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Modeling Calcium Carbonate Precipitation in the Acıgöl Lake Using AQUATOX

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Abstract

Due to the low costs of production processes, many industries use $CaCO_3$ broadly as an inorganic mineral that appears in forms of limestone. The aim of this research is to model $CaCO_3$ precipitation in the Acıgöl Lake, using water quality data obtained from the field measurements and meteorological data from the Turkish State Meteorological Service (TSMS) for the years 2013 and 2015. To achieve this aim, Environmental Protection Agency's (EPA) AQUATOX model is used to model the lake's water quality and $CaCO_3$ precipitation. Firstly, a surrogate site is selected from AQUATOX library, which would represent the lake's characteristics in the best possible manner. The model is then calibrated for nine stations of the lake using parameters related to nutrients, plants, water quality, site characteristics, inflow loadings and lake hydrodynamics. Calibration dataset is obtained from field measurements and meteorological data for the year 2013. Model validation is conducted both using data from the laboratory experiments carried out in 30^0C, and field observations obtained in August, 2015. Model results suggest that the amount of $CaCO_3$ precipitation in the system ranges between 35.16 to 128.48 $mgL^{-1}d^{-1}$. The NRMSE between the modeled and observed values are found to be 0.29.

Keywords: Modeling, Lake, $CaCO_3$ precipitation, AQUATOX

1. Introduction

$CaCO_3$ is one of the most common forms of Calcium (Ca^{2+}), which constitutes 4.9% of the earth's crust (APHA 1999). Production of $CaCO_3$ in the industry includes carbonation of lime and crystallization of $CaCO_3$ processes, which is a complex process comprising three forms of $CaCO_3$, including calcite, aragonite, and vaterite (Jung *et al*. 2000). Many industries use $CaCO_3$ broadly as an inorganic mineral that appears in forms of chalk or limestone (Shirsath *et al*. 2015). Due to low costs of the production process, $CaCO_3$ is being used in numerous manufacturing fields such as dye production, textiles, plastics, adhesives, toothpaste, rubber, paper, ink, ceramic materials, food and horticulture, and wastewater treatment (Chen and Xiang 2009). The crystal growth is highly affected by the variables, such as pH of the solution, solute concentration, and temperature (Shirsath *et al.* 2015). Photosynthetic activity results in an increase of pH of lakes, which causes a rise for $CaCO_3$ precipitation. As a consequence, an increase in pH may contribute to the increase of bicarbonate in the lake, which could proliferate the precipitation of $CaCO_3$ in lake's sediment composition (APHA 1999). $CaCO_3$ precipitates when it is over saturated, while it tends to dissolve in water when it is under saturated. When saturated, water is assumed to be in equilibrium with $CaCO_3$, meaning it neither precipitate, nor dissolve, in an aquatic environment (Merrill and Sanks 1977). AQUATOX, which is a simulation model for aquatic ecosystems developed by United States Environmental Protection Agency (USEPA) is a mechanistic ecological risk assessment model intended to be used to evaluate the past, present, and future direct and indirect effects of various stressors including nutrients, inorganic, sediments, and temperature on aquatic ecosystems. The model has a quite flexible structure providing multiple analytical tools useful for the evaluation of ecological effects, including uncertainty analysis, nominal range sensitivity analysis, comparison of perturbed and control simulations, and graphing and tabulation of predicted concentrations, rates, and photosynthetic limitations. AQUATOX also can simulate the fate of organic compounds, nutrients, and other pollutants in the water environment systems, as well as their impacts on invertebrates and aquatic plants. The aim of this research is to model $CaCO_3$ precipitation in the Acıgöl Lake, using water quality data obtained from the field measurements and meteorological data from Turkish State Meteorological Service (TSMS) in 2013 and 2015. The AQUATOX model by Environmental Protection Agency's (EPA) is used to model the lake's water quality and $CaCO_3$ precipitation, and to produce a calibration file for the state variables of the site.

2. Materials and Methods

2.1 Site Description

Acıgöl Lake named the bitter lake in Turkish, is a saline water lake, in the southwestern part of Turkey, between Denizli and Burdur provinces. It is located at 37^0 55' 27.98"- 37^0 45' 7.41" N and 29^0 41' 11.72" – 30^0 0' 17.24" E coordinates, and has an elevation of 836 m above mean sea level. With its 15 km length and 14 km width, Acıgöl Lake has a surface area of 43.3 km^2 and 82.3 km^2 in summer and winter, respectively. The depth of the lake increases from North to South, and depth varies from 1 m (August-September) to 2.1 m (December-January) (Mutlu *et al*. 1999). Groundwater is the main inflow, and the lake has no outflow except by evaporation. One unique process that controls the lake's hydrochemistry is the continuous dissolution of soluble salts during wet seasons (Balci *et al*. 2016). Figure 1 represents the locations of water quality sampling stations in the Acıgöl Lake.

