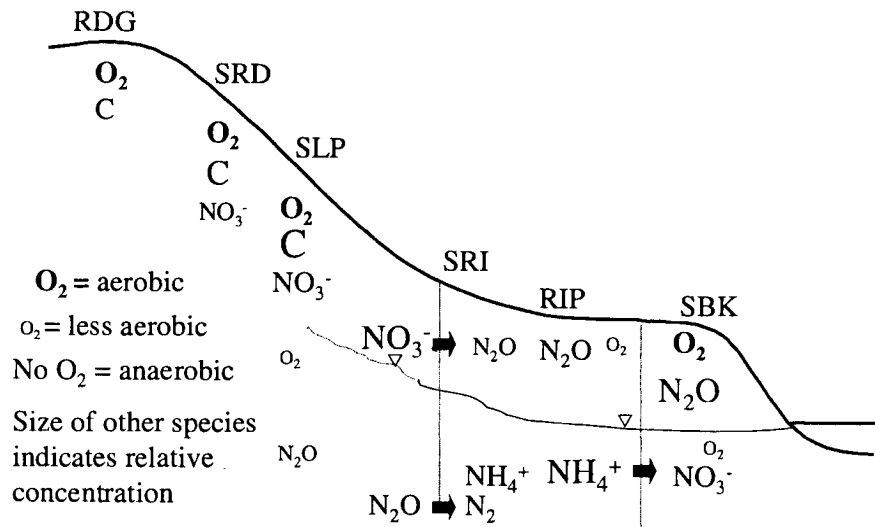
b.



## DISCUSSION

The findings of this geochemical model can begin to expand the conceptual model (Figure 4) of N speciation and related redox processes in the Rio Icacos basin proposed by McSwiney, McDowell and Keller by shedding light on the quantities of carbon electron donor associated with the reduction of dissolved oxygen and nitrate (McSwiney et al. 2001). Specifically, results help quantify the oxidation of carbon material at the critical region of the interface between the slope and the riparian zone. According to McSwiney et al, “ abrupt decreases in soil water  $\text{NO}_3^-$ , DOC,  $\text{O}_2$  along with an increase in soil  $\text{N}_2\text{O}$  at the slope-riparian break lead us to conclude that denitrification was the main source of  $\text{N}_2\text{O}$  at this topographic position” (McSwiney et al. 2001). Bowden found

Figure 4. “Conceptual model for N processing in the Rio Icacos Basin” (McSwiney et al. 2001)



that ground water conditions corresponded with these soil conditions such that dissolved N<sub>2</sub>O fully depleted most likely to N<sub>2</sub> gas at the slope–riparian zone interface of the Icacos well field (Bowden et al. 1992). Modeling results of the present analysis suggest that 0.42 mg/L of dissolved N<sub>2</sub> are produced from the oxidation of approximately 10 mg/L of DOC at the slope riparian interface. Further discussion of products follows later in this section of the paper.

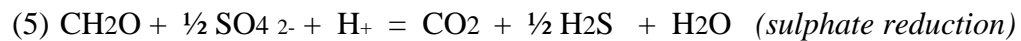
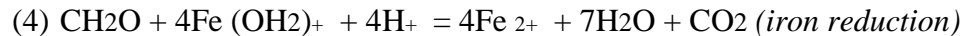
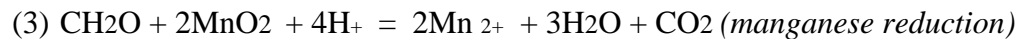
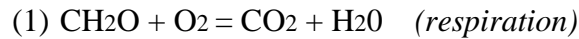
### ***Aerobic Respiration, Denitrification and DOC Oxidation***

