MODELING CALCIUM CARBOBATE PRECIPITATION IN THE ACIGÖL LAKE USING AQUATOX

by

Fereshteh Karami

BS., in Stat., University of Science and Culture, Tehran, 2011

Submitted to the Institute of Environmental Sciences in partial fulfillment of
the requirements for the degree of
Master of Science
in
Environmental Sciences

Boğaziçi University
2017

To Lake Urmia...

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my advisor Dr. Başak Güven for the useful comments, remarks and engagement through the learning process of this master thesis. I am gratefully thanks to her patience, kind personality and her trust me by providing research experiences in my academic life which all will be a great pattern in my future.

My sincere thanks also go to my thesis committee: Dr. Nurgül Çelik Balcı, Dr. Işıl Balcıoğlu, Dr. Nadim Copty, and Dr. Nazlı Olgun Kıyak for their supports regarding this work and their instructive contributions to move forward this thesis.

I also would like to express my acknowledgment to my family who always been kind and supportive to me. Finally, This thesis is dedicated to my husband, Mohammad, who has been a constant source of support and encouragement during the challenges of graduate school and life. I am truly thankful for having you in my life.

MODELING CALCIUM CARBOBATE PRECIPITATION IN THE ACIGÖL LAKE USING AQUATOX

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°C, and field observations obtained in August, 2015. Next, sensitivity of $CaCO_3$ precipitation to the variations in major input parameters was assessed. Finally, scenario analysis was undertaken to investigate the effect of meteorological changes on $CaCO_3$ precipitation. Model results suggest that the amount of $CaCO_3$ precipitation in the system ranges between 35.16 to 128.48 mg $L^{-1}d^{-1}$. The NRMSE between the modeled and observed values are found to be 0.41. Parameters related to primary productivity, especially those related with blue-greens are found to be the most significant parameters affecting $CaCO_3$ precipitation in the lake.

ACIGÖL'DEKİ KALSİYUM KARBONAT ÇÖKELİMİNİN AQUATOX İLE MODELLENMESİ

Düşük maliyetli üretim süreçleri sebebiyle, birçok endüstri kireçtaşı formundaki $CaCO_3$ mineralini kullanmaktadır. Bu araştırmanın başlıca amacı, 2013 ve 2015 yıllarına ait, saha çalışmalarından elde edeilen su kalitesi ve Meteoroloji Genel Müdürlüğü'nden elde edilen meteorolojik verileri kullanarak Acıgöl'deki $CaCO_3$ çökelimini modellemektir. Bu amaca yönelik olarak, su kalitesi ve $CaCO_3$ çökeliminin modellenmesi için Çevre Koruma Ajansı'nın (Environmental Protection Agency, EPA), AQUATOX modeli kullanılmıştır. İlk olarak, AQUATOX modelinin veritabanından gölün karakteristik özelliklerini mümkün olan en iyi şekilde tanımlayacak olan bir vekil model seçilmiştir. Daha sonra model, göle ait dokuz istasyondan elde edilen besin, bitki, su kalitesi, saha karakteristikleri, giriş yükleri ve göl hidrodimaği verileri kullanılarak kalibre edilmiştir. Kalibrasyon verisi 2013 yılına ait saha ve meteorolojik gözlemler kullanılarak gerçekleştirilmiştir. Model validasyonu 30°C altında yürütülen labaratuvar sonuçları ve 2015 Ağustos ayına ait saha verileri kullanılarak yapılmıştır. Daha sonra başlıca model girdilerindeki değişimlerin $CaCO_3$ çökelimi üzerindeki etkileri hassasiyet analizi ile değerlendirilmiştir. Son olarak ise, meteorolojik değişimlerin $CaCO_3$ çökelimi üzerindeki etkilerini araştırmak amacıyla senaryo analizleri yapılmiştir. Model sonuçlarına göre sistemdeki $CaCO_3$ çökelimi miktari 35.16 ve 128.48 mg $L^{-1}d^{-1}$ aralığında değişmektedir. Modellenen ve gözlenen veriler arasında NRMSE 0.41 olarak bulunmuştur. Birincil üretime, özellikle mavi-yeşil alglere air parametreler, göldeki $CaCO_3$ çökelimini etkileyen en belirgin parametreler olarak bulunmuştur.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS/ABBREVIATIONS

Symbol	**Explanation**	**Units used**
A	Drainage Area	(m^2)
APHA	American Public Health Association	
BOD	Biological Oxygen Demand	
c	Rational Run off Coefficient	
Ca^{2+}	Calcium	(mg L^{-1})
$CaCO_3$	Calcium Carbonate	(mg $L^{-1}d^{-1}$)
CBOD	Carbonaceous Biochemical Oxygen Demand	
C_f	Field measured calcium carbonate	(mg $L^{-1}d^{-1}$)
Cl^-	Chloride	(mg L^{-1})
C_m	Modeled calcium carbonate	(mg $L^{-1}d^{-1}$)
C2OM	Stoichiometric constant for & organic carbon matter	
CO_3^{2-}	Carbonate	(mg L^{-1})
CSTR	Continuously Stirred Tank Reactors	
d	day	
Emort	Mortality coefficient	(g $g^{-1}d^{-1}$)
EPA	Environmental Protection Agency	
H^+	Hydrogen	(mg L^{-1})
H_2CO_3	Carbonic Acid	(mg L^{-1})
H_2O	Water	(mg L^{-1})
HCO_3^-	Bicarbonate	(mg L^{-1})
i	Precipitation intensity	
IAP	Ion Activity Product	
IC	Ion Chromatography	

ICP-MS	Inductively Coupled Plasma-Mass Spectrometer	
k_f	Calcium carbonate precipitation coefficient	(L^2 $mol^{-1}m^{-2}min^{-1}$)
KN	N Half-Saturation	(mg L^{-1})
KP	P Half-Saturation	(mg L^{-1})
L	Litre	
Ly	Radiation Langley	
Mg^{2+}	Magnesium	(mg L^{-1})
$MgCO_3$	Magnesium carbonate	(mg L^{-1})
Na^+	Sodium	(mg L^{-1})
NH_3^+	Ammonia	(mg L^{-1})
NH_4^+	Ammonium	(mg L^{-1})
NO_2^-	Nitrite	(mg L^{-1})
NO_3^-	Nitrate	(mg L^{-1})
O_2	Oxygen	(mg L^{-1})
NRMSE	Normalized root mean square error	
P	Phosphorus	(mg L^{-1})
PCB	Poly Chlorinated Biphenyl	
Pmax	Maximum photosynthetic rate	(d^{-1})
PO_4^{2-}	Phosphate	(mg L^{-1})
Q	Water discharge	(m^3 d^{-1})
QGIS	Quantum Geographic Information System	
r_p	Calcium carbonate precipitation rate	(mol $L^{-1}min^{-1}$)
S	Particulate surface area	(m^2 L^{-1})
s	Second	
Scen.	Scenario	
Sed	Sedimentation rate	(g $g^{-1}d^{-1}$)
S_c	Surface area provided by existing calcite particles	(m^2 L^{-1})
Set.	Dataset	

SO_4^{2-}	Sulphate	(mg L^{-1})
S_p	Surface area provided by existing non-calcite particles	(m^2 L^{-1})
SPSS	Statistical Package for the Social Sciences	
St.	Station Number	
Std.	Standard Deviation	
T	Temperature	(°C)
TDS	Total Dissolved Solids	
Tmax	Maximum temperature	(°C)
Tmin	Minimum temperature	(°C)
Topt	Optimum temperature	(°C)
TOC	Total Organic Carbon	
TSMS	Turkish State Meteorological Service	
TSS	Total Suspended Solid	
RMSE	Root mean square error	
USEPA	United States Environmental Protection Agency	
γ_2	Activity Coefficient for Divalent Ions	

1. INTRODUCTION

Acıgöl Lake is an alkaline lake in the southwest of Turkey. One of the major precipitation is attributed to $CaCO_3$. The various chemical, meteorological and plant parameters cooperate together to shape the $CaCO_3$ precipitation quantity in this lake. The $CaCO_3$ precipitation is a dynamic occurrence which responds to the various geographic, climatic, chemical and physical characteristics of Acıgöl Lake.

The amount of CO_2 varies with precipitation locations and conditions with saturation being greatest in warm shallow water with lower levels of , because of photosynthesis and temperature [1]. In these locations, $CaCO_3$ precipitates readily either inorganically or with the help of organisms.

As the organisms die their hard or mineralized parts, shells, fall to the ocean floor and accumulate or dissolve depending on depth, temperature, and pressure. Shells and such which fall to the bottom of the deep parts of the lake are most often redissolved because the deeper waters can hold more CO_2 and are colder [2].

Usually, modeling $CaCO_3$ precipitation is associated with the occurrence of blue-green algae, and autochthonous formation and subsequent precipitation of calcium carbonate is an important process in the carbon and calcium cycling in many hard waters.

Both phytoplankton groups, blue-green algae, and cyanobacteria calcify when they grow in oligotrophic, carbonate and calcium-rich lake water. Once formed, $CaCO_3$ has a number of environmental impacts. Because of their size, $CaCO_3$ crystals settle slowly and scatter irradiance quite efficiently. As a consequence, they remain in suspension with a significant reduction in water clarity [3].

The most spectacular cases of seasonal $CaCO_3$ precipitation are called as “whiting events”. These are very fast large-scale precipitations of fine-grained $CaCO_3$ creating white waters that occur during the summer months because in summer increasing the temperature reduce the solubility of $CaCO_3$. Beyond water clarity and irradiance transmission, $CaCO_3$ precipitation serves as a safety valve that moderates pH rises by removing carbonate [4].

1.1. Aim of the Study

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. Different scenarios are implemented for various meteorological, mineralogical and environmental conditions to simulate the lake's water quality prediction. The AQUATOX model by Environmental Protection Agency's (EPA) is used to model the lake's water quality and $CaCO_3$ precipitation.

This thesis contains five main objectives; (a) to gain an understanding of the major mechanisms involved in the precipitation of $CaCO_3$; (b) to produce calibration table for conditions of effective parameters on $CaCO_3$ precipitation such as plants life conditions; (c) to examine the sources and effects of parameters on modeling of $CaCO_3$ precipitation by applying sensitivity analysis; (d) to utilize AQUATOX software (by EPA) in order to fulfill the $CaCO_3$ precipitation modeling objectives; (e) to apply lake's scenario analysis in different conditions for Lake environments and predicted new meteorological data.

1.2. Structure of the Thesis

Chapter 2 provides a background discussion on the significance of $CaCO_3$ in Lakes and the mechanisms of $CaCO_3$ precipitation with respect to major environmental factors such as irradiance, nutrients, and temperature in the Acıgöl Lake. There are several studies published in literature researches about modeling $CaCO_3$ precipitation in lakes with various approaches and with the focus on chemical processes of $CaCO_3$ precipitation. This chapter provides information about applications of Aquatox in

Environmental Modeling other than $CaCO_3$ precipitation.

Chapter 3 describes the methodology used to model the precipitation of $CaCO_3$ in Acıgöl Lake. This chapter provides all the information about physical, meteorological, mineralogical and chemical characteristics of Acıgöl Lake. The chapter also provides the description of the model algorithms which AQUATOX use together with the modeled processes. Section 3.2 is allocated for the description of the computer simulation program and how to set up the model in AQUATOX.

The initial conditions and information about required data for modeling with AQUATOX are, Concentrating on sampling approaches to obtain that how data are measured in the field and laboratory measurements are presented in Section 3.2.2. Steps for the calibration and different validation of the model with analytical chemical formulas required by in the model are described in Sections 3.2.3 and 3.2.4.

In the context of Chapter 3, a technique called Nominal Range sensitivity analysis is described in order to identify the sensitivity of parameters used in the model. The generated results of the Sensitivity Analysis are also included in this chapter. Section 3.3 is concerned with the sensitivity of the model outputs to the key parameters of the model. Section 3.4 describes the scenario analysis to evaluate different conditions of Acıgöl by applying these differences in both lake environment variables and predicted meteorological data.

Chapter 4 include all of the results and outputs of all the modeling steps including calibration, validation, sensitivity and scenario analysis. Discussion about the most sensitive parameters and their relationship with the mechanism of $CaCO_3$ precipitation are elaborated in this chapter. Finally, Chapter 5 presents a number of important conclusions of the works presented in this thesis.

2. THEORETICAL BACKGROUND

2.1. Significance of $CaCO_3$ in Lakes

$CaCO_3$ is one of the most common forms of Calcium (Ca^{2+}), which constitutes 4.9% of the earth's crust [5]. 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 [6].

Many industries use $CaCO_3$ broadly as an inorganic mineral that appears in forms of chalk or limestone [7]. 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 [8].

Calcite is a cold anoxic marine sediment which comprise the largest organic carbon sink on Earth and is a carbonate mineral with crystal structures of rhombohedra, and the most stable polymorph is $CaCO_3$.

The crystal growth is highly affected by the variables, such as pH of the solution, solute concentration, and temperature [7]. 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 [5].

$CaCO_3$ precipitates when it is over saturated, while it tends to dissolve in water when it is under saturated. When $CaCO_3$ is saturated, water is assumed to be in equilibrium with $CaCO_3$, meaning it neither precipitate, nor dissolve, in an aquatic environment [9].

2.1.1. Mechanism of $CaCO_3$ Precipitation

Almost all $CaCO_3$ is formed biogenically, primarily by plants using bicarbonate and carbonate as a source of carbon. Even "whitings" (sudden precipitation of fine-grained calcite) have been shown to be a consequence of cynobacteria photosynthesis [10]. Calcareous plants are characterized by pH polarization with acidic and alkaline poles; calcification occurs at the alkaline pole. Proton generation leads to the formation of twice as much CO_2 than is used in the process, providing CO_2 that is immediately taken up for photosynthesis. As a result, calcification and photosynthesis use equivalent moles of carbon, as shown by both theory and experiments. The chemical process of $CaCO_3$ production can be represented by the following equations [11].

$$Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_{3(aq)} + 2H^+ \tag{2.1}$$

$$2H^+ + 2HCO_3^- \rightarrow 2CO_2 + 2H_2O \tag{2.2}$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_{3(s)} + CO_2 + H_2O \tag{2.3}$$

Organic carbon existing in microorganisms are either dissolved in water or they are in sediments of lakes and their effect on $CaCO_3$ precipitation is shown by these equations as follows,

$$OrgC + O_2 \rightarrow CO_2 \tag{2.4}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)} \qquad pH < 7 \tag{2.5}$$

$$H_2CO_{3(aq)} \rightleftharpoons H^+ + HCO_3^- \qquad pH > 7 \tag{2.6}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad pH > 8 \tag{2.7}$$

And CO_3^{2-} reacts with Ca^{2+} in alkaline conditions and Calcium Carbonate is precipitated as solid.

$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_{3(s)} \tag{2.8}$$

Not all plants can use bicarbonate. However, it is difficult to generalize; mosses do not and many chrysophytes (golden algae) do not. Evidence suggests that other groups, including greens, cynobacteria, diatoms, and macrophytes, have species that use bicarbonate and that these are dominate in alkaline systems [3].

2.2. Modeling $CaCO_3$ Precipitation in Different Lakes

Several studies have focused on the formation, reactions, settling processes, and deposition of $CaCO_3$ in lakes similar to Acıgöl Lake such as in Pyramid Lake, Nevada [12], Lake Constance with focus on chemical equilibrium, sedimentation, and nucleation by algae [13], in addition to modeling the impacts of $CaCO_3$ precipitation on the epilimnion of an ultraoligotrophic, and hard-water Torch Lake [4] which is an important similar lake modeling studies to the Acıgöl Lake.

2.3. Application of Aquatox in Environmental Modeling

AQUATOX has successfully been applied to model various processes in aquatic systems including, ecological assessment of pesticides in an Iowa reservoir, fish dynamics in a North Carolina stream [14], nutrients and suspended sediments in a Minnesota River [10], fate of PCB in a Georgia reservoir and the food web dynamic characteristics of PCB in Lake Hartwell [14]. AQUATOX model also used to simulate the changes of plants and nutrients in Omerli reservoir and used under three specific scenarios [15].

Aquatic ecosystem model is developed by AQUATOX to simulate the seasonal changes of algae and the changes of the water quality indexes in the Dianshan Lake ecosystem [16], and analyzed the factors affecting blue-green algae. The indexes to focus and control the process of landscape lakes ecological restoration in north China HM ecological towns are determined and presented by AQUATOX [17].

3. METHODOLOGY

3.1. 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°55'27.98"-37°45'7.41"N and 29°41'11.72"E-30°0'17.24" 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 varies from 1 m (August-September) to 2.1 m (December-January) [18].

Groundwater is the main inflow to Acıgöl 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 [19]. Figure 3.1 presents the locations of sampling stations in the Acıgöl Lake in July, 2013 and August, 2015 used in this study.

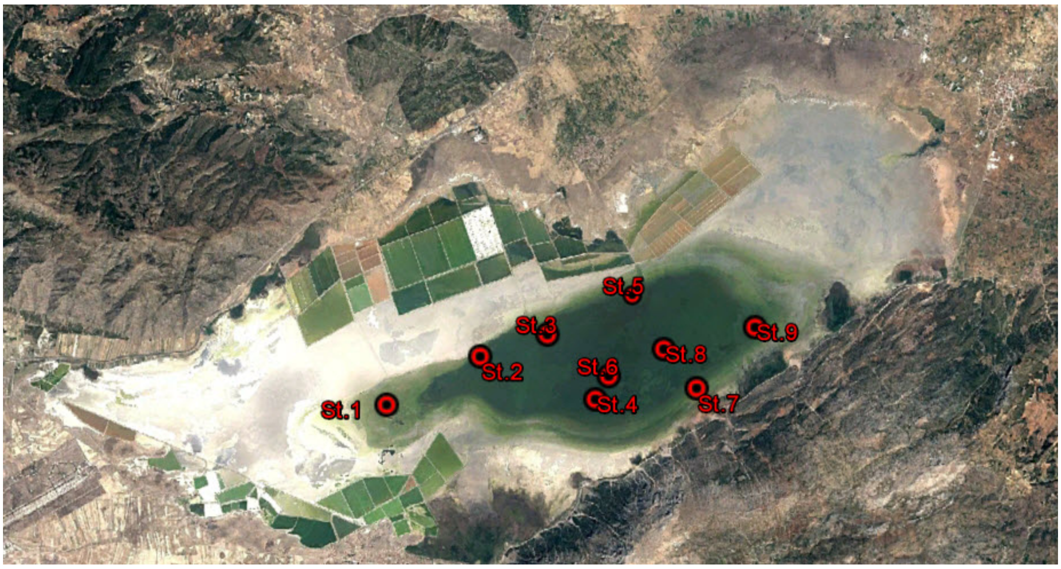


Figure 3.1. Acıgöl Lake sampling stations.

Figure 3.2. Acıgöl Lake [20].

3.1.1. Meteorological Characteristics

Semiarid continental climate governs Acıgöl Lake [19], with a mean daily temperature ranging from 3.3°C and 24.4°C in January and July, respectively [21]. Lake's area may be subject to desertification, during extreme temperatures in the summer period, due to the increases in evaporation with yearly mean of 120 cm and agricultural water consumption [22]. The mean annual wind velocity is obtained from (TSMS) around 2.1 m s^{-1}, and its dominant direction is towards South-East.

Although receiving around 40 cm mean precipitation annually, the evaporation and precipitation ratio is drastically high around 174 cm, being one of the most important factors influencing the geolimnology of Acıgöl Lake. Notable variations of evaporation are not observed from the lake's surface [21]. Due to the fact that lake has no outlets, evaporation plays an important role in water level variations of the lake. Human activities such as the use of karstic sources for agricultural and the other purposes are cause water level decrease. Meteorological data used in this study such as temperature, irradiance, precipitation, and evaporation are obtained from TSMS and further discussed in Section 3.2.2.