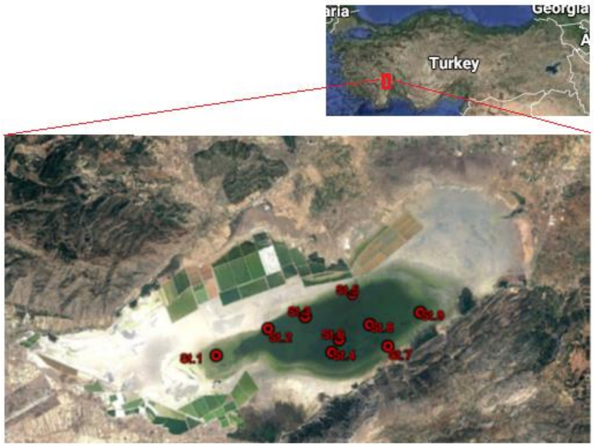

Figure 1. Acıgöl Lake sampling stations.

2.2 Model Description

AQUATOX has been used for the prediction of $CaCO_3$ precipitation in the Acıgöl Lake. AQUATOX establishes a causal chain of biological response between water quality and bioavailability, and thus, is able to predict the effects of different environmental variables on aquatic ecosystems. A conceptual representation of the ecosystem modeling procedure, with variable interactions and interrelations in AQUATOX, is depicted in Figure 2 (Park *et al*. 2013). In order to be able to apply AQUATOX for simulating $CaCO_3$ precipitation, main steps of the general modeling procedure need to be undertaken. These steps include calibration by setting up the model for initial conditions and model validation for each station. Model calibration is done using meteorological and field data obtained in 2013, and validation is carried out by laboratory data, and field data obtained in 2015. The schematized methodological approach and modeling procedure undertaken in this study is demonstrated in Figure 3.

2.3 Data Requirements

Meteorological data including temperature, precipitation, evaporation, and irradiance are obtained from Turkish State Meteorological Service for years 2013 and 2015, and used in the model both for setting up the initial conditions and as time series data. Field measurements were carried out in the sampling sites indicated in Figure 1 in July 2013 and August 2015. The type of water quality data obtained from the field, and plant type used in the model are given in Tables 1 and 2, respectively.

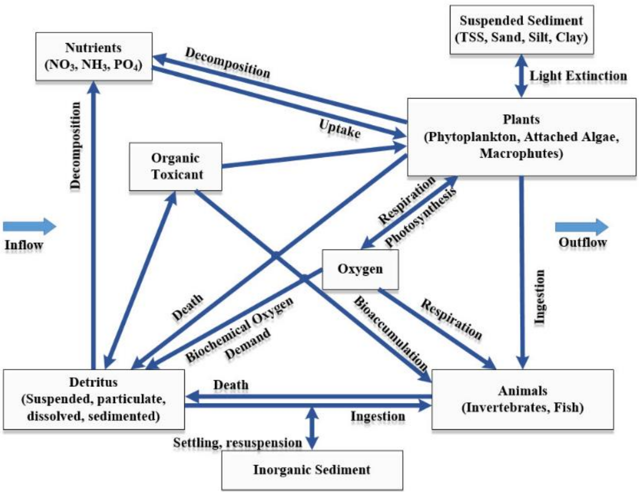

Figure 2. Conceptual model of ecosystem in AQUATOX (Park *et al*. 2013)

Table 1. Type of water quality data used in the model

Water Quality Data
pH (mg L^{-1})
O_2 (mg L^{-1})
NO_3-N (mg L^{-1})
NH_4-N (mg L^{-1})
PO_4-P (mg L^{-1})
HCO_3^- (mg L^{-1})
Ca^{2+} (mg L^{-1})
TSS (mg L^{-1})
TDS (mg L^{-1})
TOC (mg L^{-1})

3. Results and Discussion

3.1 Results of Model Calibration

Depending on the modeling purpose, specific aspects of modeling may require particular attention for the determination of model parameters. $CaCO_3$ precipitation has a biogenic origin as depicted in Figure 2. Due to the fact that $CaCO_3$ precipitation modeling with AQUATOX is highly related to the aquatic plants, in this study, photosynthesis rates of different plant groups (Table 2) and their carbon uptake from either nutrients or inorganic carbon from the atmosphere as CO_2, were paid much attention for process selection and the determination of the calibration values of related parameters within these processes. During calibration step seasonal variations of $CaCO_3$ are taken into account (Wainwright and Mulligan 2005) (Figure 4). Calibration of model is completed by comparison of the simulated $CaCO_3$ against observed $CaCO_3$ concentrations obtained from the field measurements in 2013 (Figure 5).