The geochemical analysis presented in this study indicates that in order to reach oxygen concentrations of 1.6 mg/L at the slope-riparian interface from 3.79 mg/l O<sub>2</sub> found in the Oxic slope zone, approximately 2.06 mg/L of DOC needs to be oxidized. An additional .309 mg/L of DOC are oxidized in order to reach the mean riparian zone oxygen concentration of 1.27 mg/L. From equilibrium concentrations of oxygen (9.46 mg/L), approximately 8.8 mg/L of DOC are oxidized by oxygen before nitrate becomes more thermodynamically favorable as the electron acceptor and begins decreasing in concentration. Comparatively, in a review of biogeochemical controlling processes of nitrate attenuation, Rivett et al suggest that in ground water saturated with air at 12 C and 10.3 mg/L O<sub>2</sub>, as much as 3.8 mg/L of C must be oxidized prior to the start of denitrification. These results were based on the assumptions that there was no reentry of C or N, that the death of bacteria was unaccounted for and that there was complete coupling (Rivett et al. 2008). Utilizing a PHREEQC equilibrium model approach similar to the one presented in the present study, researchers analyzed the geochemical reactions

along shallow ground water flow paths of an agricultural region and found that after reacting 0.17 mmol of CH<sub>2</sub>O (5.12 mg/L), approximately 0.17mmol of O<sub>2</sub> (5.44mg/L) were completely consumed (Saad et al. 1998). After 0.34 mmol of CH<sub>2</sub>O had been reacted, the initial concentration of approximately 0.135 mmol NO<sub>3</sub> (1.89 mg/L NO<sub>3</sub> as N) was completely reduced to .068 mmol (.95 mg/L N<sub>2</sub> as N) of dissolved N<sub>2</sub> gas. This study indicates that nitrate at the Icacos well field begins to deplete once oxygen has reached approximately 0.01 mg/L confirming that 1-2 mg/L of O<sub>2</sub> can be considered a general threshold below which denitrification occurs as suggested by Rivett et al (Rivett et al. 2008). The discrepancy, however that exists between the measured oxygen concentration from a piezometer versus the scale (10 x -9) at which water surrounding a microbe 1 um in diameter is measured underscores the general nature of the threshold offered (Rivett et al. 2008). In order to reduce the nitrate concentration of 0.47 mg/L found in the Oxic (slope) region to the lowest measured mean values of .01 mg/L NO<sub>3</sub> found in the Transitional zone, model results suggest that 1.19 mg/L of DOC need to be oxidized. From equilibrium and including the reduction of oxygen, approximately 10.01 mg/L of DOC have been oxidized when nitrate has reached .01 mg/L. Much like Hedin et al found in a study of the relationship between thermodynamics and spatial patterns of electron donors and acceptors at the soil-stream interface, results of this study demonstrate the oxidation of carbon and corresponding reduction of oxygen and nitrate between slope, slope-riparian interface and riparian-floodplain of the Icacos watershed (Hedin et al. 1998).

## *pH*

The thermodynamic equations of electron acceptor consumption during carbon oxidation (see following Equations 1-5) can help explain the pH behavior captured during modeling simulations.



In model simulation sets 1 and 3, the goals were to identify how existing field carbon values affected oxygen values and how much carbon would be needed in order to reach values of oxygen in the field. In the first set of runs, pH decreased from 4.8 to 4.75 and in the third set of modeling runs pH decreased from 4.8 to 4.68 (Tables 3 and 5). This general trend was to be expected as weak carbonic acid is added to the water with the oxidation of CH<sub>2</sub>O by means of aerobic respiration thereby decreasing the pH (Equation 1). The purpose of the fourth and final set of modeling runs was to identify the specific amount of carbon needed to reduce the nitrate to field values and to follow oxygen concentrations as nitrate reduced (Tables 6a and 6b). Referring to both the denitrification and respiration equations (Equations 1 and 2) we would expect the pH to decrease as

these reactions produce weak carbonic acid without consuming a strong acid. The simulated pH in fact decreases from 4.8 in the initial solution to 4.68 in the oxic zone and then increases to as much as 5.23 in the transitional break zone. The mean field values do not demonstrate an initial decrease in pH. Upon looking at specific mean pH data for well I-9, a decrease of pH to 4.74 does in fact occur. This decrease could be the result of respiration and denitrification. Further study would be needed to verify this. PH values also exhibit a much larger increase of up to 5.68 in the field. We hypothesize that the larger increasing trend is a result of manganese, iron or sulphate reduction (Equations 3-5). During manganese and iron reduction, one mole of weak carbonic acid is produced. This quantity of weak carbonic acid cannot make up for the 4 moles of strong acid consumed in the reaction. The pH therefore must increase. In the case of sulfur, the one mole of weak carbonic acid produced does not completely address the one mole of strong acid consumed in the reaction. As a result the pH would then increase. Further exploration of iron, manganese and sulfur at the slope-riparian interface along with further study of respiration and denitrification at the slope and slope-riparian interface could help further clarify the behavior of pH.