3.1.2. Mineralogical and Chemical Characteristics

Acıgöl Lake contains a salty composition of Na-Cl-SO_4 [21]. Groundwater is the major water inflow to the lake, and is governed by two specific contributors; the Mg-HCO_3 containing groundwater discharge, and the Na-SO_4 rich spring water [18].

Concentrations of Na^+, Mg^{2+}, Cl^-, Ca^{2+}, SO_4^{2-}, and HCO_3^- increase with progressive evaporation of lake water in the dry season, and decrease via autogenic carbonate precipitation. The maximum salinity in the Acıgöl Lake is about 211 g L^{-1}. The main contributor to the lake's salinity are the sulfate springs, which are notable for lake's sodium sulfate Na_2SO_4 reserves, supplied by a fault line on its southern side [23]. The substantial amount of Na_2SO_4 used in industries of Turkey is provided from the Acıgöl Lake. Water chemistry analysis of the relatively warm Acıgöl Lake, reveals that the lake is dominantly comprised of Ca-Na-HCO_3-Cl [22]. Due to this special water chemistry Na^+=27 mg L^{-1}; Mg^{2+}=82-3,425 mg L^{-1}; Cl^-=290-35,320 mg L^{-1}; Ca^{2+}=102-745 mg L^{-1}; SO_4^{2-}=112-15,232 mg L^{-1} the lake has a high microbial diversity, also exhibiting some unique microorganisms [20].

Acıgöl Lake contains dark colored and soft mud sediments saturated by rich organic material, which lays over the southeastern zone. Relatively high values of Total Organic Carbon (TOC) found in lake's sediments demonstrate a considerable bacterial activity. Authigenic precipitation of various phases of $CaCO_3$ polymorph minerals occurs in the Acıgöl Lake. For example, moderately halophilic bacteria such as Halobacterium salinarum, Duniella species that originate from the deposits and sediments of the lake have been used in experiments and successfully demonstrated the formation of a variety of calcium or magnesium carbonates, such as hydromagnesite, dypingite, huntite, monohydro calcite and aragonite [20].

3.2. Model Description

In this thesis, AQUATOX model has been used for the prediction of $CaCO_3$ precipitation in the study area. AQUATOX, which is a simulation model for aquatic ecosystems developed by United States Environmental Protection Agency (USEPA). It 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, flow, 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. AQUATOX includes five parameter libraries including, "Animal", "Chemical", "Plant", "Site" and "Remineralization"; each containing a large number of model parameters. The model parameters provide coefficients for relevant process functions. While default input parameters of the model can be used in the model, users can also specify values for specific conditions of simulated objects or processes.

AQUATOX, generally, utilizes differential equations to represent changing values of state variables, normally with a reporting time step of one day. These equations require calibration values or initial conditions for running a simulation. Altering the beginning of simulation time may also affect the initial conditions for the simulation. A simulation can start on any date and may last for any length of time from a few days, corresponding to a microcosm experiment, to decades, accounting for to an extreme event followed by long-term recovery [3].

AQUATOX can establish 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. Moreover, it is possible to model nutrient cycle dynamics and their relations with environmental variables, via AQUATOX. A conceptual representation of the ecosystem modelling procedure, with variable interactions and interrelations in AQUATOX, is depicted in Figure 3.3 [3].

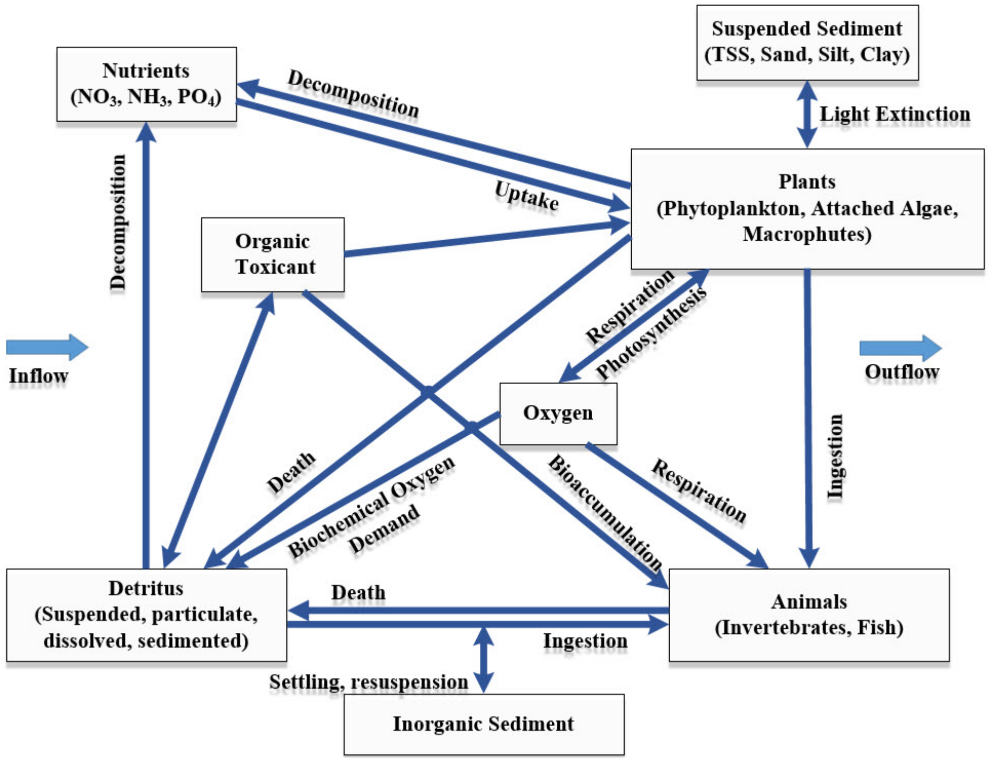


Figure 3.3. Conceptual model of ecosystem in AQUATOX [3].

Depending on the modeling purpose, specific aspects of Figure 3.3 may require particular attention for the determination of model parameters. $CaCO_3$ precipitation has a biogenic origin. 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 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.

$CaCO_3$ precipitation is simulated as a function of pH by AQUATOX. Calcite precipitation takes into account the molar equivalent of photosynthesis for most plants and precipitation occurs, when pH is around 7.5 [2]. The algorithm simulates precipitation of $CaCO_3$ as being the molar equivalent to photosynthesis of most plants is reached when pH is equal or bigger than 7.5 [2].

$$CalcitePcpt = C2Calcite.\frac{Photosynthesis_{PlantSubset}}{C2OM} \tag{3.1}$$

where CalcitePcpt is the precipitated calcite (mg $L^{-1}d^{-1}$), C2Calcite is a stoichiometric constant 8.33, g calcite g C^{-1}, PlantSubset represents plants except Bryophytes and Other Algae, C2OM is a stoichiometric constant for carbon and organic matter (1.9, g C g OM $^{-1}$).

As with most of the modeling studies, here, some assumptions are also made in order to simplify the modeling of $CaCO_3$ precipitation in the lake. For example, sorption of dissolved phosphate to $CaCO_3$ is modeled, but desorption process is ignored. Precipitated $CaCO_3$ is protected, in part, by sorbed organic material. Therefore, it is assumed to be insoluble [2]. Because the settling rate is high in case of Acıgöl Lake, it is also assumed that the $CaCO_3$ directly becomes a part of the sediment.

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; model verification with test runs for nine stations, and model validation. Model calibration is done using meteorological data field data obtained in 2013. Model validation is carried out by Laboratory Data in 2013 and field data of 2015. After validation is completed, parametric sensitivity analysis is undertaken to evaluate the sensitivity of simulated $CaCO_3$ to the alterations in input parameters. Finally, eight different scenarios were generated to account for various meteorological conditions and analyzed for their effects on $CaCO_3$ precipitation in the lake.

The schematized methodological approach and modeling procedure undertaken in this thesis are demonstrated in Figure 3.3

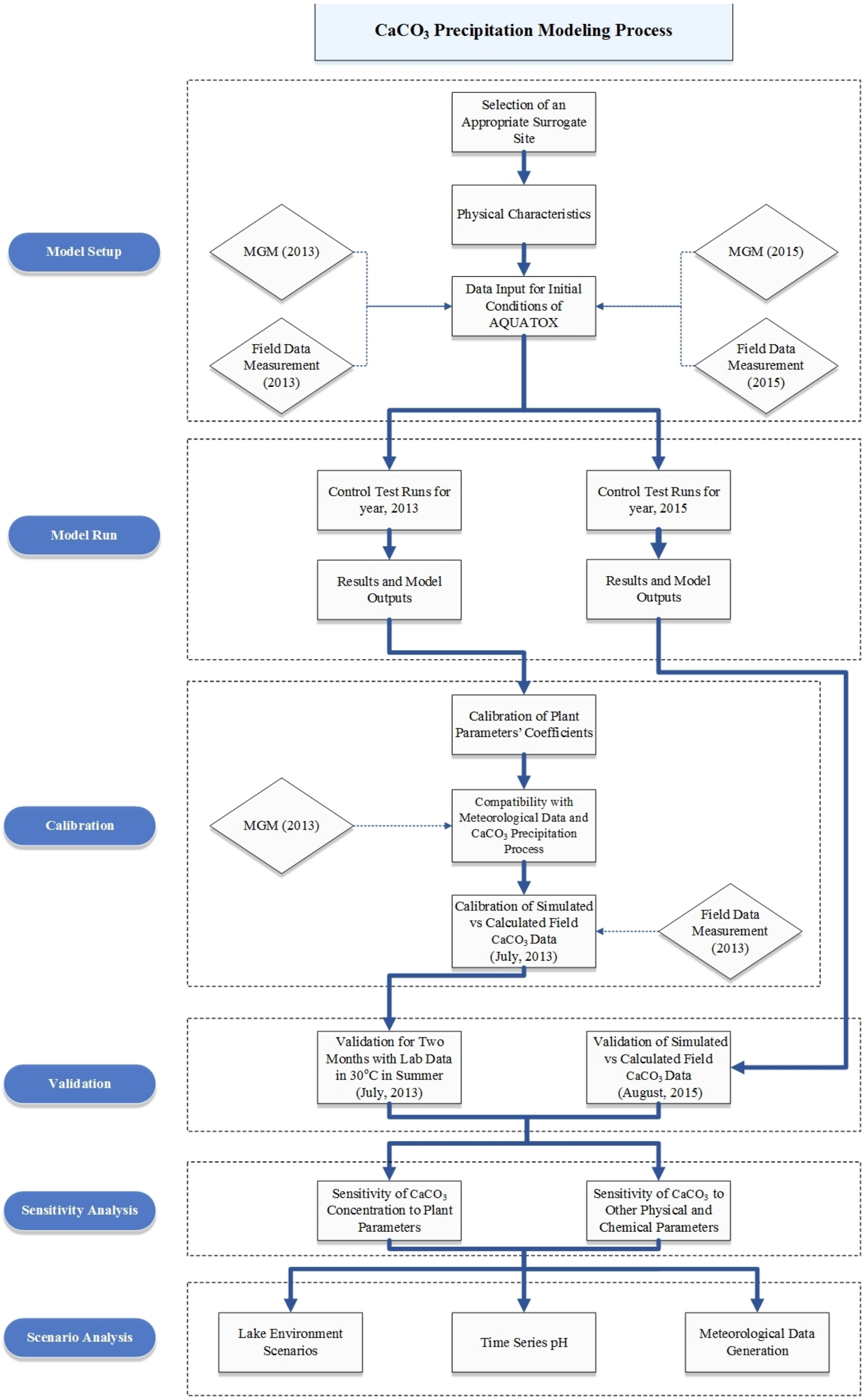


Figure 3.4. Methodological approach and modeling flowchart.

3.2.1. Model Setup

From environmental modeling viewpoint, it is possible to explore a natural lake system through the use of 'box models'. In these type of models, the lake can be considered to be a well-mixed compartment, or completely mixed system, where no concentration gradients occur within the system. These models are aimed to simplify the complex behavior of fate and transport mechanisms taking place in a natural water body. Generally, 'box models' are derived from the concept of Continuously Stirred Tank Reactors (CSTRs). Chemical kinetics and reactor theory are widely used in defining physicochemical and biochemical systems modeling, such as processes that occur in freshwater. In this thesis, Acıgöl is considered to be a CSTR. This application allows the assumption of a homogeneously distributed concentration of chemicals in the lake environment.

For simulating $CaCO_3$ in the lake, nine test runs are carried out for nine different stations, which are demonstrated in Figure 3.1. Daily meteorological data including temperature, precipitation, evaporation and irradiance, and water quality data for the year 2013 are used as model input.

Setting up the model in AQUATOX requires some basic steps including; (i) finding an appropriate surrogate site, (ii) modifying site's hydrodynamic, chemical and biological characteristics based on the study area, (iii) applying the best available field and meteorological data to set the initial conditions. The simulation can then start from any selected day and the model can run for any duration on a daily time step basis. It should be noted that $CaCO_3$ precipitation is assumed to be influenced by the total biomass of the system, hence biomass of individual organism groups are modeled.

As with any modeling study, AQUATOX sometimes may require parameters and variables that are not always possible to measure in the field, due to cost or lack of appropriate techniques. To overcome such limitations, some of these parameters and variables are derived from the surrogate site's library [24]. In this study, Onondaga

Lake, from northwest of Syracuse in USA, was selected as the surrogate site. The main reason for selection of Onondaga Lake as the surrogate is the hydrogeologic and water quality similarities between the surrogate and Acıgöl. Onondaga Lake is an oligotrophic, highly alkaline lake that has high salinity, similar to the Acıgöl.

Following the selection of the surrogate site, all initial conditions for nutrients, biota, detritus, water quality, and hydrogeometry are entered to AQUATOX to set up the model. The first step in model set up is the calculation of lake's volume. The rational method is chosen for the determination of water volume based on water depth, surface area and precipitation amounts. Volume of lake can then be computed in a dynamic manner, given the dynamically contributing inflow, outflow and evaporation factors governed by Equation 3.2.

$$\frac{dVolume}{dt} = Inflow - Outflow - Evaporation \tag{3.2}$$

where, the *dVolume/dt* represents the change of lake's volume in time unit (m^3 d^{-1}), *Inflow* is the amount of water entering to the lake (m^3 d^{-1}), *Outflow* is the discharge of water from the lake (m^3 d^{-1}) and *Evaporation* represents the evaporation rate of the lake (m^3 d^{-1}) [3].

There are no direct inflows from surface water sources, such as rivers, to the Acıgöl Lake. The only water inflow the lake is the springs that are filled by rainfall in wet seasons groundwater. In addition, there is no outflow from lake except evaporation during the hot season as it is discussed in Section 3.1.1. Hence, in Equation 3.2 the final model of the volume model contains just inflow and evaporation terms, with zero discharge, which AQUATOX can compute by the following formula:

$$\frac{dVolume}{dt} = Inflow - Evap \tag{3.3}$$

To calculate amount of rainfall inflow to the lake rational method is applied as following equation, [25],

$$Q = ciA \tag{3.4}$$

where Q is peak discharge (m^3 d^{-1}) and c is runoff coefficient for unimproved areas and i is rainfall intensity (mm d^{-1}) and A is drainage area (m^2).

AQUATOX cannot successfully produce the simulation, when the volume of water in a site falls to zero, or when it is more than a value that may interfere with the amount of biota or other parameters. Therefore, c is taken as 0.1 out of a range of (0-1), for unimproved areas [25]. Time series precipitation are entered into the model from the data obtained from TSMS for the year 2013, and drainage area is calculated by QGIS as 1,116 km^2.

3.2.2. Data Requirements

Water quality sampling is a crucial step in developing models for freshwater systems. When carried out cautiously, sampling strategy can assist the modeler, in terms of obtaining the accurate values for environmental variables and parameters to be used for model parameterizations, calibration, and validation. Direct or indirect techniques can be used in the measurement.

Due to the spatial sampling scheme, models can be represented as distributed, semi-distributed or lumped. The temporal sampling scheme, on the other hand, depends on a models' duration and temporal resolution. The spatial sampling scheme usually acts as a compromise between what best represents the system under consideration and the computational resources and data available for that system [24].

3.2.2.1. *Field Measurement.* Field measurements and water sampling were carried out in the sampling sites indicated in Figure 3.5 at July 2013 and August 2015 for nine stations as depicted in Figure 3.1. pH and salinity were measured in situ with pH and conductivity probes (WTW). Colorimetric measurements with Hach kits (DR2800 Hach Company) were used to measure SO_4^{2-}, PO_4^{3-}, NO_2^-, and NO_3^- concentrations in the lake water. All water samples were filtered on site with a sterile syringe and single-use membrane filters (0.45 μm millipore) and stored in 50 mL and 500 mL polyethylene bottles and refrigerated at 4°C until further analysis. The 500 mL samples were used for anion and cation analysis. Water samples (for major ions and elements) were analyzed with Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) and Ion chromatography (IC). Spectrophotometry is used to measure chlorophyll-a in surface water.

Figure 3.5. Field measurements in Acıgöl Lake [20].

3.2.2.2. *Laboratory Experiments.* In addition to the field data, experimental data are also used for validating the model. The laboratory data were performed at 30°C that is appropriate for validation of simulated $CaCO_3$ against July 2013 dataset, which is further discussed in detail in Section 3.2.4.

Experimental $CaCO_3$ precipitation experiments were performed with artificial lake water that is simulated to aaker2010strategicrepresent the biogeochemical conditions and their influences on carbonate precipitation in Lake Acıgöl. The water chemistry of the lake is seasonally monitored by measuring pH, Electrical Conductivity Meter, Temperature, Mg^{2+}, Ca^{2+}, K^{+}, Na^{+} , SO_4^{2-}, Cl^{-}, NO_3^{-}, and NH_4^{+}. The experimental solution for the precipitation experiments is prepared based on the water chemistry of Acıgöl Lake. The chemical composition of the liquid culture medium used for the precipitation experiments is given in Table 3.1. The medium is prepared with 1% (w/v) yeast extract, 0.5 % (w/v) proteose-peptone, 0.1% (w/v) glucose and 7.5% NaCl supplemented to provide a Mg^{2+} and Ca^{2+} as acetate. The medium is modified by adding varying amounts of Na_2SO_4 to obtain final sulphate concentrations of 14 $mmolL^{-1}$, 28 $mmolL^{-1}$ and 56 $mmolL^{-1}$, representing the range of seasonally (March through August) varying sulphate concentrations in the lake water.

Table 3.1. Chemical composition of liquid medium used in the experiments.

Chemical Composition	**Unit**	**Value**
pH	-	7.2
SO_4^{2-}	$mmolL^{-1}$	0.14-28.56
Ca^{2+}	$mmolL^{-1}$	11
Mg^{2+}	$mmolL^{-1}$	85
K^{+}	$mmolL^{-1}$	17
Na^{+}	$mmolL^{-1}$	1,329
Cl^{-}	$mmolL^{-1}$	1,285
Proteose Peptone	(w/v)%	0.50%
Glucose	(w/v)%	0.10%
Yeast extract	(w/v)%	1%

3.2.2.3. *AQUATOX Initial Conditions and Data Requirements.* Data requirements in AQUATOX depend considerably on the site characteristics that is being modeled and the goal of the modeling. Any ecosystem model consists of multiple components requiring input data. In AQUATOX, there are two main forms of driving variables, being abiotic and biotic state variables. Biotic variables are those related to the organisms, whereas abiotic variables are the ones that describe the physical and chemical environment, such as temperature, irradiance, and nutrient loadings. There are also some point estimate parameters that have default values set in the database. These databases are called 'Libraries' in AQUATOX and include information on plants, animals, remineralization, chemicals, and site characteristics, which can be modified based on the needs of the modeler.

In$CaCO_3$ precipitation modeling, different categories of parameters and variables are effective. Some of the driving variables, which can also be called as 'forcing functions' for AQUATOX simulations are the meteorological data, which are obtained from TSMS. Table 3.2 provides information on meteorological data.