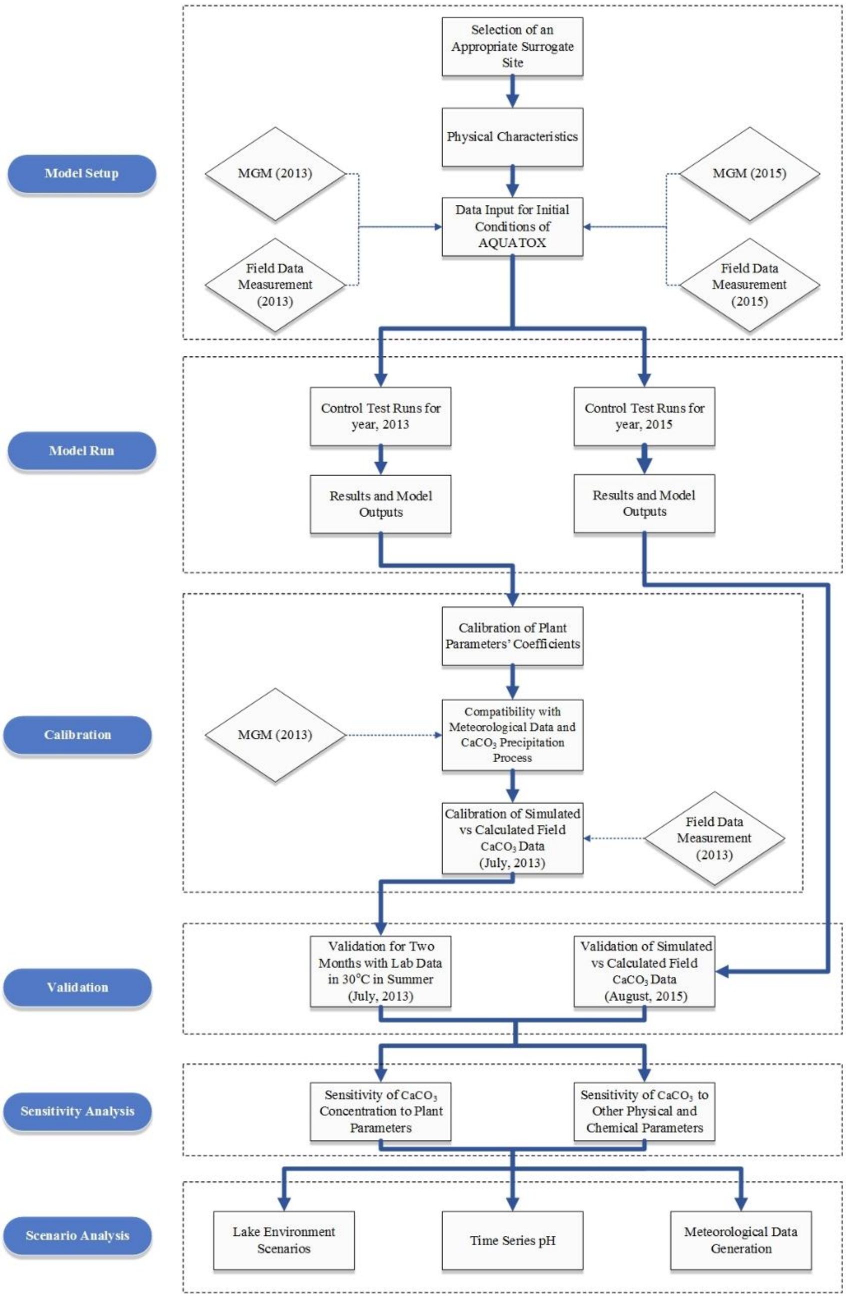

Figure 3. Methodological approach and modeling flowchart

Table 2. Type of plant data used in the model

Plant Name	Scientific Name	Taxonomic Type	Plant Type
Greens	Scenedesmus	Greens	Phytoplankton
Hydrilla	Hydrilla	Macrophytes	Macrophytes
Phyt, Blue-Green HiLt	Microcystis	Blue-Greens	Phytoplankton
Phyt, Blue-Greens Mar	Trichodesmium	Blue-Greens	Phytoplankton
Phyt, Blue-Green max	Anabaena	Blue-Greens	Phytoplankton
Phyt, Blue-Greens CR	Microcystis	Blue-Greens	Phytoplankton
Phyt, Blue-Greens DR	Aphanizomenon	Blue-Greens	Phytoplankton
Phyt, Blue-Greens JC	Cyanobacteria	Blue-Greens	Phytoplankton
Phyto, Green		Greens	Phytoplankton
Phyto, Green, Marine	Chlorophyceae	Greens	Phytoplankton
Phyto, Hi-Nut, Diatom	Scenedesmus	Diatoms	Phytoplankton