### ***Products of Aerobic Respiration and Denitrification***

The geochemical products that were followed in this modeling study in order to verify both respiration and denitrification were specifically  $N_2$ ,  $HCO_3^-$  and  $CO_2$ . While little data exists for these particular species during the study period for direct comparison, we can note interesting trends about the predicted products of denitrification as they

relate to bioavailability of dissolved organic carbon and the range of carbon oxidation at which these species emerge (Table 7). The specific behavior of these products within distinct narrow ranges of carbon oxidation as predicted by our geochemical model suggests general confirmation of observations made by Jacinthe, Groffman and Gold in their 2003 study of dissolved organic carbon dynamics in a riparian aquifer (Jacinthe et al. 2003). They found that additional DOC added to the aquifer mesocosm from an external source increased CO<sub>2</sub> production yet did not produce more N<sub>2</sub> gas and thus denitrification. According to their observations, “production of CO<sub>2</sub> is an index of overall microbial activity, while N gas production reflects the response of a special group of denitrifiers. This differential response (N gases –vs- CO<sub>2</sub> production) to DOC addition suggests that denitrifiers can utilize a narrow range of substrates compared to the general heterotrophic population” (Jacinthe et al. 2003). The findings of our geochemical model simulations suggest that between 8.68 mg/L and 10.7 mg/L of carbon oxidation as much as 0.42 mg/L of dissolved di-nitrogen are produced while both CO<sub>2</sub> and HCO<sub>3</sub> generally increase steadily. The concentration of HCO<sub>3</sub> increases from 0.33 mg/L to 2.64 mg/L while CO<sub>2</sub> increases up to 13.8 mg/L and then slightly decreases to 13.7 mg/L before increasing again as more carbon is reacted. In the same range of carbon oxidation, nitrate decreased from 0.47 to 0.0 mg/L. Figure 7 and table 7 illustrate the possible range of carbon oxidation where denitrification occurs at the slope-riparian region of the Icacos well field. When put in the context of large carbon pulses from hurricane litter falls occurring frequently at the Icacos site (Lodge and McDowell 1991, Lodge et al. 1994, McDowell et al. 1996, Ostertag et al. 2003), the observation of a narrow range of C reacted at which denitrification takes place suggests that despite an availability of large

quantities of labile carbon with these events, only very fine amounts of DOC are ultimately utilized for aerobic respiration and denitrification. Study of this narrow range of carbon oxidation under pulsed conditions deserves further investigation.

### ***Patterns of Electron Donors and Acceptors***

Key field studies of C and N dynamics in the riparian zone have focused on general patterns of electron donors and acceptors in the riparian zone in order to deduce regions of respiration and denitrification (Hill et al. 2000, McDowell et al. 1992, Vidon and Hill 2004). The present modeling study allows us to identify if any differences exist between the amount of carbon electron donor measured in a particular region of the slope-riparian zone and the actual amount utilized in microbial metabolism. We hypothesize that DOC concentration values reported in the wells are excess or oversupply of DOC that is unutilized in microbial metabolism. Table 8 illustrates the specific differences in mean concentration values of DOC reported at each zone versus the actual DOC utilized to reach oxygen and nitrate values at each zone in the geochemical model.

**Table 8. Comparison of Reported Mean C values and the C reacted in PHREEQC in order to Reach Mean Field Oxygen and Nitrate Concentrations at Oxidic, Transitional and Anoxic Zones.**

<b>Zone</b>	<b>Mean C Field Values (mg/L)</b>	<b>Model C Values Reacted in order to Reach Mean Oxygen Zone Values (mg/L)</b>	<b>Model C Values Reacted in order to Reach Mean Nitrate Zone Values (mg/L)</b>
<b>Oxic</b>	<b>0.48</b>	<b>5.33 (from Equilib. to Oxidic zone)</b>	<b>.02 (from 8.80 C where nitrate begins to reduce to Oxidic zone)</b>
<b>Transitional</b>	<b>0.75</b>	<b>2.06 (from Oxidic)</b>	<b>1.19 (from Oxidic zone)</b>
<b>Anoxic</b>	<b>2.68</b>	<b>0.309 (from Transitional)</b>	<b>1.18 (from Oxidic zone)</b>