Table 3.2. Meteorological data used in the model.

State Variables	**Unit**
Mean Daily Temperature	(°C)
Total Daily Precipitation	(mm)
Total Daily Evaporation	(mm)
Total Daily Light Radiation	(Ly d^{-1})

Water temperature is an important controlling factor for all physical, chemical, and biological processes take place in aquatic environments. In addition to the temperature, irradiance amount is also very effective for the processes governing primary productivity [26]. Meteorological data including temperature, precipitation, evaporation, and irradiance are used in the model both for initial conditions and as time series data as Langleys per day 'Ly d^{-1}' [27]. Daily precipitation data is used both as time series data and for the determination of water volume through the rational method.

Surrogate site's characteristics, including length, mean and maximum depths, surface area and latitude are modified based on the characteristics of Acıgöl Lake obtained from field studies and literature. In lake systems modeling, site length is the fetch or distance across the lake, which is 15 km for the Acıgöl Lake [18], [21] . In the model the mean and maximum depth values are used. The average depth of Acıgöl

Lake is taken as 1.6 m based on this study, and depths regarding individual stations are obtained from field studies. Surface area and latitude information are obtained through QGIS software.

Input data, used in the model for predicting $CaCO_3$ precipitation via AQUATOX, are obtained from field measurements, and presented in Tables 3.3 and 3.4.

Table 3.3. List of field measurements values in nine stations in 2013.

	Unit	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9
pH	-	8.2	8.4	7.8	8.3	8.1	7.8	7.9	8.1	7.9
O_2	mg L^{-1}	6.3	7.8	9.4	8.7	6.5	7.5	8.2	10.1	11.2
NO_3-N	mg L^{-1}	35.4	37.7	33.2	42.3	35.6	32.1	31.3	30.6	18.3
NH_4-N	mg L^{-1}	11.2	14.2	8.4	6.2	3.4	0.9	0.8	0.1	0.1
PO_4-P	mg L^{-1}	4.2	3.1	3.2	0.2	0.3	0.01	0.23	0	0
HCO_3	mg L^{-1}	2.98	1.91	3.83	1.49	2.45	3.5	3.75	4.72	125
CO_3^{2-}	mg L^{-1}	2.46	1.78	4.2	2.31	1.23	2.3	1.4	6.2	1.6
SO_4^{2-}	mg L^{-1}	22,173	21,501	17,120	35,639	32,459	31,270	31,500	32,450	12,750
Ca^{2+}	mg L^{-1}	83,683	74,580	19,095	16,030	14,131	13,240	14,570	5,670	4,575
Mg^{2+}	mg L^{-1}	7,895	6,573	7,560	3,450	4,570	1,389	1,673	1,560	1,450
Na^{2+}	mg L^{-1}	678	451	411	341	432	351	345	560	451
TSS	mg L^{-1}	15.3	13.6	12.2	10.3	6.2	9.1	25.6	22.1	19.5
TDS	g L^{-1}	21.7	21.1	23.4	12.1	9.5	12.5	15.6	15.2	16.3
TOC	mg L^{-1}	34.21	41.67	46.2	24.16	22.94	16.9	19.1	22.4	12.3

Table 3.4. List of field measurements values in nine stations in 2015.

	Unit	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9
pH	-	8.5	8.8	7.6	7.6	8.4	8.2	8.3	7.9	7.9
O_2	mg L^{-1}	12.1	9.5	11.6	8.5	7.2	8.2	5.1	11.2	9.3
NO_3-N	mg L^{-1}	36.5	37.5	48.1	26	23.1	20.1	22.3	14.2	21.3
NH_4-N	mg L^{-1}	15.2	17.3	9.6	7.2	5.4	1.2	2.1	0.3	0.3
PO_4-P	mg L^{-1}	4.5	3.1	4.2	0.5	0	0	0.3	0	0
HCO_3	mg L^{-1}	1710	1850	1520	1490	1590	1850	1650	305	275
CO_3^{2-}	mg L^{-1}	3	4	-	3	2	-	2	5	1
SO_4^{2-}	mg L^{-1}	22,100	22,305	16,500	18,560	18,520	19,530	29,200	15,660	11,200
Ca^{2+}	mg L^{-1}	650	351	312	320	450	351	342	450	375
Mg^{2+}	mg L^{-1}	6,950	6,530	5,560	5,450	3,750	1,263	1,572	1,563	1,350
Na^{2+}	mg L^{-1}	82,300	64,520	18,092	15,230	14,520	12,360	11,570	4,500	3,750
TSS	mg L^{-1}	16	15	12	12	5	7	16	21	20
TDS	mg L^{-1}	23.4	24.5	22.1	10.4	8.2	9.6	11.2	10.5	16.2
TOC	mg L^{-1}	45.2	51.2	42.5	25.1	21.9	15.2	17.5	23.2	11.3

Essential nutrients for aquatic food web, such as NH_4^+, NO_3^-, PO_4^{3-}, and dissolved oxygen are entered to the model from the field data. In AQUATOX, one of the most effective parameters in calcite precipitation modeling is pH, mainly because (i) $CaCO_3$ precipitation is predicted as a function of pH, (ii) conversion of refractory detritus to labile detritus is affected by pH, (iii) decomposition of organic matter is affected from variations in pH. In model set up, pH values are obtained from field measurements [3].

There are two types of detritus in AQUATOX which are named as 'labile' and 'refractory' detritus and include all non-living organic material and associated decomposers (bacteria and fungi). Labile detritus is readily decomposed and assimilated, while refractory detritus is resistant to decomposition [3]. Initial conditions and daily loadings of detritus in the water column can be entered as organic matter (dry weight), organic carbon, or Carbonaceous Biochemical Oxygen Demand (CBOD).

AQUATOX can then make the necessary conversions for simulations. Suspended and dissolved detritus initial conditions and loadings are divided into four groups being particulate refractory, labile detritus, dissolved refractory and labile organic matter. Initial conditions and loadings are described by specifying percent particulate and percent refractory. According to available field data for 2013 in Table 3.3, Total Organic Carbon (TOC) is used in AQUATOX to model the precipitation of $CaCO_3$ in each station. Detrital boundary conditions are selected from the surrogate's data.

Total Suspended Solid (TSS) have significant effects on irradiance, hence primary productivity which is one of the factors governing calcite formation. In this study, based on the availability of data, TSS inputs are entered as constant values.

In AQUATOX, different plant groups and associated inputs are classified as Diatoms, Greens, Blue Greens, Other Algae, and Macrophytes. Except 'Other Algae', all of these categories use carbon source, which is effective in the precipitation of $CaCO_3$. Biomass is entered into the model as dry weight (mg L^{-1} dry weight). Field measurements in Acıgöl Lake suggest a value of 200 mg L^{-1} for algal biomass in 1 kg salt, which consumes organic carbon in by Equation 3.1. The most common form of existing algae in Lake Acıgöl are blue-greens, especially *Spirulina sp* and phytoplankton named as *Dunaliella Salina*.

Among all the plants' libraries in AQUATOX, all the species that may be present in the lake are selected for simulations. These selected plants are either salt tolerant or $CaCO_3$ precipitating plants, which use carbon source for calcite precipitation. The selected species and associated taxonomic types are presented in Table 3.5.

Table 3.5. Plants 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	Scenedesmus	Greens	Phytoplankton
Phyto, Green, Marine	Chlorophyceae	Greens	Phytoplankton
Phyto, Hi-Nut, Diatom	Cyclotella nana	Diatoms	Phytoplankton
Phyto, Navicula	Navicula	Diatoms	Phytoplankton

Input data for invertebrates in the AQUATOX model are classified as shredders, sediment feeders, suspension feeders, calms, grazers, snails, and predatory invertebrates. Except for shredders, calms and grazers, field measurements in Acıgöl Lake demonstrated 100 mg L^{-1} of invertebrates in 1 kg of salt. The most common form of sediment feeders are Artemiidae, Protozoa and Fabrea Salina in the lake. Moreover, there is no fish living in Acıgöl Lake due to its high salinity. Therefore, ostracode, daphnia, gastropod and shrimp are entered to the model as to account for invertebrates.

For all biota, AQUATOX uses a fixed value of 10^{-5} g m^{-2} as constant loading. This value is small enough that it does not affect the results during the growing season, yet high enough to prevent extinction.

Following the entrance of required input data with their initial conditions in AQUATOX, test runs are carried out for nine stations, and output results for each station are calibrated. These results represent the initial model runs for $CaCO_3$

simulation in the lake. In this part of the study, to test and verify initial model runs, techniques such as visualization, comparison with other surrogates models and predictive validation are used. Visualization techniques are often associated with a statement that declares how well the modeled results match the observed data. General comparison with other surrogate models to choose better simulation trend for a specified purpose is one of the initial calibration techniques applied in this study and discussed in detail in Section 3.2.3. Predictive validation is the comparison of model output with the actual behavior of the system in question. During calibration and validation steps seasonal variations of $CaCO_3$ are taken into account [24]. The techniques of initial testing (verification), calibration and validation are discussed in detail in the following sections.

3.2.3. Model Calibration

Model calibration can be described as the process of modifying the input parameters of a model until the output from the model matches an observed set of data. Therefore, calibration is a necessary step in every modeling exercise to gain better and more accurate results predictive simulation modeling. According to the modeling procedure flowchart given in Figure , following verification, the calibration step is undertaken by modifying the parameters of the surrogate site. During calibration, $CaCO_3$ precipitation simulation results are also compared with the meteorological data, especially temperature, since there is a close relationship with increasing temperature and irradiance, and $CaCO_3$ precipitation, due to photosynthetic activity.

Perhaps, the most effective process responsible for calcite formation and precipitation is the processes carried out by plants, therefore parameters describing plant growth and plant characteristics are amongst the most significant ones [3]. Coefficients in the plant's library are carefully calibrated, using trial and error technique by modifying parameter values within ranges reported in the literature, to attain better agreement between simulated and observed.

As plants' photosynthesis and growth rates are quite sensitive to the saturating irradiance and nutrient half-saturation coefficients along with optimum temperature and the maximum photosynthetic rate, algae are differentiated on basis of these parameters; consequently, altering the values of these parameters based on literature in the plants' libraries effects in the simulation of $CaCO_3$. There are also differences in the sedimentation rate of phytoplankton among different aquatic systems, and in the case of lakes, these values are larger.

AQUATOX biotic state variables are also quite sensitive to temperature related parameters. These parameters include optimal temperature, maximum temperature, and temperature response slope [3]. The most effective plants in precipitation of $CaCO_3$ are nitrogen-fixing species of blue-green algae (cyanobacteria), including the *Anabaena* sp. and *Aphanizomenon* sp. For example, calibration of coefficients regarding *Anabaena* sp. indicated a positive impact on the trend of the model in comparison with temperature, irradiance, evaporation; and these are discussed in Section 4.1. Table 3.6 shows the calibration parameters for *Anabaena sp.* Representative figures of what it has been discussed in this section regarding initially calibrated control test runs, in other words, verification, are shown in Section 4.1.

When using a surrogate simulation, it is crucial to check whether food-web described by the surrogate site is stable and matches the current conditions of the study site. This can be done in a qualitative or quantitative manner due to the availability of biomass data for the site under study. Biota facts of the lake, which is previously discussed in Section 3.2.2. provide another valid reason for selection of the Onondaga Lake as a surrogate model for the Acıgöl Lake.

Consequently, control test runs are done in AQUATOX, for nine stations using required initial conditions for the model from field measurements. Some of the hydrodynamic variables such as surface area and water volume are assumed to be the same for all stations.

Finally, calibration is completed by comparison of simulated and observed $CaCO_3$. Calculation of the amount of $CaCO_3$ is explained in detail in the following section.

Table 3.6. Calibration values for *Anabaena* sp.

Anabaena	**Chemical Record**	**Unit**	**Range**	**Value**	**Source**
Light Saturation	Sat Light	(Ly d^{-1})	18-350	85	[28]
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	[28]
Inorganic. C Half saturation	-	(mg L^{-1})	0.01-1	0.1	[28]
Optimum Temperature	Topt	(°C)	15-28	28	[28]
Maximum Temperature	Tmax	(°C)	35	35	[28]
Min Adabtation Temperature	Tmin	(°C)	7-12	7	[28]
Maximum Photosynthetic Rate	Pmax	(d^{-1})	0.1-4	3.9	[29]
Photorespiration Coefficient	-	(d^{-1})	0.01-1	0.14	Calibrated
Mortality Coefficient	EMort	(g $g^{-1}d^{-1}$)	0.001-1	0.002	[29]
Light Extinction	-	(1/m-g/m^3)	0.01-1	0.144	[30]
Sedimentation Rate	Sed	(g $g^{-1}d^{-1}$)	0.01-1	0.01	[28]

3.2.3.1. *Calculation of $CaCO_3$ concentration from Field Measurements.* When the solids precipitate over time, it is not possible to measure the exact value of precipitated $CaCO_3$, because precipitated white solids may not only contain calcium. Likewise, in natural aquatic systems, water is not only comprised of included pure Ca^{2+}, to cause the precipitation of $CaCO_3$, other divalent cations like Mg^{2+} may also cause the precipitation of $MgCO_3$. The rate equation used in the determination of the amount of precipitated $CaCO_3$ is proposed by Inskeep and Bloom [31] , and provides an excellent fit for precipitation processes occurring in natural waters, especially with high alkalinity, where pH is higher than 7.5. AQUATOX also suggests the same threshold for pH, for calcite precipitation (Equation 3.1). Therefore, both methods are considered to be appropriate for carrying out a modeling study in an extreme environment, such as Acıgöl Lake [32] and [4].

The precipitation rate is driven by the dissolved concentrations of Ca^{2+} and CO_3^{2-} in relation to the solubility product, as well as the particulate surface area available for crystal growth. As a result, $CaCO_3$ amount is obtained from field measurements of

Ca^{2+} and CO_3^{2-}, using plummer method given by the following formula.

$$r_p = k_f S \gamma_2^2 \left[Ca^{2+}\right] \left[CO_3^{2-}\right] \tag{3.5}$$

Where r_p (mol $L^{-1}min^{-1}$) is the $CaCO_3$ precipitation rate. S (m^2 L^{-1}) is the available particulate surface area for $CaCO_3$ precipitation, is modeled as the sum of the surface area provided by existing calcite particles S_c and the surface area provided by non-calcite particles such as picoplankton S_p in Equation 3.6 which is dominant in an oligotrophic lakes such as Acıgöl lake.

$$S = S_C + S_P \tag{3.6}$$

where Sc and Sp are the volume-specific surface areas of calcite particles and non-calcite particles, respectively. As described by Kalff [33], picoplankton (plankton between 0.2 and 2 m^2 L^{-1}) are the dominant forms of plankton in ultra-oligotrophic and Oligotrophic lakes such as Acıgöl Lake. Value for S obtained from a similar environment, Torch Lake [4], it is equal to 123 m^2 L^{-1}.

Ion activity product (IAP) shows this relationship between ion activity and ion concentration in form of Equation 3.7 [34].

$$IAP = \left\{Ca^{2+}\right\} \left\{CO_3^{2-}\right\} = \gamma_2^2 \left[Ca^{2+}\right] \left[CO_3^{2-}\right] \tag{3.7}$$

Where Gamma (γ_2) is the activity coefficient for divalent cations and anions. The value for activity coefficient of divalent Ca^{2+} and CO_3^{2-} are obtained from chemical coefficients from [1] and [35].

In the formula, Ca^{2+} and CO_3^{2-} concentrations are used from field measurements of July 2013. $CaCO_3$ precipitation coefficient's (k_f)($L^2mol^{-1}m^{-2}min^{-1}$) calibration value are compared with model predictions in order to estimate the most appropriate of k_f based on the lake's conditions and literature. In order to calibrate this coefficients in nine stations, the relationship between depth and k_f are considered.

During calibration, it is observed that $CaCO_3$ precipitation coefficients decrease with increasing depth. For instance, station six as shown in Figure 3.1 is the deepest point of the lake, which has the lowest value of the k_f as depicted in Table 3.8.

The reason for this relationship between depth and k_f coefficients is related to the chemical processes involved. As the organisms die, their hard or mineralized parts, shells, fall to the lake floor and accumulate or dissolve depending on depth, temperature, and pressure. Shells and such which fall to the bottom of the deep parts of the lake are most often redissolved because the deeper waters can hold more CO_2 and are colder [2].

Temperature assists chemical reactions, so $CaCO_3$ precipitation as well increases with temperature. Moreover, $CaCO_3$ precipitation decreases with pressure, and pressure increases with increasing depth. More $CaCO_3$ is deposited in shallower water than deeper water due to the lower depth such as Acıgöl Lake. As pressure increases, more $CaCO_3$ dissolves [2].

Depth is typically around 2 m, with variation around depending on stations as it can also be seen in Figure 3.1. Acıgöl Lake can be classified as a shallow lake with low depth and low pressure. Consequently, stations must have high precipitation of $CaCO_3$ particularly in summer. According to the lake's characteristics, k_f values should change within a range between 0 and 1 according to [32]. Therefore, the sequence of k_f for nine stations with relation to depth are assumed as Station 6 $<$ Station 8 $<$ Station 3 $=$ Station 5 $<$ Station 4 $<$ Station 1 $<$ Station 2 $<$ Station 7 $<$ Station 9 [4].

As a result of discussion about this method and coefficient determination, Table 3.7 depicts these relationship between depth and $CaCO_3$ precipitation coefficients for nine stations in Acıgöl Lake.

Table 3.7. Values of coefficients and variables in determination of $CaCO_3$.

Stations	**Depth (m)**	**k_f ($L^2 mol^{-1} m^{-2} min^{-1}$)**
9	0.1	0.3
7	0.2	0.25
2	0.25	0.2
1	>0.3	0.15
4	<0.7	0.1
5	<1	0.06
3	<1	0.06
8	<1.5	0.055
6	>1.5	0.05

As a result of all explanations about this method and its coefficients, Table 3.8 shows all estimated k_f and literature coefficients for calculation of $CaCO_3$ by Equation 3.5.

Table 3.8. Chemical Plummer method for calculation of $CaCO_3$ by measured Ca^{2+} and CO_3^{2-} from field data in 2013.

St.	**k_f**	**γ_2 (Ca^{2+})**	**γ_2 (CO_3^{2-})**	**[Ca^{2+}]**	**[CO_3^{2-}]**	**$CaCO_3$**	**Field $CaCO_3$**
				(mol L^{-1})	(mol L^{-1})	(mol $L^{-1}min^{-1}$)	(mg $L^{-1}d^{-1}$)
St.1	0.15	0.98	0.08	0.01696	0.00004	1.01E-06	144.85
St.2	0.2	0.98	0.08	0.01129	0.00003	6.46E-07	92.98
St.3	0.06	0.98	0.08	0.01029	0.00007	4.17E-07	59.99
St.4	0.1	0.98	0.08	0.00853	0.00004	3.17E-07	45.60
St.5	0.06	0.98	0.08	0.01080	0.00002	1.28E-07	18.45
St.6	0.05	0.98	0.08	0.00878	0.00004	1.62E-07	23.37
St.7	0.25	0.98	0.08	0.00863	0.00002	4.85E-07	69.91
St.8	0.055	0.98	0.08	0.01400	0.00010	7.67E-07	110.51
St.9	0.3	0.98	0.08	0.01128	0.00003	8.70E-07	125.34

Finally, after calculation of $CaCO_3$ by plummer method, the modeled $CaCO_3$ is drawn by AQUATOX and compared with field measurements as in Section 4.1. Calculated $CaCO_3$ by plummer method, is used as the observed data to compare with modeled $CaCO_3$, which will be discussed in the following section.