Phyto, Navicula	Navicula	Diatoms	Phytoplankton

Table 3. Calibration values for blue-green algae

Blue-Green Algae	Chemical Record	Unit	Range	Value	Source
Light Saturation	Sat Light	Ly d^{-1}	18-350	85	Wlosinski and Collins 1985
P Half-Saturation	KP	mg L^{-1}	0.001-1	0.2	Calibrated
N Half-Saturation	KN	mg L^{-1}	0.01-1	0.06	Wlosinski and Collins 1985
Inorganic C Half-Saturation	-	mg L^{-1}	0.01-1	0.1	Wlosinski and Collins 1985
Optimum Temperature	Topt	^{o}C	15-28	28	Wlosinski and Collins 1985
Max. Temperature	Tmax	^{o}C	35	35	Wlosinski and Collins 1985
Min. Adaptation Temperature	Tmin	^{o}C	7-12	7	Wlosinski and Collins 1985
Max. Photosynthetic Rate	Pmax	d^{-1}	0.1-4	3.9	Collins and Wlosinski 1983
Photorespiration Coefficient	-	d^{-1}	0.01-1	0.14	Calibrated
Mortality Coefficient	EMort	g $g^{-1}d^{-1}$	0.001-1	0.002	Collins and Wlosinski 1983
Light Extinction	-	1/m-g/m^3	0.01-1	0.144	Megard and Berman 1989
Sedimentation Rate	Sed	g $g^{-1}d^{-1}$	0.01-1	0.1	Wlosinski and Collins 1985

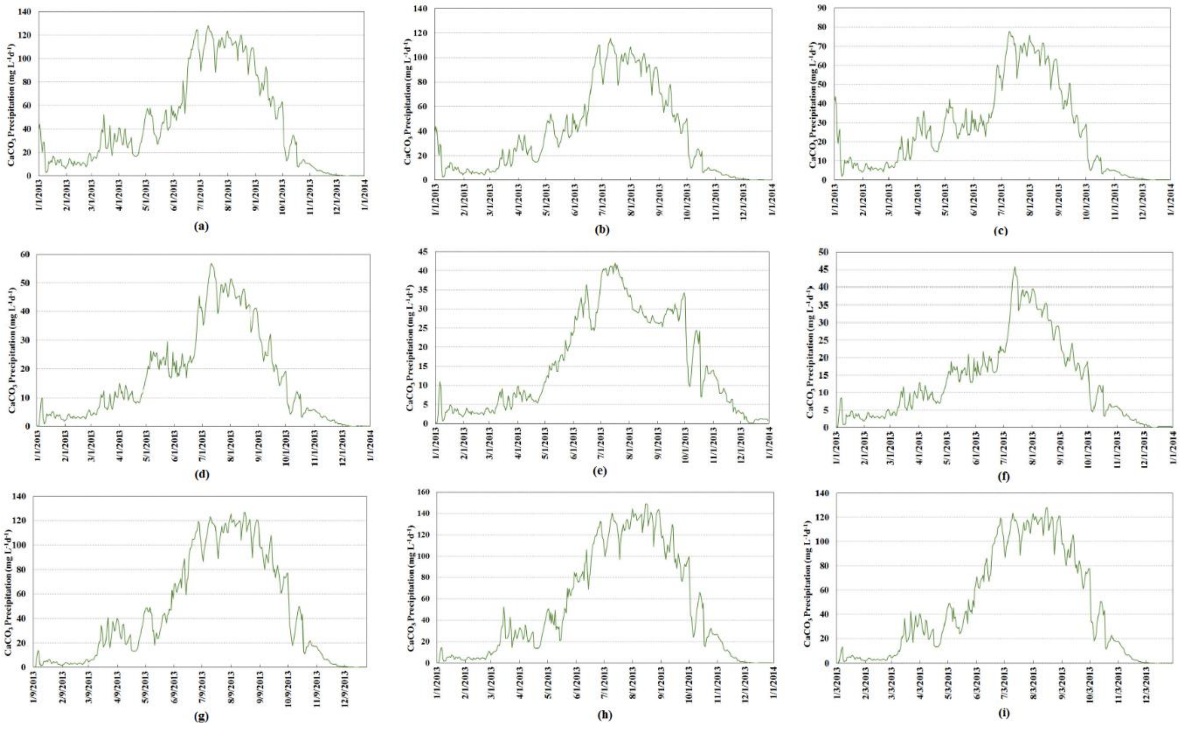

Figure 4. Model calibration results for nine stations (a: St.1, b: St.2, c: St.3, d: St.4, e: St.5, f: St.6, g: St.7, h: St.8, i: St.9)