## CONCLUSIONS

In quantifying the carbon electron donors needed to reduce oxygen and nitrate to reported field concentrations across Oxidic, Transitional and Anoxic zones of the Icacos watershed, we have been able to identify several key characteristics of C and N dynamics in the riparian zone. This study has helped us identify the amount of carbon electron donors involved in respiration and denitrification at the critical slope-riparian interface. Our results also reveal the following:

- Confirmation of a narrow range of carbon oxidation identified in a previous study on riparian DOC dynamics at which denitrification occurs and beyond which CO<sub>2</sub> continues evolving. This suggests possibly a specific range at which denitrifiers metabolize versus the range at which a larger heterotrophic population metabolizes.
- Confirmation of general concentration thresholds of O<sub>2</sub> previously identified in field studies after which nitrate begins to attenuate.
- Identification of a possible discrepancy between measured concentration values of DOC, (whose general aggregate patterns in previous studies have been used to identify regions of respiration and denitrification in the riparian zone) versus the carbon amounts actually utilized in microbial metabolism. Results suggest that reported DOC values made in field measurements could be residual or oversupply of DOC unutilized in microbial metabolism.

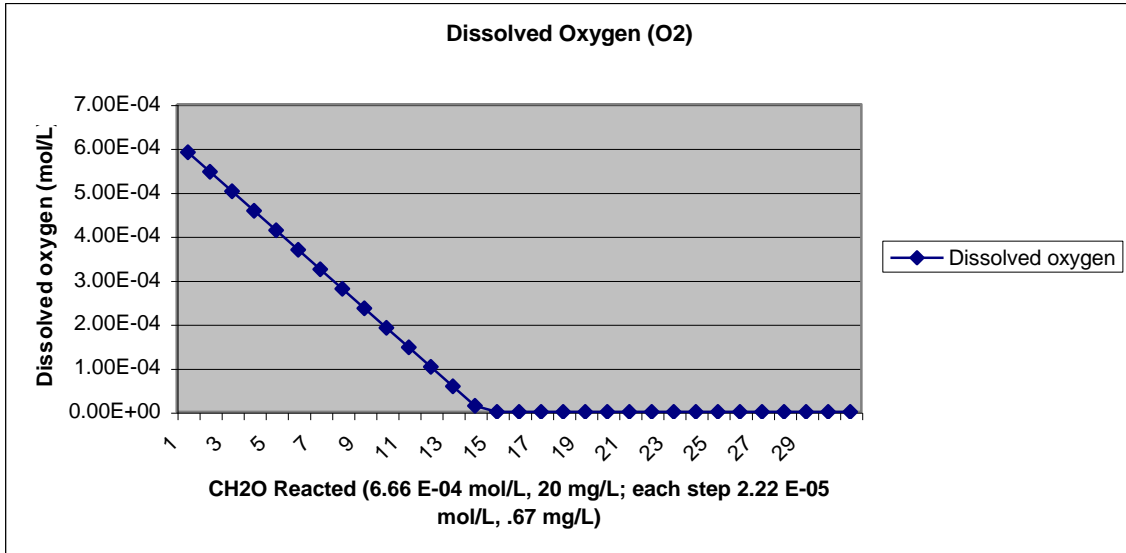
- As a result of this previous conclusion, once correlated to a particular site, this modeling approach can help identify specific quantities of DOC needed during microbial metabolism in order to reduce nitrate for issues of bio-remediation in the environmental science and engineering fields.

While this geochemical modeling study has identified general trends related to carbon oxidation, respiration and denitrification across three redox zones, the following questions still remain. If answered they could offer a more complete picture of riparian processes in the Icacos stream basin, specifically of the slope-riparian interface:

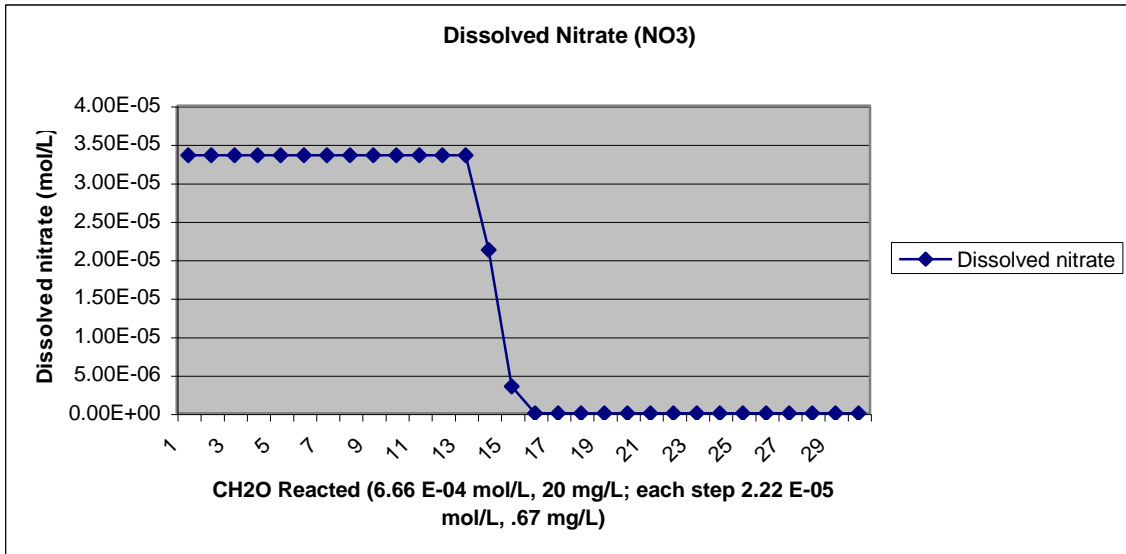
- How much of the carbon oxidation is a result of iron, manganese or sulfate reduction?
- Can a further investigation of the whole thermodynamic sequence explain discrepancies observed in the pH levels of this modeling study?
- What is the role of Fe <sup>2+</sup> in sorption processes at the slope riparian interface?
- Given the presence of sulfur and iron at this site, does the oxidation of ferrous disulfide (pyrite) have any role in the reduction of nitrate?
- How are riparian groundwater redox reactions affected by pulsed or hot moment conditions representative of hurricanes?

Figures 5 a. and b. Simulated DO and NO3 values with respect to CH2O reacted.

a.

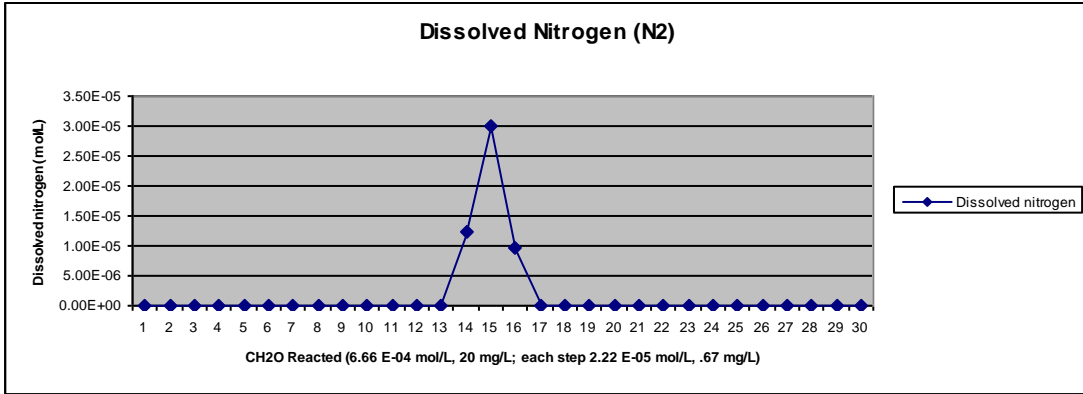


b.