3.2.4. Model Validation

As also depicted in the modeling flowchart (Figure 3.4), for validation of $CaCO_3$ precipitation modeling by AQUATOX, two different approaches are applied. Firstly, laboratory data obtained for two months under in 30°C are used. In this part, in order to obtain $CaCO_3$ from laboratory data, an analytical method, which is explained in Section 3.2.3.1 is applied. The validation is carried out, for the summer months, for nine stations with laboratory derived $CaCO_3$ precipitation. The amount of $CaCO_3$ precipitation is obtained by the Plummer method, using Ca^{2+} and CO_3^{2-} concentrations obtained from laboratory experiments undertaken in 30°C, and provided in Table 3.9.

Table 3.9. Laboratory $CaCO_3$ precipitation data obtained at 30°C.

Date	**Day**	**$CaCO_3$ (mg L^{-1})**
6/12/2013	2	4.478
6/14/2013	4	18.680
6/17/2013	7	23.277
6/25/2013	15	132.539
7/1/2013	21	82.671
7/10/2013	30	128.673

As a result, the values are given in Table 3.9 from laboratory data are used to validate the model against the simulated $CaCO_3$ precipitation in the Acıgöl Lake by AQUATOX for 2013. The results of validation with laboratory data are shown in Figure 4.9 for the first station only, and validation results for other stations are presented in Appendix C.

After validation of modeled $CaCO_3$ precipitation by AQUATOX with laboratory data, the second step of validation is carried out. In this part model control test runs are done based on field data and using the initial conditions obtained from field measurements in 2015. This increases confidence proving the model has the capability to effectively capture alternative scenarios. The results of these validation using August 2015 dataset for nine stations are shown in Section 4.2.

3.3. Sensitivity Analysis

The input data of the model could be affected by different uncertainties due to different sources such as measurement errors and uncertainties introduced by inadequate definition. Hence, the model may not be sufficiently reliable for correct conclusions [36]. In this context sensitivity analysis, which contributes to understanding how a given model depends upon the information fed into it, are applied to identify the relationships between the outputs and the inputs and to explore the most sensitive parameters. Since analyzing how much each individual input contributes to the output variance, parametric sensitivity analysis is crucial to the validation and calibration of numerical models. Sensitivity analyses generally involve the illustration of the impact of introducing small changes to specific input parameters on evaluation outcomes [37].

In this study, parametric sensitivity analysis is undertaken by altering the values of model variables by 10% increments within a range of 100%, from -50% to +50%, to determine the most significant ones affecting the model output. AQUATOX determines the parametric sensitivity by the following formula [3]:

$$Sensitiviy = \frac{|Result_{Pos} - Result_{Baseline}| + |Result_{Neg} - Result_{Baseline}|}{2 \times |Result_{Baseline}|} \times \frac{100}{\%Changed} \tag{3.8}$$

where, sensitivity is the normalized sensitivity statistics %, result scenario is the average AQUATOX result for an endpoint given a positive or negative change in the input parameter, or no change in the input parameter (baseline), and % Changed is the percent that the input parameter is modified in the positive or negative directions.

The method of AQUATOX for analyzing the sensitivity is a nominal range sensitivity analysis test, which is suitable as a screening method to identify the parameters and drivers that are most important to the simulation results applied for the sensitivity analysis of calcite simulation [38].

AQUATOX use many parameters to run the model, moreover, in this model, the effect of plants are very substantial with many different parameters. Therefore, these effective parameters are separated into two categories being chemical and plant related parameters. The results for sensitivity analysis of $CaCO_3$ precipitation modeling undertaken in this thesis are presented in Section 4.3, with Figures 4.11 and 4.12 and for plant and chemical conditions, respectively.

3.4. Scenario Analysis

Environmental research very often concerns developing scenarios for change and understanding the impacts of different environmental conditions (scenarios) on systems upon which humans depend. The strength of modeling is the ability to run the model under different environmental conditions to aid in understanding the impact of events that have not happened yet. Scenario Analysis is the process of analyzing possible future events by considering alternative possible outcomes. Thus, the scenario analysis does not try to show one exact picture of the future. Instead, it presents consciously several alternative future developments. Consequently, a scope of possible future outcomes becomes observable [39].

In order to observe the effects of different scenarios and the capability of applying future scenarios, perturbation runs are used in AQUATOX. Perturbation runs are useful in recognizing the differences between the initial control and perturbed runs simulated after modification of environmental variables.

In $CaCO_3$ precipitation modeling by AQUATOX, two different categories of scenarios were considered, including the modification of chemical properties of lake environment and modification of meteorological data, which will be elaborated in detail, in the following Sections 3.4.1 and 3.4.2.

3.4.1. Lake Environment Scenario

In this part, different scenarios related to the lake environment are applied in the model and the changes in results are represented by perturbation runs in AQUATOX to recognize the difference with control run. Firstly, as the simulation of $CaCO_3$ precipitation is a function of pH in AQUATOX [3], a random time-series dataset is produced for pH within the range of 6-9 and compared with constant pH conditions, to see the effects of changing alkaline conditions in the precipitation of $CaCO_3$. The results of this scenario for the first station and other stations are shown in Sections 4.4 and Appendix E, respectively.

Another scenario analysis is undertaken to see the effect of varying inflow. In the control runs, it is assumed that there was no inflow into the lake. For scenario analysis, variable inflow loading data are entered to the model to account for groundwater contribution, since groundwater is the major water inflow to the lake, entering from five different locations. Table 3.10 provides the inflow data used for AQUATOX scenario analysis.

Table 3.10. Inflow data from groundwater in St.1.

Variables in 1st station	Value	Unit
Inflow NH_4-N	14.2	[mg L^{-1}]
Inflow NO_3-N	37.7	[mg L^{-1}]
Inflow PO_4-P	3.1	[mg L^{-1}]
Inflow CO_2	0.7	[mg L^{-1}]
Inflow Oxygen	4	[mg L^{-1}]
Inflow of dissolved detritus	2.1	[mg L^{-1}]

The results of scenario analysis for the changing lake environment and inflow to the lake is demonstrated and interpreted in detail in Section 4.4.

3.4.2. Meteorological Data Generation

In this part, it is aimed to generate a future meteorological dataset including temperature, irradiance, evaporation, and precipitation using data from the past. SPSS software is applied as a synthetic weather generator.

To accomplish this step, firstly, daily meteorological data from 2011 to 2015 are entered as input data for SPSS. Afterward, the traditional forecast model is applied for the analyzing with SPSS. SPSS software uses time series to generate these type of data by forecast analyses and creates a model. The analysis, then, predicts five different predicted datasets for each category of meteorological data. Generated meteorological data including temperature, irradiance, evaporation, and precipitation are outlined in Table 4.1.

To use these predicted dataset as input in AQUATOX, statistical analysis with different indexes are applied to select an appropriate data set for each category among five sets of the generated data. Tables 3.11 and 3.12 shows the results of the statistical analysis, which are undertaken by SPSS for synthetic temperature and evaporation data, respectively.

To observe effects of temperature on $CaCO_3$ precipitation more vividly, maximum and minimum conditions are applied in the modeling. These datasets are named as Set.4 and Set.5, and provided in Tables 3.11 and 3.12 for temperature and evaporation, respectively. The reason of selection of these two dataset is related to the statistical analysis, for instance in Table 3.11, mean of Set.4 are the biggest, and it shows that it has the maximum temperature set.

Table 3.11. Temperature statistics for 5 dataset in scenario analysis.

Statistics of Temperature [°C]					
Dataset	**Set.1**	**Set.2**	**Set.3**	**Set.4**	**Set.5**
Mean	16.23	17.56	17.60	17.75	15.91
Std. Error of Mean	0.45	0.49	0.43	0.38	0.44
Median	13.81	17.96	16.44	16.38	14.37
Mode	27.20	1.86	1.51	28.65	6.63
Std.Deviation	8.63	9.43	8.26	7.34	8.46
Variance	74.50	89.01	68.22	53.89	71.51
Range	29.52	34.53	30.73	24.75	35.30
Minimum	1.53	-1.45	0.58	6.18	-2.69
Maximum	31.05	33.08	31.31	30.93	32.61

Evaporation and temperature have the similar effects on the precipitation of $CaCO_3$ due to the fact that there is direct relationship between this two variables, so the evaporation amount responds to temperature proportionally. Consequently, the reason for selection of Set.1 and Set.4 as maximum and minimum, respectively are similar to the reason for temperature in Table 3.11. Table 3.12 shows statistical index for evaporation to use in scenario analysis.

Table 3.12. Evaporation statistics for 5 dataset in scenario analysis.

Statistics of Evaporation [mm]					
Dataset	**Set 1**	**Set 2**	**Set 3**	**Set 4**	**Set 5**
Mean	130,678.60	127,525.09	126,198.24	109,451.06	125,011.95
Std. Error of Mean	11,145.69	10,923.53	10,120.13	7,420.00	8,669.21
Median	108,245.30	89,102.10	121,671.23	83,551.00	129,211.39
Mode	3.99	9.35	5.26	2,133.80	11.39
Std.Deviation	117,427.14	114,566.98	106,140.77	77,821.63	90,923.44
Range	402,957.63	411,772.01	335,265.63	297,623.64	367,388.20
Minimum	3.99	9.35	5.26	2,133.80	11.39
Maximum	402,961.62	411,781.36	335,270.89	299,757.44	367,399.59

As plants activity and photosynthesis of the plants have crucial role in precipitation of $CaCO_3$, knowing their behaviour in maximum and minimum irradiance conditions are also asset us to understand about the complex process in the mechanism of $CaCO_3$. Selected dataset for maximum and minimum conditions of solar radiation are Set.3 and Set.1 respectively based on Table 3.11.

Table 3.13. Light statistics for 5 dataset in scenario analysis.

Statistics of Light (Ly d^{-1})					
Dataset	**Set 1**	**Set 2**	**Set 3**	**Set 4**	**Set 5**
Mean	397.75	423.40	431.67	413.39	402.64
Std. Error of Mean	8.87	9.72	9.69	9.57	8.53
Median	375.30	421.13	431.33	428.59	383.75
Mode	134.54	241.87	99.07a	168.80	207.48
Std.Deviation	169.71	185.76	185.09	182.89	162.99
Variance	28,801.06	34,507.74	34,259.50	33,448.97	26,566.51
Range	635.20	641.35	630.07	646.89	604.01
Minimum	73.41	93.13	99.07	77.44	122.73
Maximum	708.61	734.48	729.14	724.33	726.74

Water volume is one of the most important meteorological variables which has significant effect on $CaCO_3$ precipitation. The reason is when volume is high these $CaCO_3$ can dissolve in the water and vice versa. Table 3.14 shows the inflow statistical indexes and among this five data set, Set.3 and Set.1 are selected for scenario analysis. Inflow dataset are the only dataset that minimum value are not applied in AQUATOX, because without any water volume the perturb test run made an error.

Table 3.14. Inflow statistics for 5 dataset in scenario analysis.

Statistics of Inflow [m^3d^{-1}]					
Dataset	**Set 1**	**Set 2**	**Set 3**	**Set 4**	**Set 5**
Mean	174,603.6	2,983.4	71,110.9	163.3	95,101.1
Std. Error of Mean	13,679.1	2,411.7	8,779.6	163.3	12,051.4
Median	98,431.2	0.0	16,873.9	0.0	32,622.9
Mode	1,124.9	0.0	0.0	0.0	0.0
Std.Deviation	261,696.7	46,076.2	167,733.9	3,120.7	230,241.7
Range	2,815,694.8	847,070.8	1,958,499.7	59,621.2	3,055,304.5
Minimum	0.0	0.0	-4,499.7	0.0	-17,998.9
Maximum	2,815,694.8	847,070.8	1,953,999.9	59,621.2	3,037,305.6

After analysing all five dataset and sign the best dataset, all the possible conditions are applied to see the effect of modification of meteorological data for $CaCO_3$ precipitation in Acıgöl lake. Table 4.1 depicts the conditions for all of the scenarios for meteorological data which applied in this model.

Finally, after selection of required appropriate dataset for each scenario, these new predicted data in SPSS are extracted and entered as new sets of time series into the AQUATOX to apply scenario analysis with perturbation test runs in order to observe the behavior of $CaCO_3$ precipitation in the Acıgöl Lake when conditions are different. As a result, for each scenario in Table 4.1, one perturbation test run is conducted and the outputs of these simulation is shown in Section 4.5.

4. RESULTS AND DISCUSSION

Developing and calibrating a model for $CaCO_3$ precipitation creates a tool that can be used to quantify the interactions of physical, chemical and biological processes. This chapter starts with comparisons of model predictions with data of Acıgöl Lake for the summer 2013.

The purpose of this thesis is to demonstrate how well the Acıgöl Lake model is able to estimate values over the time horizon for the major chemical state variables, meteorological variables, cyanobacteria and sensitive parameters of plants.

The results of these model predictions are presented by comparison with meteorology and field data for calibration, and validation is done with laboratory and field measurements. The model results are followed by a sensitivity analysis that assesses the relative importance of the sensitive parameters on $CaCO_3$ precipitation in Acıgöl Lake. Afterward, the results of scenario analysis for different lake environment conditions are presented to evaluate the effects of inflow from ground water, and time series pH on $CaCO_3$ precipitation modeling. Finally, different weather conditions are modeled by different meteorological dataset to evaluate of their effects on $CaCO_3$ precipitation.

4.1. Model Calibration Results

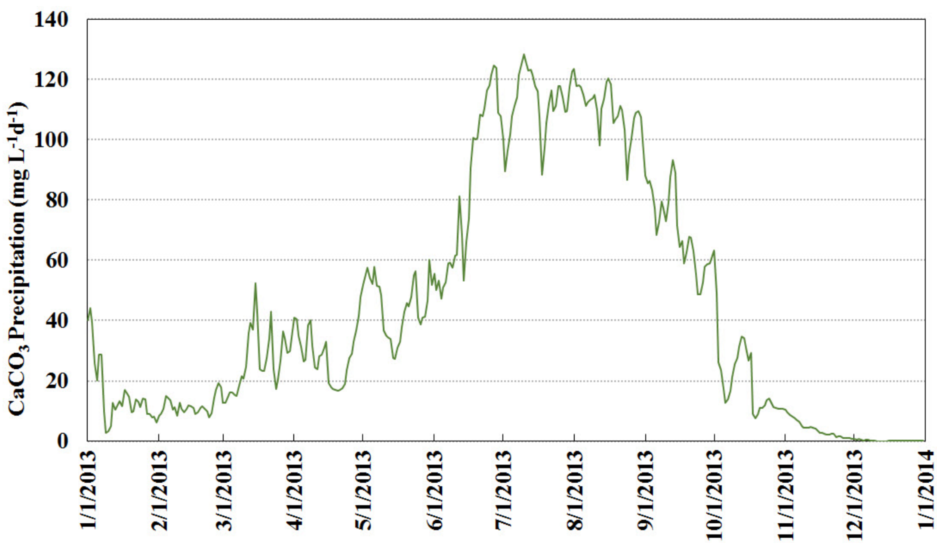
As Chapter 3 discusses calibration steps for simulation of $CaCO_3$ in Acıgöl Lake, is divided into three parts as follows:

Onondaga Lake's selection as surrogate site is due to its similar characteristics of Acıgöl Lake including pH range in alkaline condition, having high salinity, and being in the category of oligotrophic types of lake cause the high precipitation of $CaCO_3$ which is also incompatible with the result of $CaCO_3$ precipitation in Acıgöl Lake.

According to the AQUATOX and what has been discussed in Section 3.2.3 regarding calibration of the model, the results of the initial steps for calibration of $CaCO_3$ precipitation modeling which are the modifying coefficients of plants'parameters are presented for 9 stations in Figures 4.1(a) to 4.1(i).

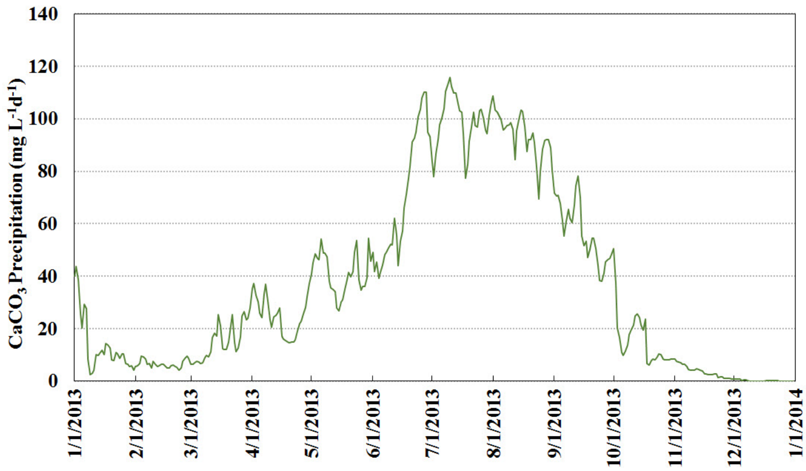
These figures show how plants calibration of the model asset the initial model to be more accurate by calibration with meteorological data in the next step of calibration which is elaborated in detail in next steps. Each time, when the coefficients of plants are modified, calibration with meteorological data are applied to see whether these changes are applied properly.

In addition, by these modifications, the trend is more adapted with the real data. For instance, with high photosynthesis activity by plants in summer due to higher solar radiation, the peak in the model is also created in this season. Further discussions are explained in next sections of calibration including Section 4.1

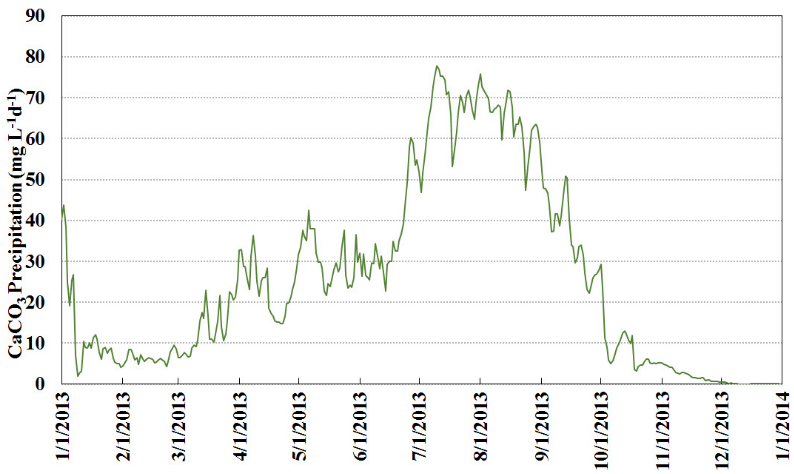


(a) Initial calibration of $CaCO_3$ in St.1

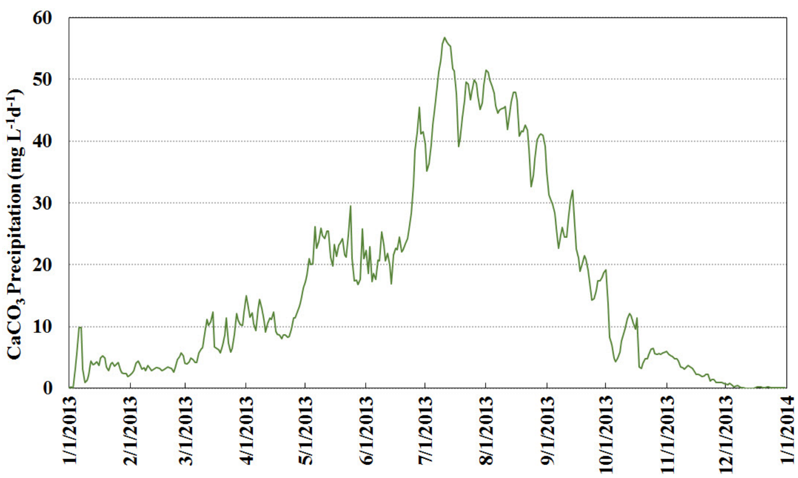
Figure 4.1. Initial calibration by modification of plant coefficients.