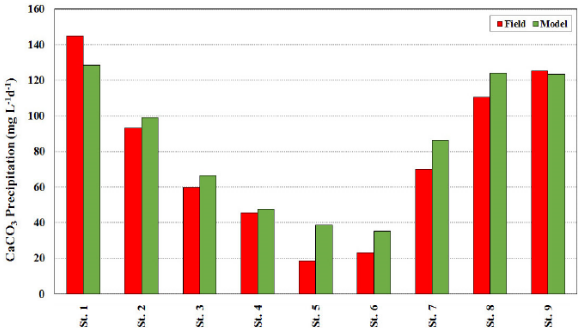

Figure 5. Model calibration with field data

3.2 Results of Model Validation

Validation was done using laboratory data performed at 30^{0}C for two months in summer to see the effect of the summer season on the precipitation of $CaCO_3$ in the lake. According to Figure 6, $CaCO_3$ precipitation starts to increase and reach its first peak after 15 days from the beginning of experiment. Model simulations corresponding to summer months are highlighted in the circular region, depicted in Figure 6, which are quite consistent with the experimental data at 30^0C. Next, modeled $CaCO_3$ is compared with observed values from the field (Figure 7), which are obtained in 2015. The NRMSE values of 2015 data for nine stations are found to be 0.29.

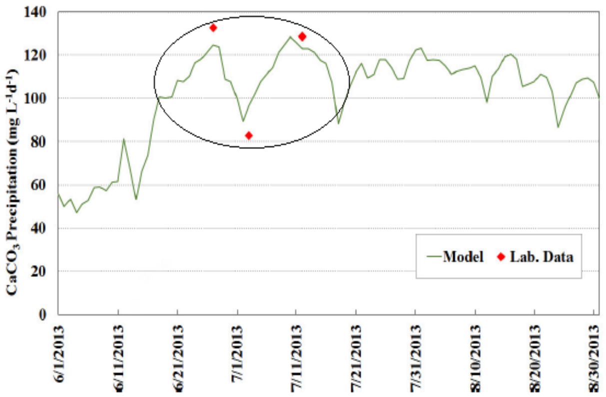

Figure 6. Model validation with experimental data

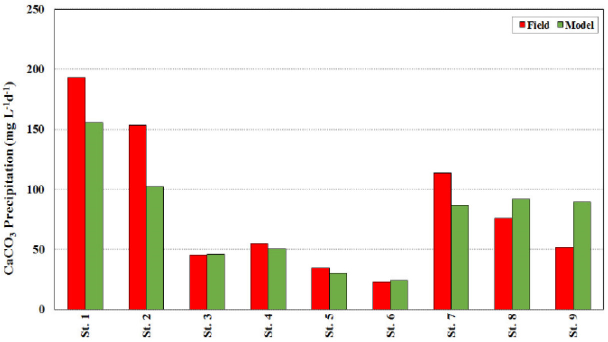

Figure 7. Model validation with field data

4. Conclusions

This study presents the first attempt to estimate $CaCO_3$ precipitation in an alkaline lake using AQUATOX. Model suggests that photosynthesis is one of the most effective processes determining the rate of precipitation. The amount of $CaCO_3$ precipitation is simulated between 35.16 to 128.48 mg $L^{-1}d^{-1}$ in nine stations. According to AQUATOX, *Anabaena* and *Aphanizomenon* sp. are the most dominantly effective species of blue-greens that use carbon source to precipitate $CaCO_3$. These two species are nitrogen fixing cyanobacteria, meaning they can easily compensate the lack of nutrients. The model showed a strong relationship between nitrogen cycles and carbonate precipitation in the lake by *Anabaena* sp. This determination is consistent with the fact that nitrogen cycles cause alkalinity increased by consuming proton and thus creating a favorable condition for carbonate precipitation. Considering that CO_2 is already in equilibrium with the atmosphere, production of CO_2 via oxidative degradation of organic matter (e.g., glucose and acetate) would not have a significant effect on the pH of the lake. Therefore ammonium production, as also suggested by the model results, could be the main control in the lake.

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