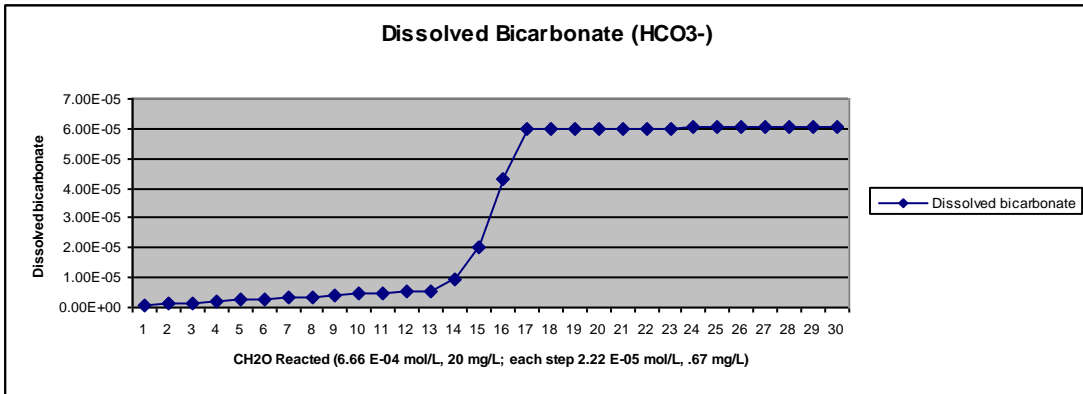


Figures 6 a., b. and c. Simulated N2, HCO3 and CO2 values with respect to CH2O reacted.

a.



b.



c.

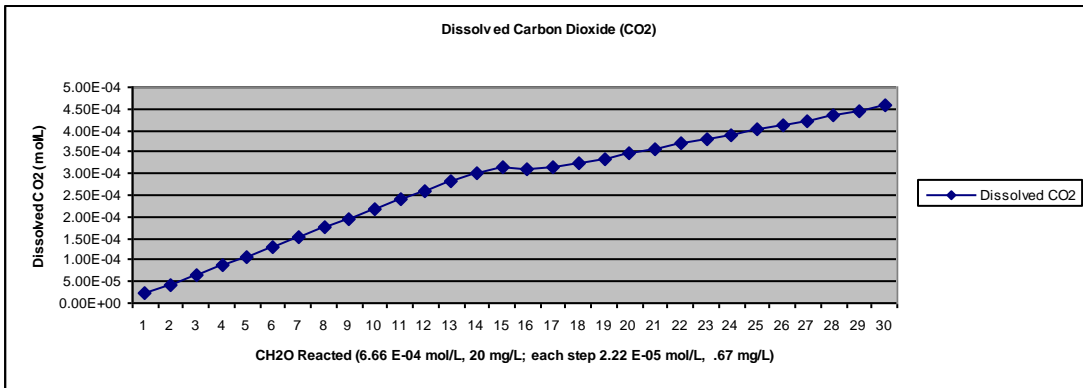
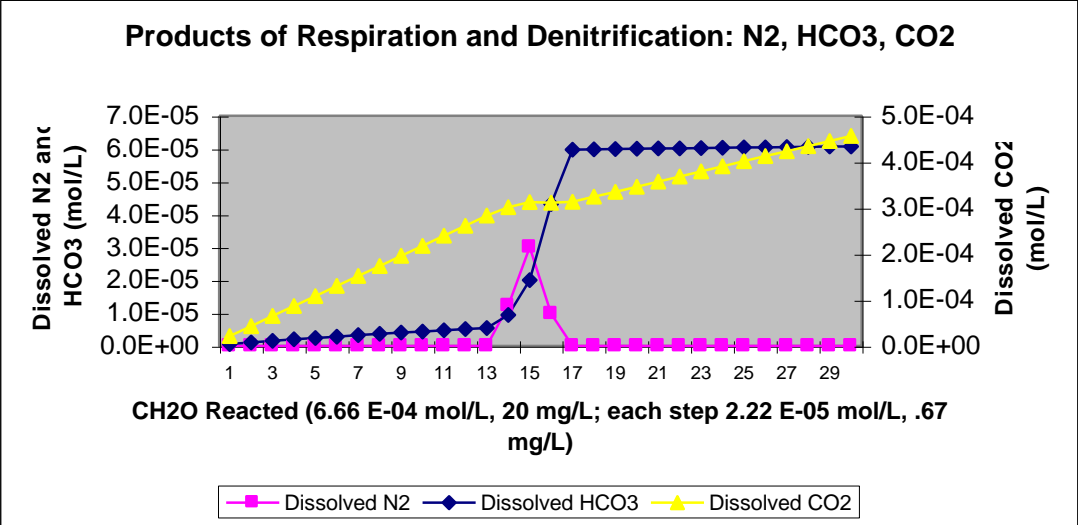


Figure 7. Simulated products of respiration and denitrification with respect to CH2O reacted.



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