(b) Initial calibration of $CaCO_3$ in St.2

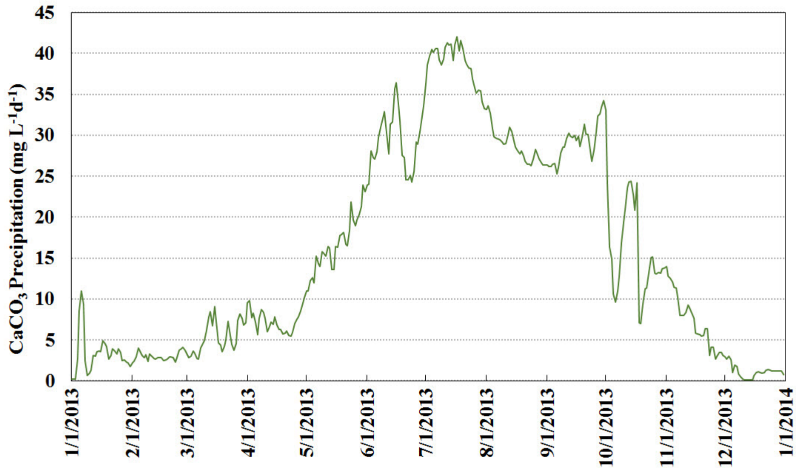


(c) Initial calibration of $CaCO_3$ in St.3

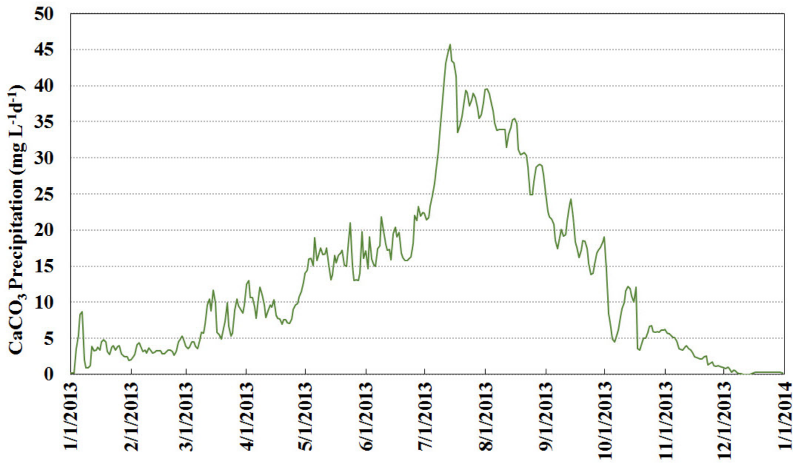


(d) Initial calibration of $CaCO_3$ in St.4

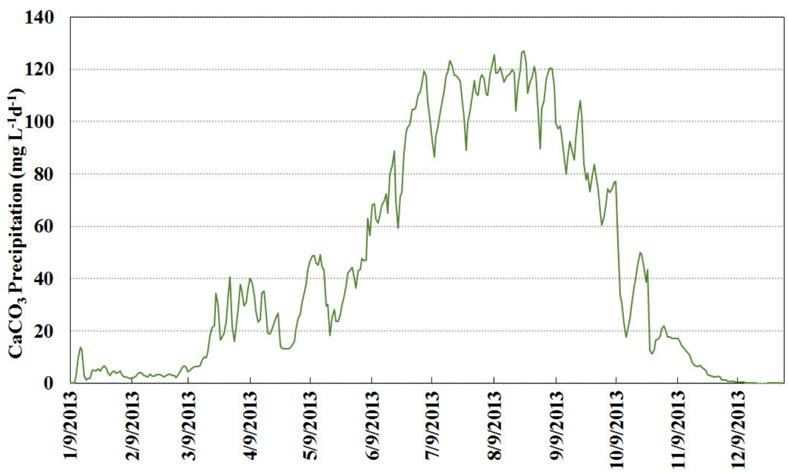
Figure 4.1. Initial calibration by modification of plant coefficients (cont.).



(e) Initial calibration of $CaCO_3$ in St.5

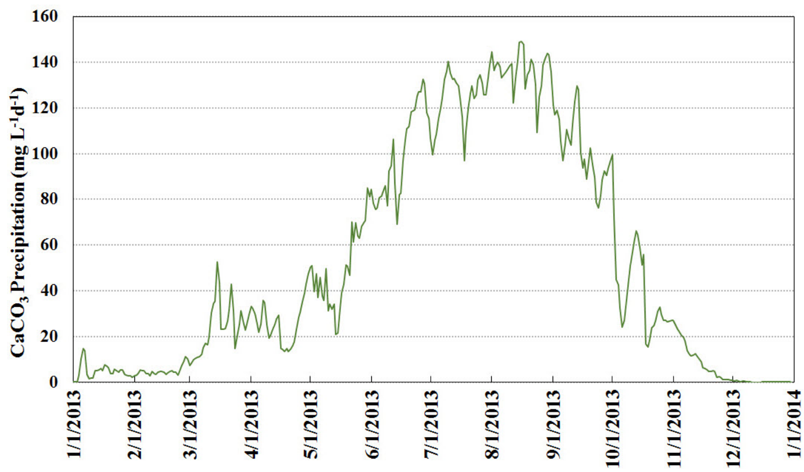


(f) Initial calibration of $CaCO_3$ in St.6

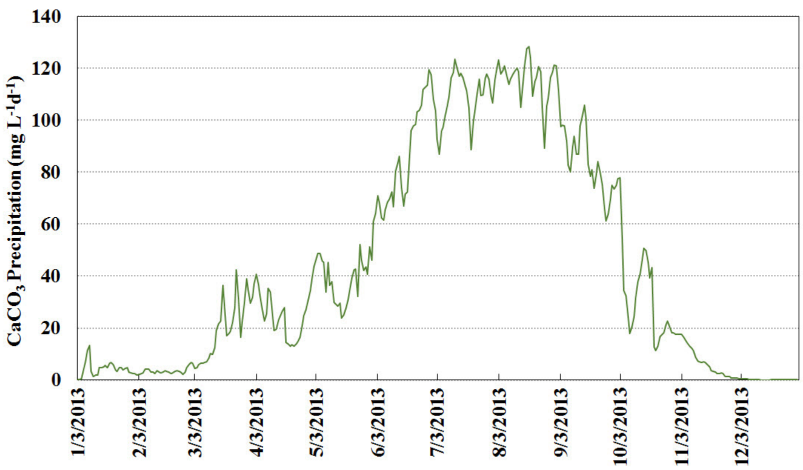


(g) Initial calibration of $CaCO_3$ in St.7

Figure 4.1. Initial calibration by modification of plant coefficients (cont.).



(h) Initial calibration of $CaCO_3$ in St.8



(i) Initial calibration of $CaCO_3$ in St.9

Figure 4.1. Initial calibration by modification of plant coefficients (cont.).

In this step, the modeled $CaCO_3$ values are compared with meteorological data to observe if the system conditions of $CaCO_3$ precipitation are compatible with Acıgöl Lake properly. For instance, the temperature is one of the most important variables that has affects directly on $CaCO_3$ precipitation and when temperature rises in summer in shallow lakes, a number of deposits have to be high value as observed with these step in calibration with temperature obtained from TSMS.

In a comparison of $CaCO_3$ precipitation simulation in nine stations with meteorological characteristics such as temperature, irradiance, evaporation and water volume, the trend of simulation is compatible with effective meteorological state variables. Consequently, the results of this compatibility are demonstrated for each meteorological category.

AQUATOX is capable of generating various related results of modeling. As precipitation of $CaCO_3$ is highly depended on algae discussed in methodology and their photosynthesis activity by AQUATOX, checking variables condition while the model is being calibrating assists in improving the model performance.

All surface water supplies support the growth of aquatic organisms. Plankton and are of great interest because of effects on water quality. The plankton is composed of animals, zooplankton, and plants, phytoplankton. The latter are predominantly algae and cyanobacteria which are effective in precipitation of $CaCO_3$ [2].

Algae use CO_2 in their photosynthetic activity during the day. Removal of carbon dioxide tends to increase the pH to between 8 and 9 in waters with moderate alkalinity. Algae, however, can reduce the free carbon dioxide concentration below its equilibrium concentration with air and consequently can cause an even greater increase in pH. The alkalinity forms change with the increase in pH. Moreover, CO_2 can also be extracted for algal growth both from bicarbonates and from carbonates in accordance with the following equilibrium equations in Section 2.1.1. Thus, the removal of carbon dioxide by algae tends to cause a shift in the forms of alkalinity present from bicarbonate to carbonate, and from carbonate to hydroxide. Noted that during these changes the total alkalinity remains constant unless removal results through precipitation of carbonate salts such as $CaCO_3$ [2].

During the dark hours of the day, algae produce rather than consume carbon dioxide. This is because their respiratory processes in darkness exceed their photosynthetic processes. This carbon dioxide production has the opposite effect and tends to reduce the pH. Diurnal variations in pH due to algal photosynthesis and respiration are common in Lake waters [2]. Generally, as in Figure 4.2 when the concentration of Algae biomass is high, the precipitation of $CaCO_3$ is much as well provided that other participating factors are available.

Hence, in this figure when the concentration of algae biomass is at its maximum value, but seasonally it is in winter time with lower temperature, the precipitation of $CaCO_3$ is lower. While the algae biomass declined and temperature increased by summer, the $CaCO_3$ precipitation is also responding to its peak value and good matching of the trend for calibration.

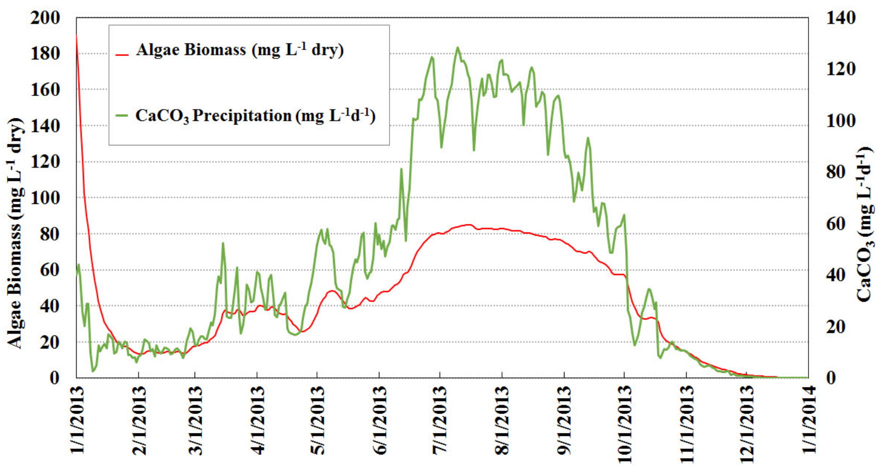


Figure 4.2. Initial calibration of $CaCO_3$ with algae biomass in St.1.

Nitrogen and phosphorus are both essential for the growth of algae and cyanobacteria and that limitation in amounts of these elements is usually the factor that controls their rate of growth. Scientific evidence has shown that such blooms do not occur when nitrogen or phosphorus or both are present in very limited amounts. The critical level for inorganic phosphorus has been established as somewhere near 0.005 mg L^{-1} or 5 mg L^{-1} under summer growing conditions in oligotrophic lakes [2].

According to the applied algorithm of AQUATOX, *Anabaena* and *Aphanizomenon* as blue-green algae use carbon source to precipitate $CaCO_3$ (Figure 4.3). These two blue-green algae are nitrogen fixing bacteria and they can compensate the lack of nutrient budgets, so in summer season especially when these two species exist, also $CaCO_3$ is precipitated [2].

As it is shown in this figure, at the initial steps of the model with colder temperature in colder seasons are affected by the amount of *Anabaena* which is more adapted with the trend of the $CaCO_3$ precipitation in cold season. Afterward, in the warmer season *Aphanizomenon* present good matching with the trend of $CaCO_3$ precipitation due to the fact that they have more maximum photosynthesis in plant's library and also higher tolerable salt conditions in much evaporation in summer. As a result, they do more photosynthesis and more effective in $CaCO_3$ precipitation among other blue-green algae.

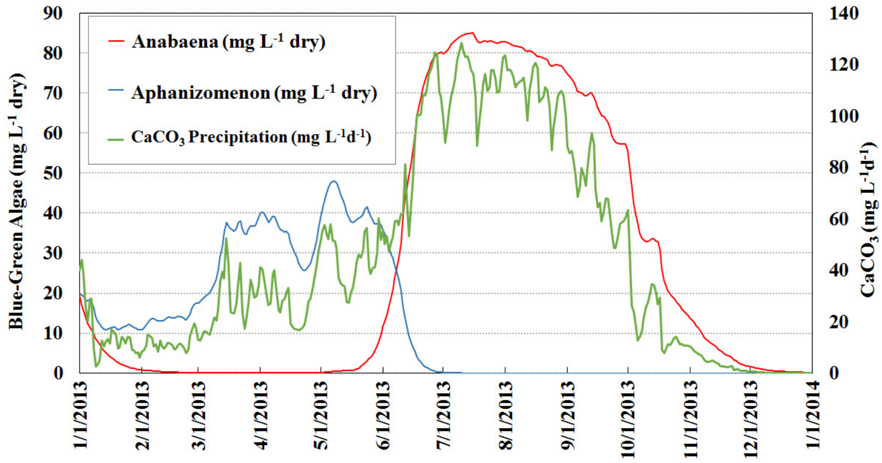


Figure 4.3. Initial calibration of $CaCO_3$ with Blue-green algae in St.1.

So far, the model is calibrated by different initial concentrations for different initial conditions in stations. In addition, the appropriate surrogate models are tested and selected to reach the basic needs of existing model by modifying the parameters.

In following, the surrogated model is calibrated with modifying the Anabaena's coefficient in four stations and the results are compared with meteorological data to see whether the model is in good agreement with the real system. Consequently, the trend-wise comparison of $CaCO_3$ precipitation versus the meteorological data are presented in Figures 4.4 to 4.7. The combination of four parameters to generate the $CaCO_3$ precipitation trend.

First comes the light effects on $CaCO_3$ precipitation; as it is discussed in Section 3.2.3 photosynthesis needs light. Consequently, the $CaCO_3$ precipitation proportionally responds to the light intensity. In winter the lack of shining sun produced less $CaCO_3$

while as the warm spring and summer seasons arrive, the $CaCO_3$ is more precipitated until it hits the peak in mid-summer and starts decreasing through autumn and winter again as it is shown in Figure 4.4.

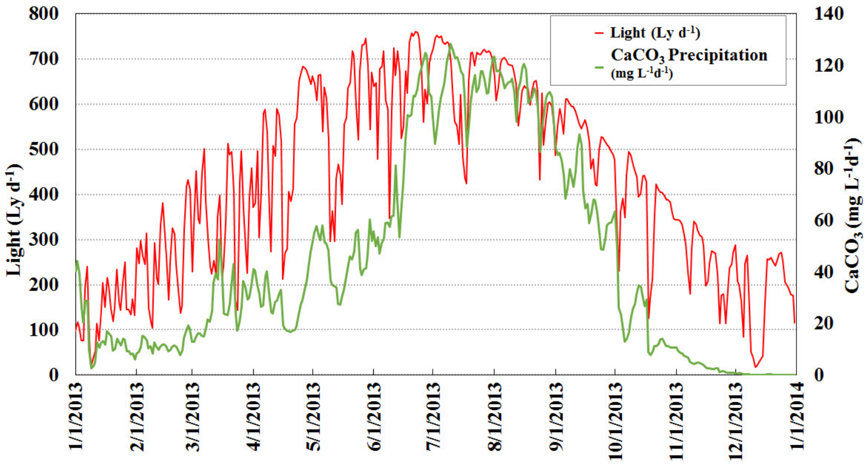


Figure 4.4. Calibration of $CaCO_3$ vs. irradiance from TSMS in St.1.

Next parameter is temperature, which generally follows the trend of light due to sun shines. The $CaCO_3$ precipitation values, fluctuate with the temperature as shown in Figure 4.5.

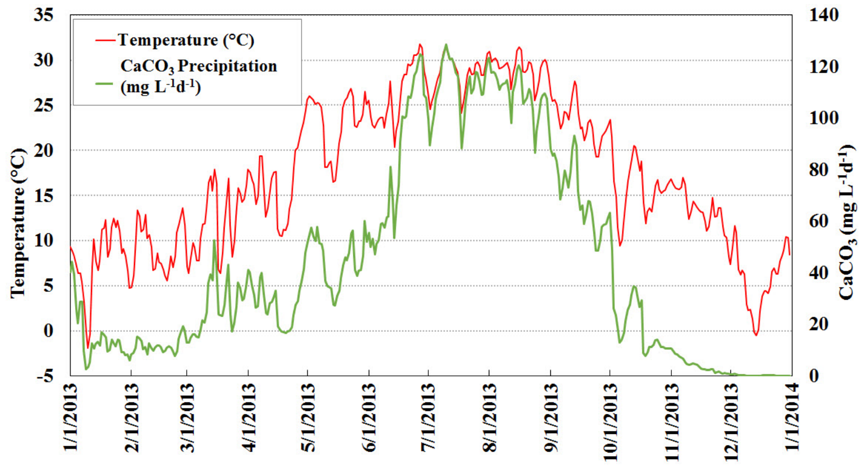


Figure 4.5. Calibration of $CaCO_3$ vs. temperature from TSMS in St.1.

Evaporation is an important parameter which affects the water volume of lake. Therefore, the high water volume, the high chance of dissolved $CaCO_3$ in the water. As the evaporation rate goes higher, the $CaCO_3$ precipitation start increasing. According to Figures 4.4 and 4.5, the winter which has less temperature and light values, the precipitation value is strongly low. In early 2013, there is no evaporation while the very small quantity of precipitation exists which seems to be due to temperature and light fluctuations or due to the cycle reaction of dissolved $CaCO_3$ and precipitation.

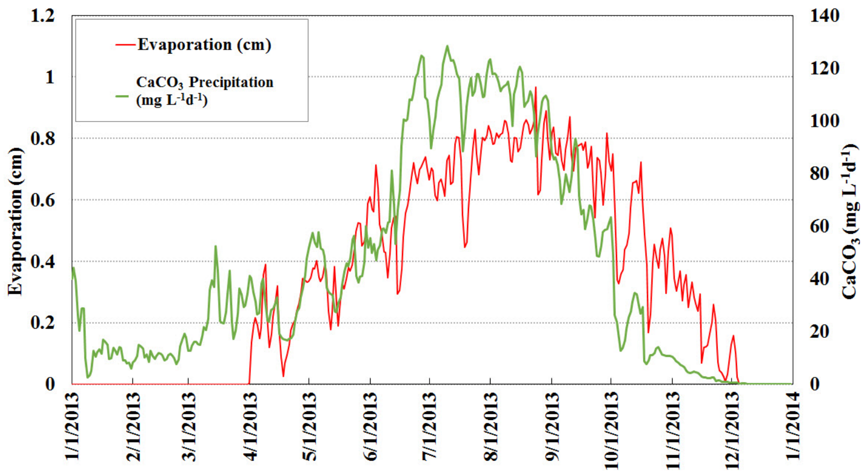


Figure 4.6. Calibration of $CaCO_3$ vs. evaporation from TSMS in St.1.

The water volume quantity of lake is a parameter which is the resultant of all above three parameters. Therefor, generally, as it is shown in Figure 4.7, the high value of water volume due to cold seasons results in less $CaCO_3$ precipitation. As the evaporation, light and temperature values increase in warmer seasons, the less water volume generates high amount of $CaCO_3$.

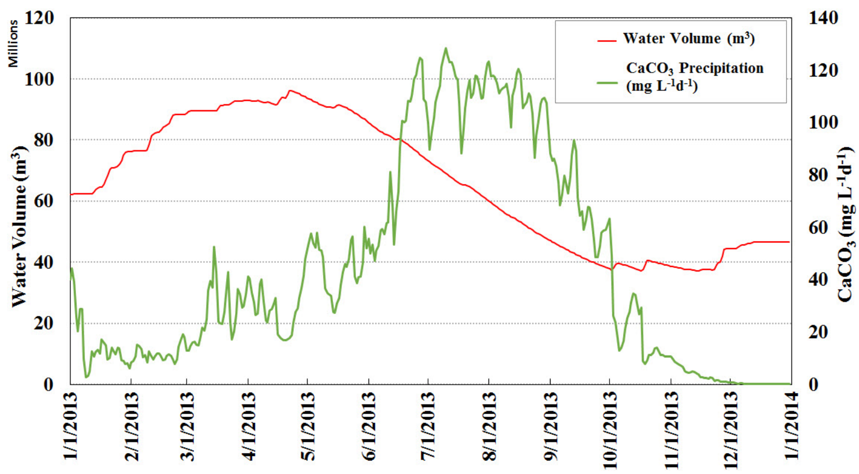


Figure 4.7. Calibration of $CaCO_3$ vs. water volume from TSMS in St.1

Generally, it is concluded that the AQUATOX program is capable to model Acıgöl Lake's $CaCO_3$ precipitation quantity by having logical behavior with existing physical and meteorological parameters. The comparison plots between meteorological Data and model results in different stations are shown in Appendix B.

4.1.1. Model Calibration result using Field Measurements

Calibration of model is completed by comparison of the simulated $CaCO_3$ by observed $CaCO_3$ concentration from the field measurements in 2013 (Section 3.2.3).

Furthermore, $CaCO_3$ from field measurements is obtained by calcium and carbonate data by the chemical analytical method explained in Section 3.2.3.1 to fulfill the last step of calibration for this model.

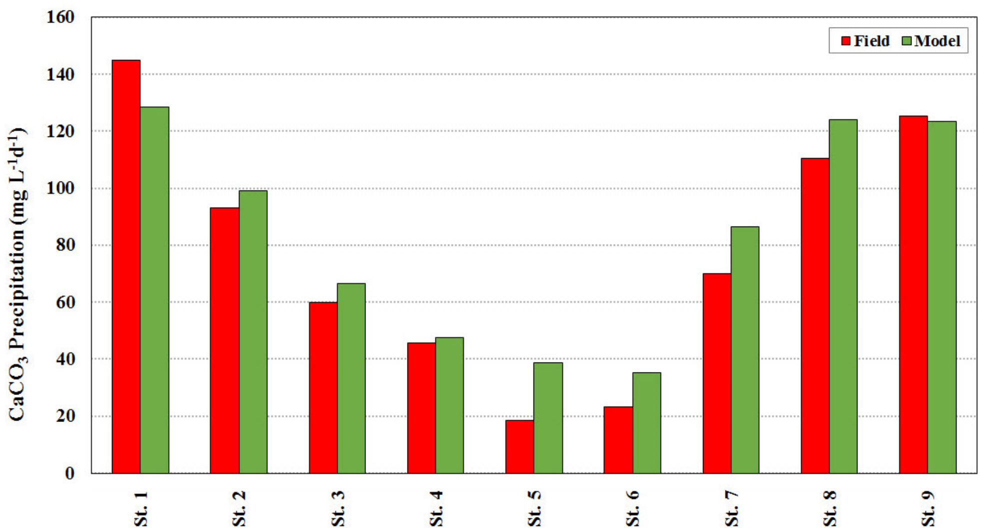


Figure 4.8. Calibration of $CaCO_3$ by field measurements for all stations.

To measure the differences between values predicted by a model and the values actually observed in the model, Root Mean Square Error (RMSE) and Normalized Root Mean Square Error (NRMSE) are applied. Equations 4.1 and 4.2 represents how this errors are obtained.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(C_m - C_f)^2} \tag{4.1}$$

$$NRMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{C_m - C_f}{C_f}\right)^2} \tag{4.2}$$

After applying these two equations in to the result outputs, RMSE and NRMSE values for n=9 stations are equal to 12.3 and 0.41, respectively, for 2013.

RMSE value shows that the deviations between the results of model is less in comparison with observed amount of $CaCO_3$ precipitation which describe the model results are obtained precisely.

4.2. Model Validation Results

After calibration of the simulated model, validation was done using laboratory data performed at 30°C for two months in summer to see the effect of the summer season on the precipitation of $CaCO_3$ in Acıgöl Lake. The results of validation is demonstrated by upcoming figures in this section.

The discussed laboratory data in Section 3.2.2.2 are compared with the $CaCO_3$ precipitation in nine stations to observe the matching of the model and laboratory data.

According to Figure 4.9 for St.1, in the laboratory condition the $CaCO_3$ precipitation starts and increase to reach the first peak after 15 days. Then reaches the crest point on 21^{st} day with the approximate value of 80 mg $L^{-1}d^{-1}$. The last value of lab data is measured in 30 days after, with the second peak value of approximately 125 mg $L^{-1}d^{-1}$.

It is concluded that the lab data need some days to reach stability, then they match the model fluctuations with the available measurement data. Hence, the trend-wise and quaintly-wise comparison state that the AQUATOX model is validated for this case study and able to predict the $CaCO_3$ precipitation in Acıgöl Lake for 2013.

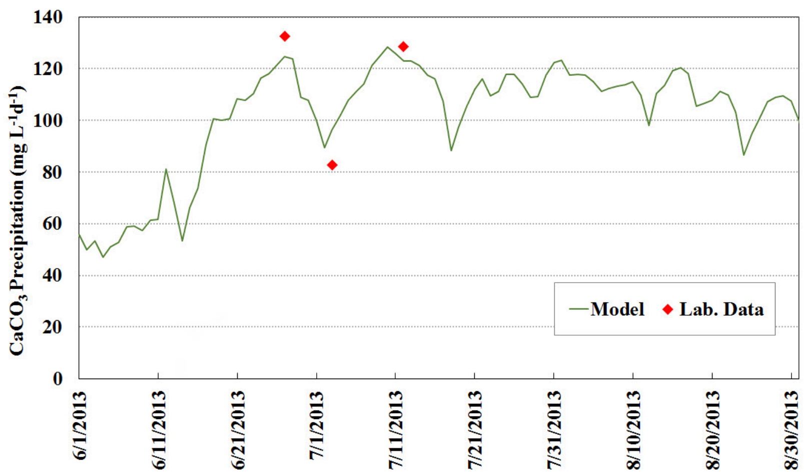


Figure 4.9. Validation of $CaCO_3$ by laboratory measurements in St.1.

In this part after the model is calibrated by field measurements and validated by laboratory experiments, the modeled $CaCO_3$ is compared with $CaCO_3$ from field measurements in 2015 in order to achieve final validation of $CaCO_3$ precipitation in Acıgöl Lake.

The following figure depicts the result of final validation of simulated $CaCO_3$ versus the 2015 field measured $CaCO_3$.

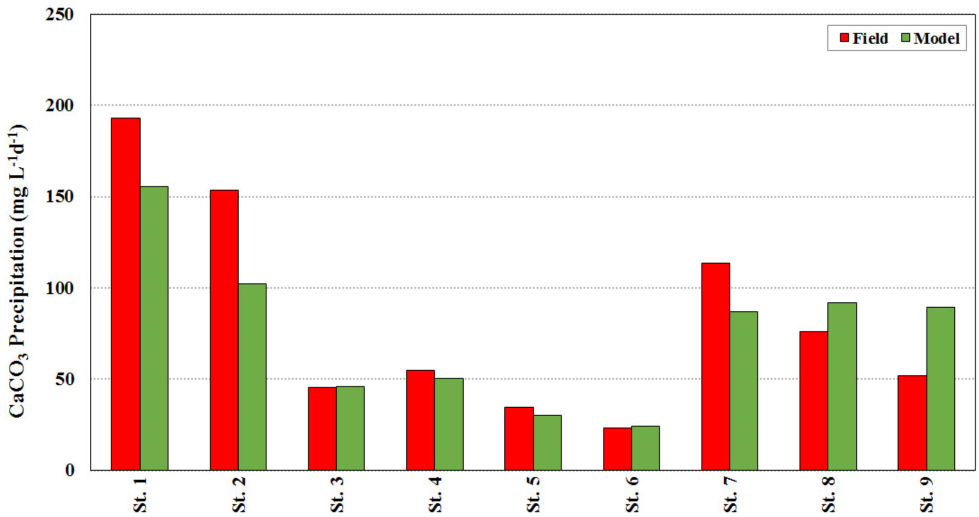


Figure 4.10. Validation of $CaCO_3$ by field measurements for all stations.

Analysis of error for the results of validation with field measurements in 2015 are also applied as it has been applied for calibration results of the model in 2013.

The RMSE and NRMSE values of 2015 data for n=9 stations are equal to 26.8 and 0.29, respectively, which also represents the less error existing in the model.

4.3. Sensitivity Analysis Results

Nominal range sensitivity analysis works well for the models with idea about plausible ranges that can be assigned to each selected input [40]. Hence, according to the $CaCO_3$ precipitation modeling algorithm by AQUATOX, these effective input are distinguished and utilize as sensitivity input parameters in AQUATOX.

The results of this approach are applied to evaluate the amount of sensitivity of $CaCO_3$ outputs towards the selected inputs parameters.

For each output variable tracked, model parameters may be sorted on the average sensitivity (for the positive and negative tests) and plotted on a bar chart. The final result is referred to as a “Tornado Diagram” as shown in Figures 4.11 and 4.12.

The vertical line at the middle of the diagram represents the deterministic model result. Red lines represent model results when the given parameter is reduced by the user-input percentage while blue lines represent a positive change in the parameter. Within this report the top 14 most sensitive variables out of all variables tested in a simulation are shown in each related tornado diagram.

In order to achieve a better evaluation of sensitivity analysis, parameters tested in the sensitivity of $CaCO_3$ precipitation are categorized in two parts of plants, and other physical and chemical parameters including important phytoplankton and blue-green algae, effective nutrients and organic matter loadings respectively as it is discussed in Section 3.3.

Biotic state variables which have significant role in the precipitation of $CaCO_3$ are sensitive to the temperature parameters including "optimal temperature", "maximum temperature", and "temperature response slope". In addition, algae are also sensitive to the temperature parameters and particularly maximum photosynthesis rate (PMAX) [38]. This relationship is especially straightforward for phytoplankton biomass [3].

In Figure 4.11 which is related to the Tornado Diagram for biotic parameters, as it is predicted in the calibration part also, the most sensitive parameters are related to the photosynthesis activity including optimal temperature for *Aphanizomenon* then it is highly sensitive to their maximum photosynthesis rate.

Hence, after selection of important parameters for biotic variables and applying control run in sensitivity mode, the sensitivity analysis are presented in Figure 4.11.

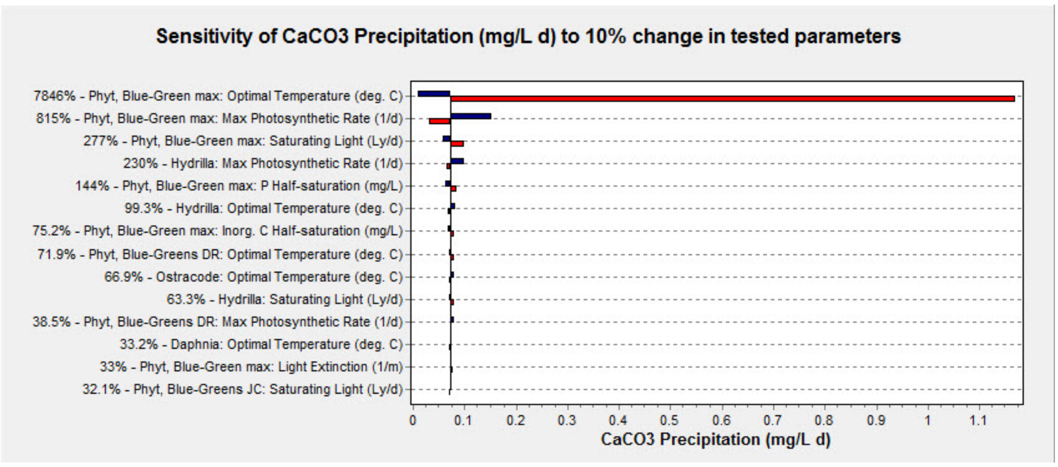


Figure 4.11. Sensitivity analysis of plant parameters.

Furthermore, in considering the most sensitive physical parameters for simulated $CaCO_3$ outputs, depth of the Acıgöl Lake, which is shallow lake is highly sensitive parameter in $CaCO_3$ precipitation modeling as it is depicted in Figure 4.12.

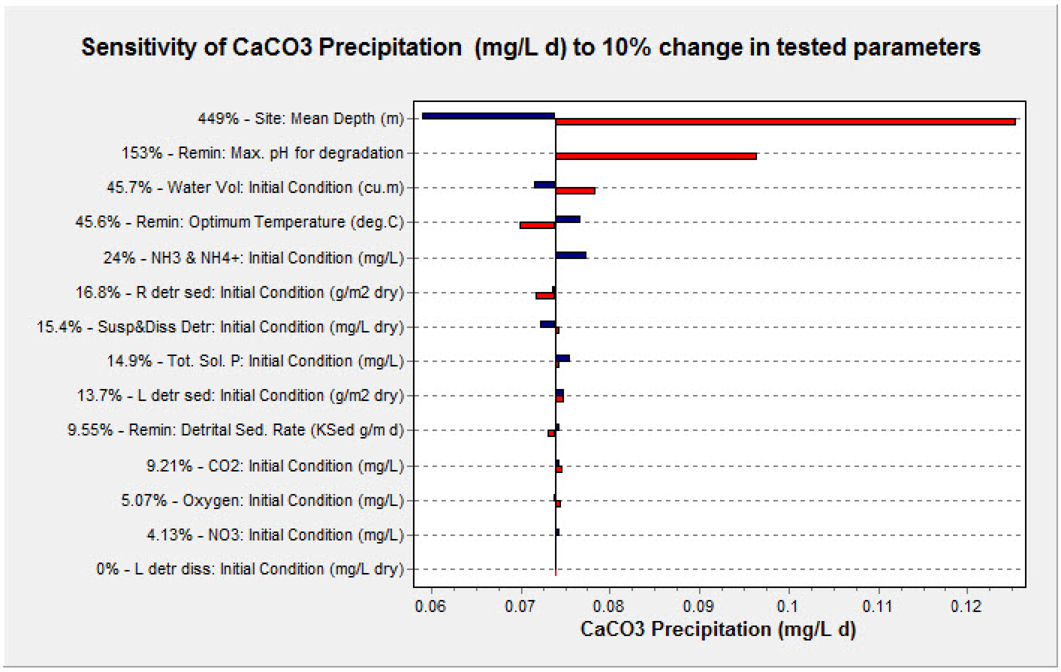


Figure 4.12. Sensitivity analysis of chemical parameters.

4.4. Scenario Analysis Results for Lake Environments

Generally, nutrient budgets affect $CaCO_3$ precipitation. Organic compounds can sorb to these particles and phytoplankton can serve as nucleus for $CaCO_3$ formation. Hence as the particle settle, they carry organic matter with them [41].

According to the scenario analysis for lake environment, addition of oxygen and suspended dissolved detritus as inflow from groundwater to the Acıgöl Lake did not have any influence on simulation of $CaCO_3$ with perturbation test runs.

Nitrogen and phosphorus are both essential for the growth of algae and cyanobacteria and that limitation in amounts of these elements is usually the factor that controls their rate of growth. Research has shown that such blooms do not occur when nitrogen or phosphorus or both are present in very limited amounts [42]

As a result, when total soluble P is entered to the lake from ground water the $CaCO_3$ simulation is changed and the result of perturbation test run for the first station is shown in Figure 4.13 and for other stations are presented in Appendix E.

The reason for increase in the amount of $CaCO_3$ is the addition of total soluble phosphorus from inflow loading data of groundwater to the Acıgöl Lake which modifies the nutrient budgets. As it is shown in below figure, at first the amount of precipitation is low due to the entrance of phosphorus and seasonal reason. This inflow causes nitrogen limiting in the Acıgöl Lake. Phosphate tends to sorb strongly to fine-grained particles. The settling of these particles, along with sedimentation of organic particles containing phosphorus, serves to remove phosphorus from the water to the bottom sediments [42]

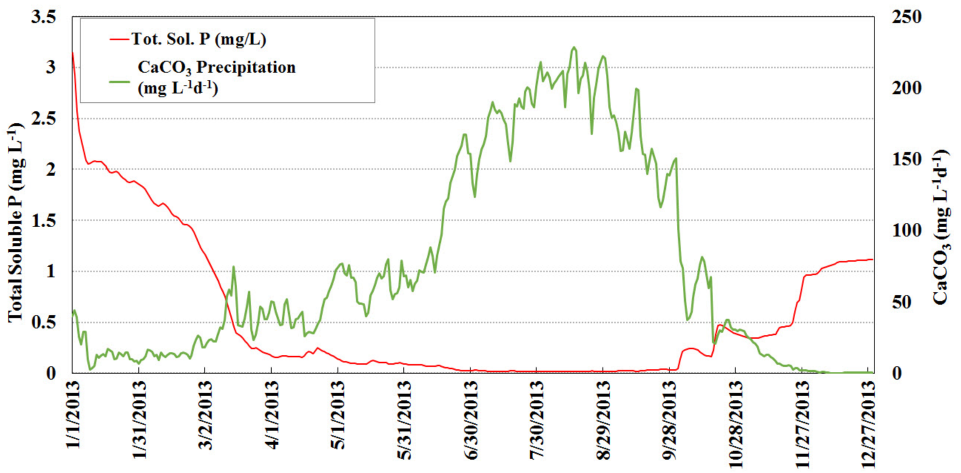


Figure 4.13. Simulated $CaCO_3$ vs. total soluble phosphorus in St.1.

In hard water systems such as alkaline Acıgöl Lake, when CO_2 reduces and pH increases, $CaCO_3$ is precipitated. Variations in pH are caused mainly by phytoplankton production and decomposition. During summer, pH values range from 7.8 to 9.2 [13]. As it is explained in Section 3.2, AQUATOX has a threshold of 7.5 for $CaCO_3$ precipitation specially when carbonate system such as alkaline Acıgöl Lake is dominant. This addition of time series pH to the model as required input for Lake environment scenarios prove this issue of threshold.

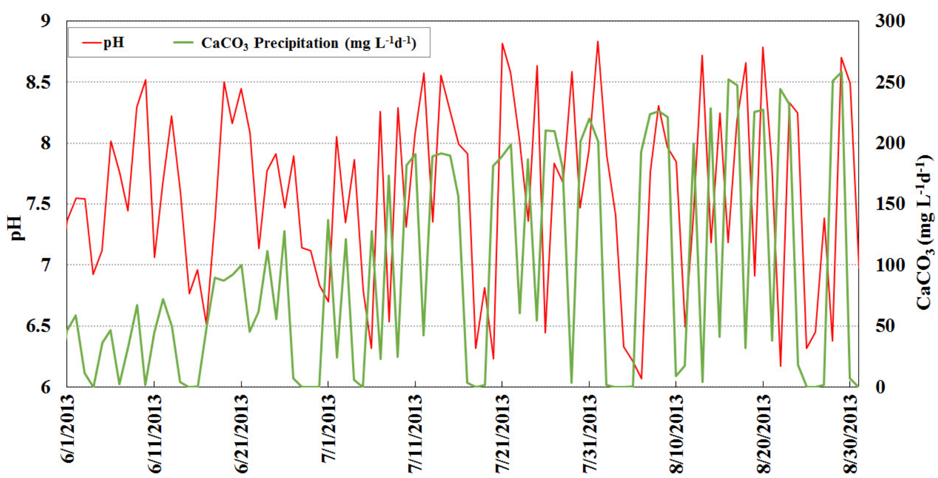


Figure 4.14. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.1.

As in Figures 4.15 and 4.16 are shown, $CaCO_3$ precipitate was high at about 50 mg L^{-1}, when pH values are higher than 7.5 meaning in alkaline condition.

Figure 4.15 depicts $CaCO_3$ precipitation modeling values when they are compared with constant pH and to evaluate the alkalinity conditions for precipitation modeling in Acıgöl Lake during two months.

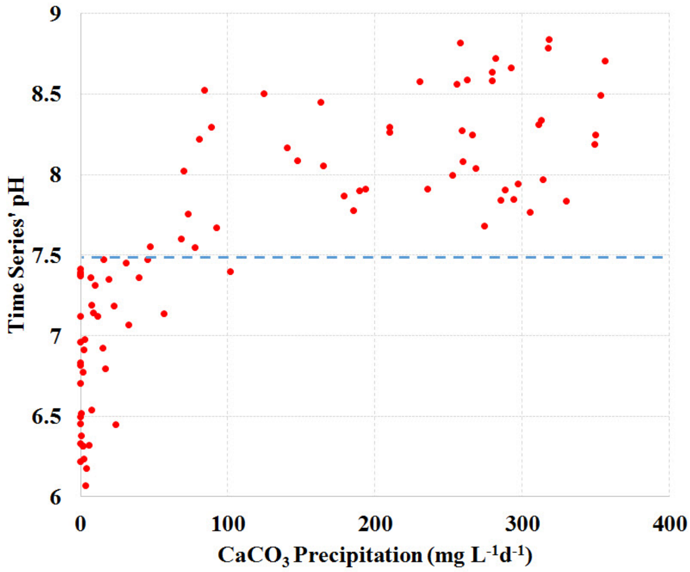


Figure 4.15. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.1.

Figure 4.16 demonstrates same scenario as it was in Figure 4.15 for one year in 2013. This makes clear again that, alkalinity conditions is responding for $CaCO_3$ precipitation in summer and other seasons.

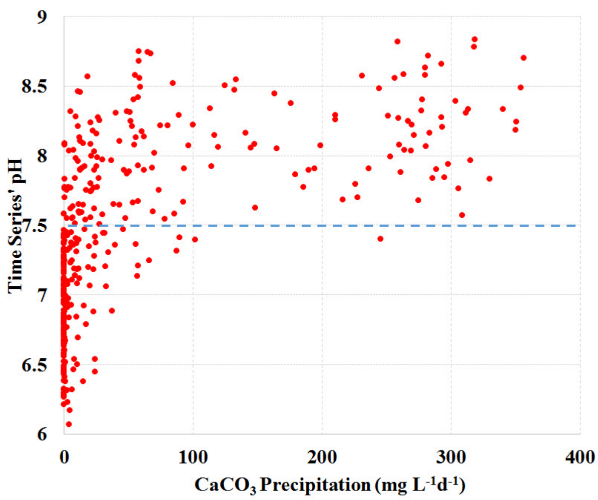


Figure 4.16. Modeled $CaCO_3$ vs. time series pH to check threshold in St.1.

4.5. Scenario Analysis Results for Meteorological Data

The predicted values of meteorological parameters expressed in Section 3.4 are categorized as Scenarios of Table 4.1. All the possible scenarios applied to obtain the results of $CaCO_3$ precipitation in Acıgöl lake when meteorological data are changed are represents as following:

Table 4.1. Various applied scenarios for Acıgöl Lake by modified meteorological data.

Different Scenarios	Water Volume	Light	Temperature	Evaporation
Scanerio 1	Max	Max	Max	Max
Scanerio 2	Min	Min	Min	Min
Scanerio 3	Max	Min	Min	Min
Scanerio 4	Max	Max	Min	Min
Scanerio 5	Max	Min	Max	Max
Scanerio 6	Min	Max	Max	Max
Scanerio 7	Min	Max	Min	Min
Scanerio 8	Min	Min	Max	Max

The model resulted for $CaCO_3$ precipitation of these scenarios are presented in Figures 4.17 to 4.24. These figures state that according to predicted scenarios, the high range of $CaCO_3$ precipitation will occur in summer, starting in early July and reaches its peak in Aug. Then starts to decrease towards the autumn and winter which is almost zero value of precipitation. Noted that, all of the figures demonstrate the same trend approximately, but differ in the $CaCO_3$ precipitation value.

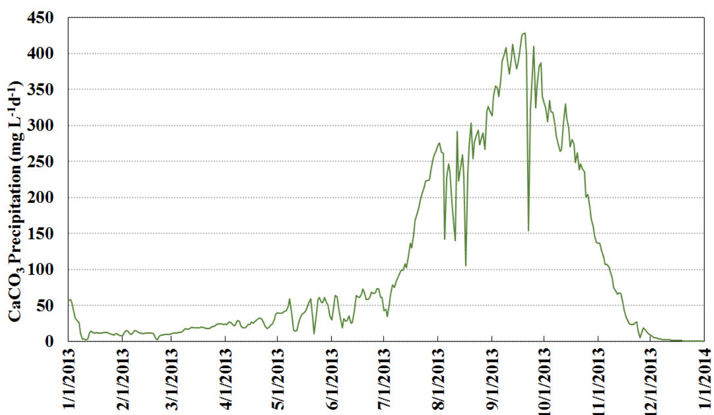


Figure 4.17. Scenario (1) for $CaCO_3$ precipitation from modified meteorological data.

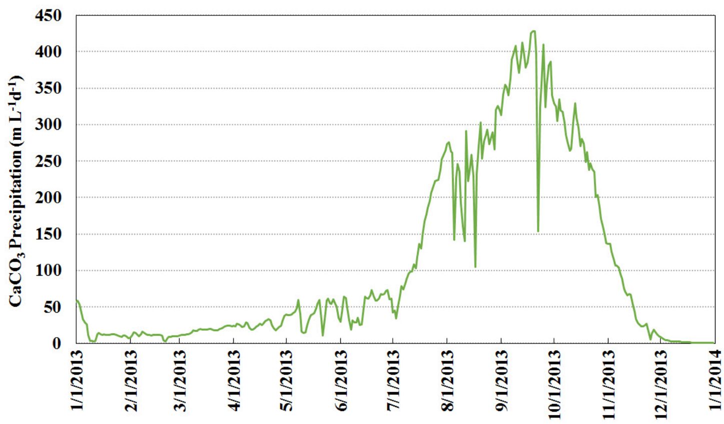


Figure 4.18. Scenario (2) for $CaCO_3$ precipitation from modified meteorological data.

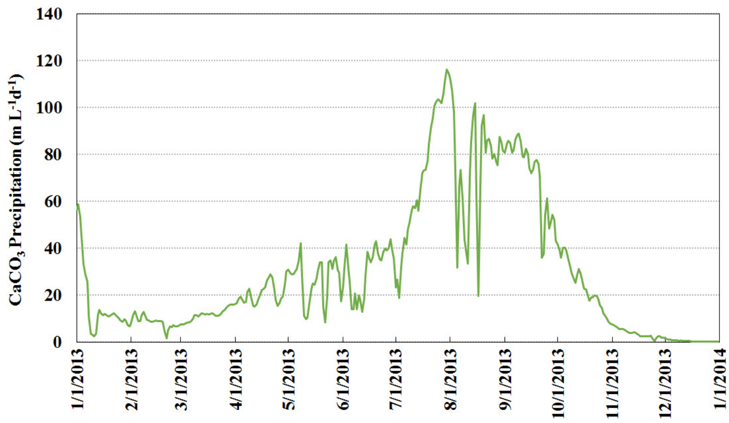


Figure 4.19. Scenario (3) for $CaCO_3$ precipitation from modified meteorological data.

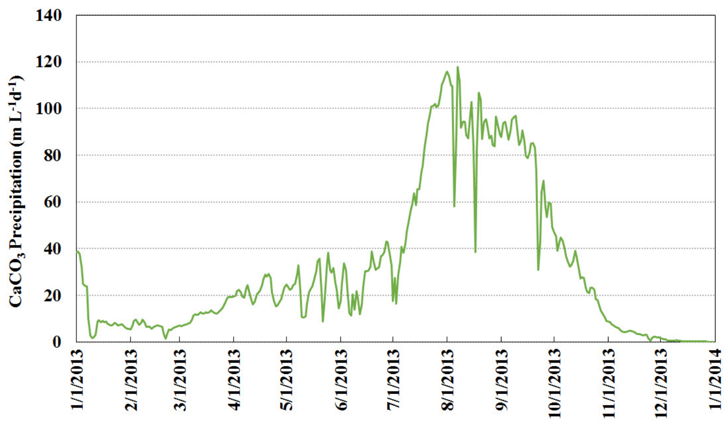


Figure 4.20. Scenario (4) for $CaCO_3$ precipitation from modified meteorological data.

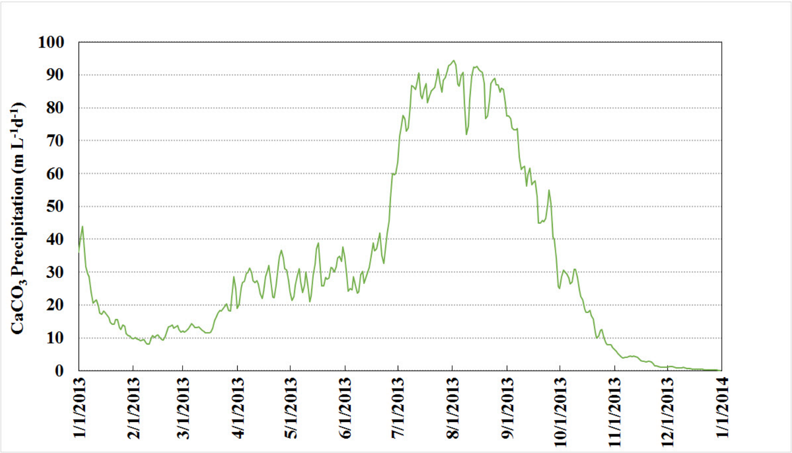


Figure 4.21. Scenario (5) for $CaCO_3$ precipitation from modified meteorological data.

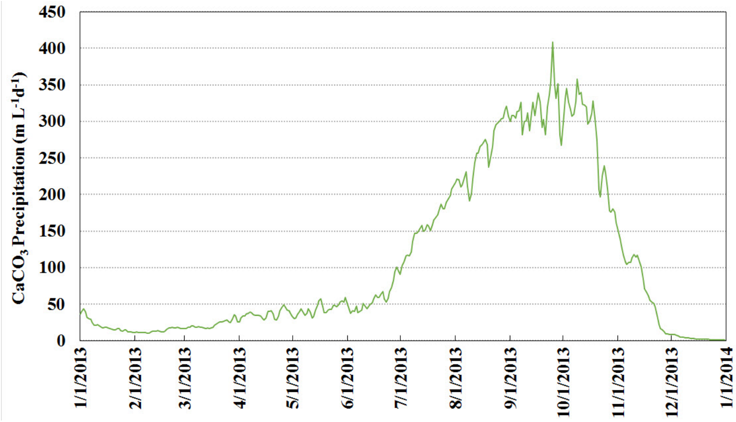


Figure 4.22. Scenario (6) for $CaCO_3$ precipitation from modified meteorological data.

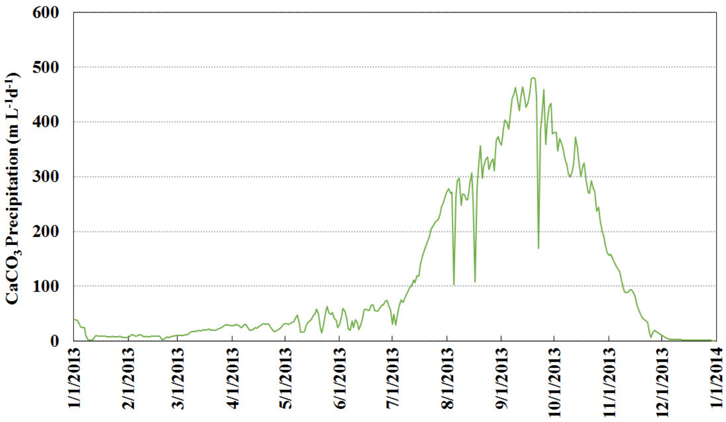


Figure 4.23. Scenario (7) for $CaCO_3$ precipitation from modified meteorological data.

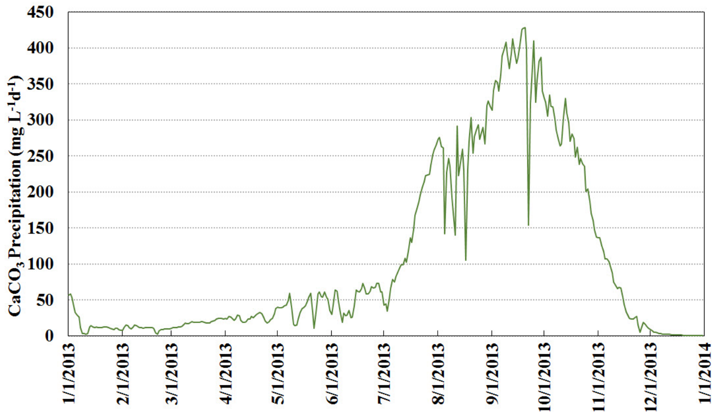


Figure 4.24. Scenario (8) for $CaCO_3$ precipitation from modified meteorological data.

Overall, to demonstrate all results of the scenario analysis in a whole to compare the different conditions with each other Figure 4.25 is drawn.

As it is expected from the mechanism of the $CaCO_3$ precipitation and results of the model, Scenario 6 has shows the maximum amount of the precipitation due to the fact that temperature, irradiation, and evaporation are in the maximum value in contradict with water volume with the minimum value.

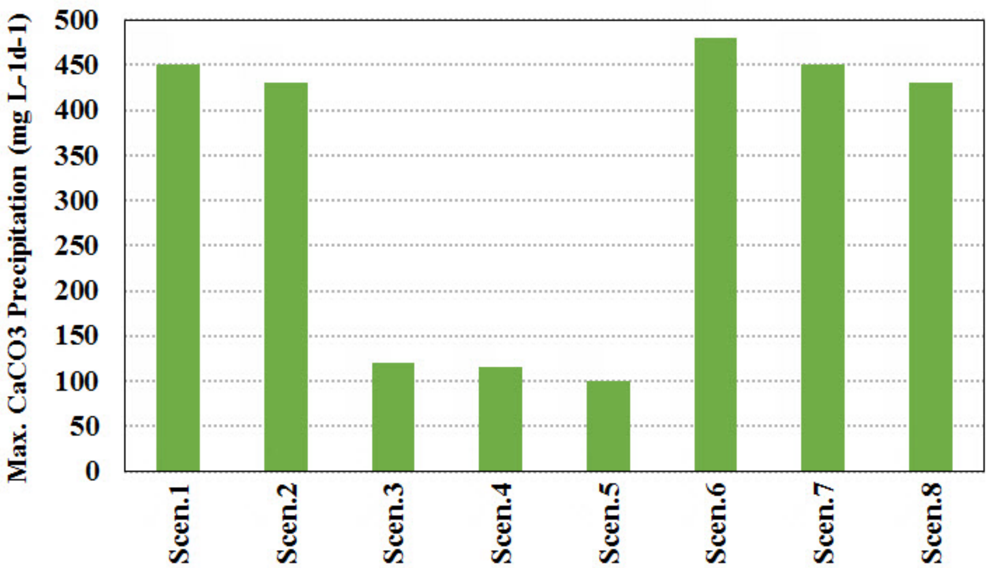


Figure 4.25. Results of the Scenarios by generating meteorological data.

5. CONCLUSION

5.1. Main Conclusion

This study presents the first attempt to estimate $CaCO_3$ precipitation in an alkaline lake using AQUATOX.

The development of a model for the $CaCO_3$ precipitation in Acıgöl Lake especially during the summer has provided insight into the annual whiting event and familiarity with effective parameters in precipitation of $CaCO_3$ in this lake.

This study provides a model of $CaCO_3$ precipitation with changing over time during one year in nine different stations, the analysis provided here shows that AQUATOX mostly focuses on photosynthesis during the period of precipitation. Blue-greens algae are especially common in calcareous and alkaline lakes such as Acıgöl Lake.

Overall, after complete all the required steps for modeling, the range for amount of $CaCO_3$ precipitation is between 35.16 to 128.48 mg $L^{-1}d^{-1}$ in different.

Since CO_2 is already in equilibrium with the atmosphere in the lake, production of CO_2 via the oxidative degradation of organic matter would not dissolved in the lake and thus not create acidic condition and further contribute to the precipitation.

According to the applied algorithm of AQUATOX, *Anabaena* and *Aphanizomenon* as blue-green algae use carbon source to precipitate $CaCO_3$ (Figure 4.3). These two blue-green algae are nitrogen-fixing algae and they can compensate the lack of nutrient budgets, so in summer season especially when these two species exist, also $CaCO_3$ is precipitated.

Our model showed a strong relationship between nitrogen cycles and carbonate precipitation in the lake as *Anabaena*. 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 in the lake, production of CO_2 via the oxidative degradation of organic matter (e.g., glucose and acetate) would not have a significant effect on pH of the solution. Therefore ammonium production as suggested by the model would be main control in the lake .

In addition to this findings, according to the trend of simulation, meteorological data also have a crucial role in the precipitation of $CaCO_3$.

Radiation, the most important meteorological variable for the photosynthesis of blue-green algae, is the highest when the temperature is high in summer, so the photosynthesis is also increased by cyanobacteria and resulting in more solubility of CO_2 in water and more utilization of carbon source which triggers precipitation of $CaCO_3$.

The direct effects of temperature include reducing the solubility, represented by the temperature dependence of K_{sp}, the shift in the carbon system, as well as the increase in the chemical reaction rate. Temperature also affects the rate of calcite precipitation indirectly through the temperature dependencies of primary production rates, the air exchange rate and the timing period in a lake [4].

Depth which is important physical characteristics of the Acıgöl Lake is around 2 m, with variation depending on stations. Acıgöl Lake can be classified as a shallow lake, with a low pressure. There is an important relationship between depth, pressure and temperature to interpret the reason for higher precipitation in summer ,particularly dependency to depth and calibration of model.

Calibration with modifying data inputs according to field measurements and literature yielded better simulations of $CaCO_3$ in AQUATOX. The relationship between depth of different stations and k_f coefficients is related to the chemical processes involved. Temperature assists chemical reactions, so $CaCO_3$ precipitation as well increases with temperature. Moreover, calcite precipitation decreases with pressure, and pressure increases with increasing depth. More $CaCO_3$ is deposited in shallower water than deeper water due to the lower depth such as the case of Acıgöl Lake. As pressure increases and temperature decreases, more $CaCO_3$ dissolves.

In this study, sensitivity analysis represents the important issue for the modeling of $CaCO_3$. In this way, the sensitivity of $CaCO_3$ outputs attributes to the coefficient's parameters of plants are indicated. The blue-green algae optimal temperature are highly effective in the precipitation of $CaCO_3$, particularly optimal temperature for *Aphanizomenon* species.

In scenario analysis for this study, modification of weather conditions by newly generated data by SPSS proves that meteorological variables are highly effective in precipitation of Acıgöl Lake.

Perturbations test runs also give the opportunity to try different scenarios to evaluate different conditions for $CaCO_3$ precipitation. When the inflow loadings such as dissolved oxygen, NO_2^-, NO_3^-, PO_4^{3-}, NH_4^+, enter to the Acıgöl Lake, nutrient budget balance is influenced. Effect of entrance of phosphate from ground water loadings are very substantial due to changes the balance between nitrogen and phosphorus in water. According to the less TN/TP in the oligotrophic lake and limiting nitrogen, nitrogen-fixing blue-green algae are compensated the lack of nitrogen and do the photosynthesis activity which triggers in precipitation of $CaCO_3$.

As it is expected from the mechanism of the $CaCO_3$ precipitation and results of the model, Scenario 6 has shows the maximum amount of the precipitation 480 (mg $L^{-1}d^{-1}$) to the fact that temperature, irradiation, and evaporation are in the maximum value in contradict with water volume with the minimum value.

Hence by changing pH from constant to time-series, it is observed that high amount of $CaCO_3$ precipitation occurs when pH is more than 7.5 means an alkaline condition for Lake.

5.2. Recommendations for Future Work

In order to obtain more precise $CaCO_3$ precipitation model in Acıgöl Lake, there are some significant implementations which would be considered.

Firstly, more field measurements are needed. The long-term and consistent field measurements of cooperating physical, chemical, biological and finally meteorological must be obtained at different points of the lake. By these data, not only the more realistic effects of each parameter can be obtained, but also the upcoming measurements can be used as validation data for continuous modeling.

Secondly, the laboratory experiment should be conducted by considering all of the realistic values of existence physical and chemical materials in the lake water. In addition, the consistent laboratory experiment with the realistic meteorological and physical parameters provide precise calibrating data for long-term modeling.

In addition to the precise laboratory $CaCO_3$ precipitated data, effective phytoplankton and algae must be cultured separately in the laboratory from the sample taken in Acıgöl Lake.

Finally, hydrodynamic characteristics of the lake should be measured comprehensively. In addition to precipitation and evaporation by meteorological record, the creeks and groundwater inflow and discharge values of the lake's water body should be modeled to distinguish the realistic interaction of chemical and hydrological conditions.

REFERENCES

1. Leyendekkers, J. V., 1973. The chemical potentials of seawater components. Marine Chemistry, 12, 75–88.

2. Stumm, W., Morgan, J. J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, Environmental Science and Technology, Wiley.

3. Park, R. A., Clough, J. S., Wellman, M. C., 2013. AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. Office of Water of United States Environmental Protection Agency, 302–344.

4. Homa, E. S., 2010. Mass balance modeling of calcite in the epilimnion of an ultraoligotrophic lake, Ph.D. Thesis, Tufts University.

5. APHA Standard Methods for the Examination of Water and Wastewater, 1999. American Public Health Association, Washington, DC, 20.

6. Jung, W. M., Kang, S. H., Kim, W. S., Choi, C. K., 2000. Particle morphology of calcium carbonate precipitated by gas–liquid reaction in a Couette–Taylor reactor. Chemical Engineering Science, 554, 733–747.

7. Shirsath, S. R., Sonawane, S. H., Saini, D. R., Pandit, A. B., 2015. Continuous precipitation of calcium carbonate using sonochemical reactor. Ultrasonics sonochemistry, 24, 132–139.

8. Chen, L., J. and Xiang, 2009. Controllable synthesis of calcium carbonate polymorphs at different temperatures. Powder Technology, 1891, 64–69.

9. Merrill, D. T., Sanks, R. L., 1977. Corrosion Control by Deposition of CaCO3 Films: Part 1, A Practical Approach for Plant Operators. American Water Works Association, 592–599.

10. Parker, J. E., Thompson, S. P., Lennie, A. R., Potter, J., Tang, C. C., 2010. A study of the aragonite-calcite transformation using Raman spectroscopy, synchrotron powder diffraction and scanning electron microscopy. CrystEngComm, 125, 1590–1599.

11. McConnaughey, T. A., LaBaugh, J. W., Rosenberry, D. O., Striegl, R. G., Reddy, M. M., Schuster, P. F.,Carter, V., 1994. Carbon budget for a groundwater-fed lake: Calcification supports summer photosynthesis. Limnology and Oceanography, 396, 1319–1332.

12. Reddy, M. M., 1995. Carbonate precipitation in Pyramid Lake, Nevada Mineral Scale Formation and Inhibition, 21–32.

13. Stabel, H. H., 1986. Calcite precipitation in Lake Constance: chemical equilibrium, sedimentation, and nucleation by algae. Limnology and Oceanography, 31, 81–94.

14. Rashleigh, B., 2003. Application of AQUATOX, a process-based model for ecological assessment, to Contentnea Creek in North Carolina. Freshwater Ecology, 184, 515–522.

15. Morkoç, E., Tüfekçi, V., Tüfekçi, H., Tolun, L., Karakoç, F. T., Güvensel, T., 2009. Effects of land-based sources on water quality in the Omerli reservoir. Environmental geology, 575, 1035–1045.

16. Yang, Y. F., Zhu, Y. Q., Lin, W. Q., 2009. Simulation Study on Eutrophication Control in DianShan Lake. Environmental Science and Technology, 2, 008.

17. Chen, Y. X., Niu, Z. G., Zhng, H. W., Mi, Z. M., Sun, J., Wang, F., 2012. Aquatic ecological modeling and remediation of landscape water based on AQUATOX. Tianjin University, 1, 006.

18. Mutlu, H., Kadir, S., Akbulut, A., 1999. Mineralogy and water chemistry of the Lake Acigol. Carbonates and Evaporites, 142, 191–199.

19. Balci, N., Menekşe, M., Karagüler, N., Sönmez, M., Meister, P., 2016. Reproducing authigenic carbonate precipitation in the hypersaline Lake Acıgöl (Turkey) with microbial cultures. Geomicrobiology, 1–16.

20. Balci, N., Menekşe, M., Karagüler, N., Sönmez, M., Meister, P., 2014. Authigenic carbonate precipitation in Lake Acigöl, a hypersaline lake in southwestern Turkey. EGU General Assembly Conference Abstracts, 16, 6038.

21. Helvaci, C., Alcicek, M. C., Gündoğan, I., Gemici, Ü., 2013. Tectonosedimentary development and palaeoenvironmental changes in the Acıgöl shallow-perennial playa-lake basin, SW Anatolia, Turkey. Turkish Journal of Earth Sciences, 222, 173–190.

22. Burçak, M., 2009. Water Chemistry and Isotope Studies In Aksaray Geothermal Fields (Acıgöl-Ziga-Şahinkalesi), Central Anatolia, Turkey. Bulletin of The Mineral Research and Exploration, 138.

23. Garrett, D. E., 2001. Sodium Sulfate: Handbook of Deposits, Processing, & Use, Academic Press.

24. Wainwright, J., Mulligan, M., 2005. Environmental modelling: finding simplicity in complexity, John Wiley & Sons.

25. Linsley, R. K., Franzini, J. B., 1979. Water-resources engineering, McGraw-Hill New York, 165.

26. Park, R. A., Clough, J. S., 2004. Modeling environmental fate and ecological effects in aquatic ecosystems volume 2: technical documentation. United States Environmental Protection Agency.

27. Pickard, G. L., Emery, W. J., 1990. Descriptive physical oceanography: an introduction, Elsevier.

28. Wlosinski, J. H., Collins, C. D., 1985. Confirmation of the Water Quality Model CE-QUAL-R1 Using Data from Eau Galle Reservoir, Wisconsin, DTIC Document.

29. Collins, C. D., Wlosinski, J. H., 1983. Coefficients for Use in the US Army Corps of Engineers Reservoir Model, CE-QUAL-R1.

30. Megard, R. O., Berman, T., 1989. Effects of algae on the Secchi transparency of the southeastern Mediterranean Sea. Limnology and Oceanography, 348, 1640–1655.

31. Inskeep, W. P., Bloom, P. R., 1985. An evaluation of rate equations for calcite precipitation kinetics at pCO2 less than 0.01 atm and pH greater than 8. Geochimica et Cosmochimica Acta, 4910, 2165–2180.

32. Nancollas, G. H., Reddy, M. M., 1971. The crystallization of calcium carbonate, II. Calcite growth mechanism. Colloid and Interface Science, 374, 824–830.

33. Kalff, J., 2002. Limnology: inland water ecosystems, 504.

34. Clair, N. S., Perry, L. M., Gene, F. P., 2003. Chemistry for environmental engineering and science, Mcgraw-Hill, New York.

35. Pytkowicz, R. M., 1975. Activity coefficients of bicarbonates and carbonates in seawater. Limnology and Oceanography, 206, 971–975.

36. Crosetto, M., Tarantola, S., Saltelli, A., 2000. Sensitivity and uncertainty analysis in spatial modelling based on GIS. Agriculture, ecosystems & environment, 811, 71–79.

37. Chen, Y., Yu, J., Khan, S., 2010. Spatial sensitivity analysis of multi-criteria weights in GIS-based land suitability evaluation. Environmental Modelling & Software, 2512, 1582–1591.

38. Park, R. A., Clough Jonathan S, 2013. Sensitivity Analysis of AQUATOX, Volume2: Technical Documentation, United States Environmental Protection

Agency.

39. Aaker, D. A., Jonathan S,McLoughlin, D., 2010. Strategic market management: global perspectives, John Wiley & Sons.

40. Christopher Frey, H., Patil, S. R., 2002. Identification and review of sensitivity analysis methods. Risk Analysis, 223, 553–578.

41. Wetzel, R. G., 2001. Limnology: lake and river ecosystems, Gulf Professional Publishing.

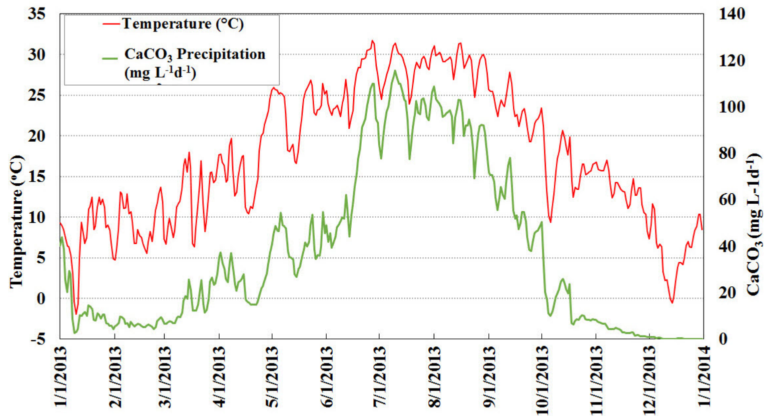
42. Chapra, S. C., 2008. Surface water-quality modeling, Waveland Press.

APPENDIX A: Site Description

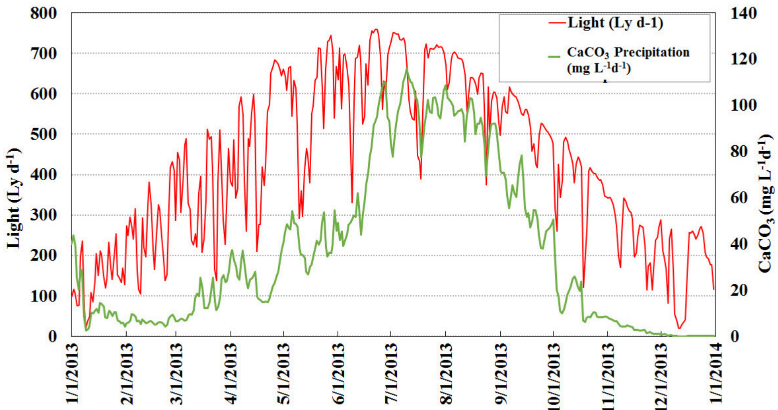
Table A.1. Site Characteristics of Selected surrogate site for the model.

Site Characteristics of Onondaga Lake	**Values**	**Unit**
Site length	7	km
Surface Area	1349400	m^2
Mean Depth	3.9547	m
Maximum Depth	4.6512	m
Evaporation	115	cm
Latitude	27.26	Degree
pH	57	-

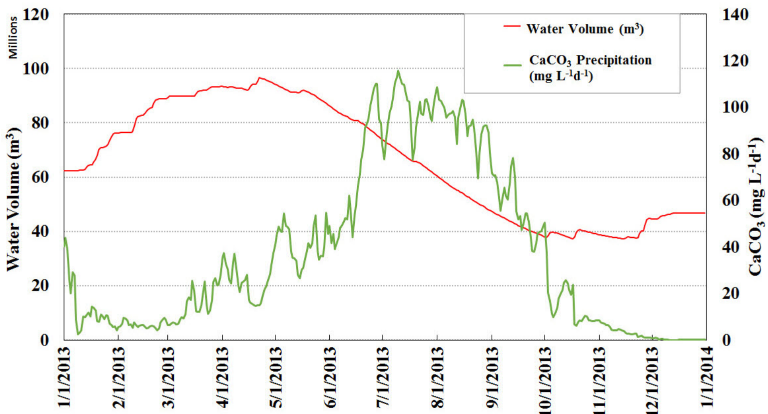
APPENDIX B: Results of Calibration



(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.2

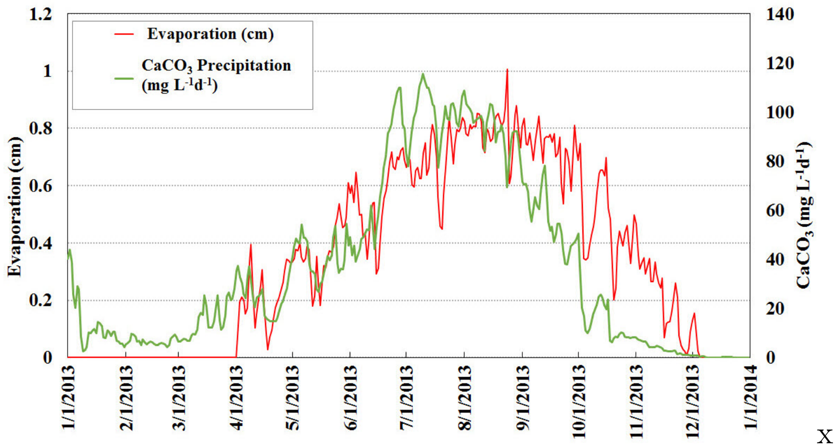


(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.2



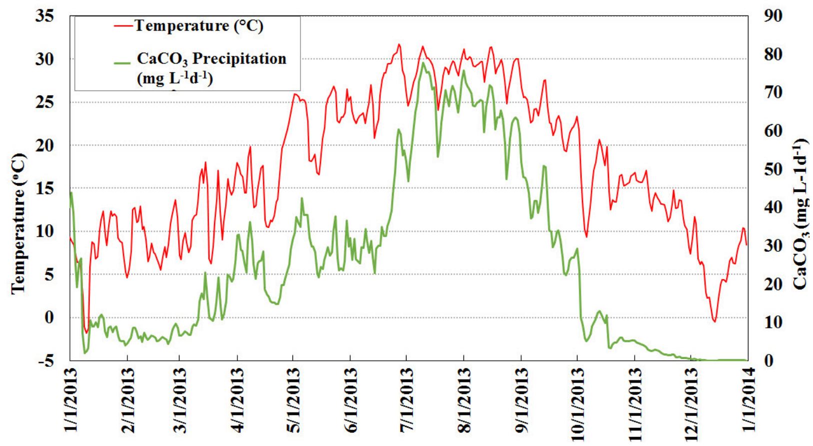
(c) Calibration of $CaCO_3$ vs water volume from TSMS in St.2

Figure B.1. Initial calibration of by modification of plant coefficients for St.2.

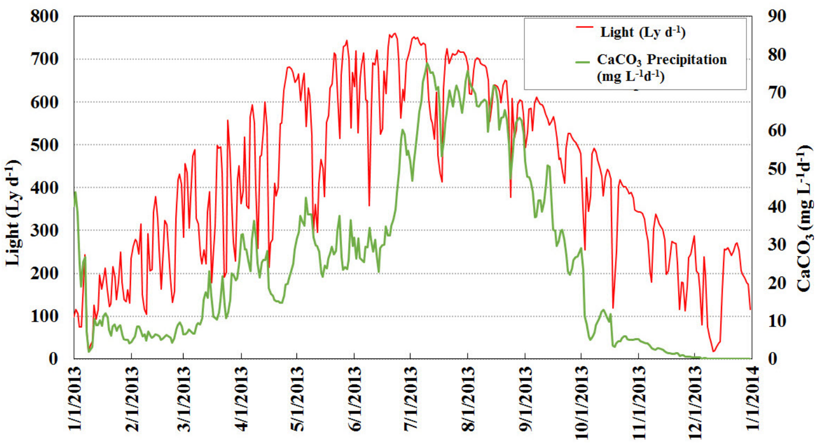


(b) Calibration of $CaCO_3$ vs evaporation from TSMS in St.2

Figure B.1. Initial calibration of by modification of plant coefficients for St.2 (cont.).

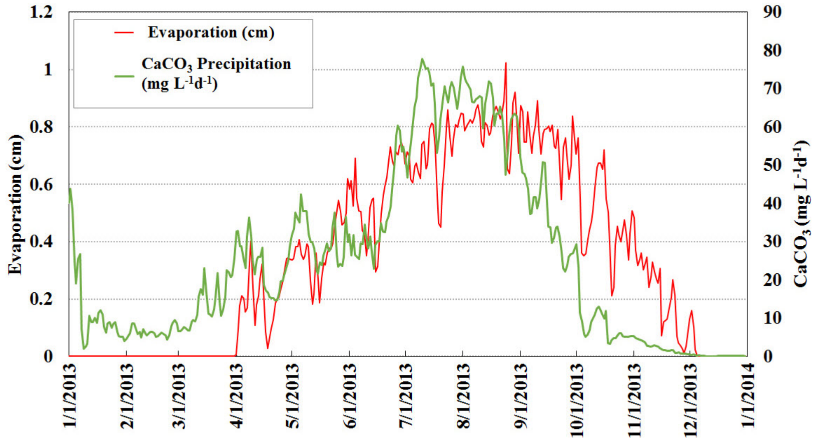


(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.3

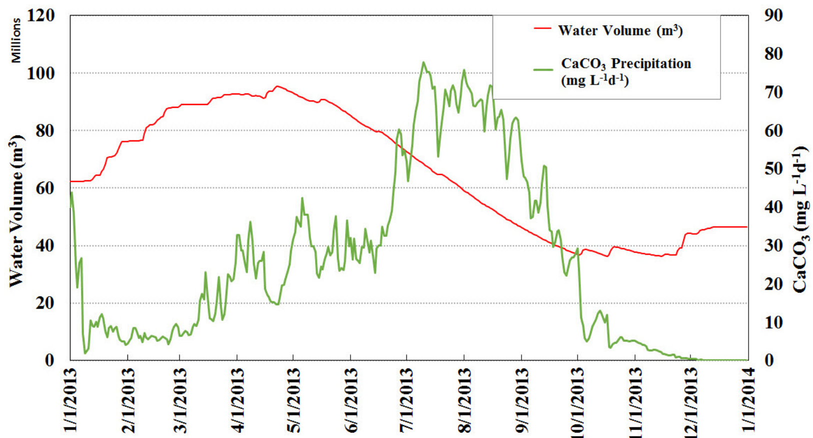


(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.3

Figure B.2. Initial calibration of by modification of plant coefficients for St.3.

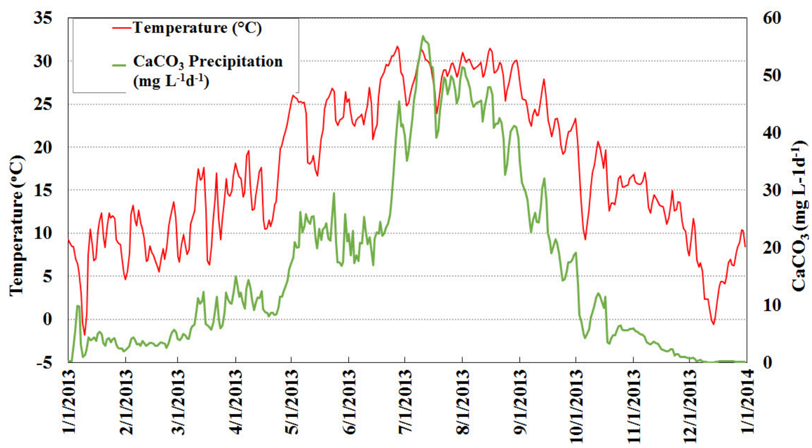


(c) Calibration of $CaCO_3$ vs evaporation from TSMS in St.3



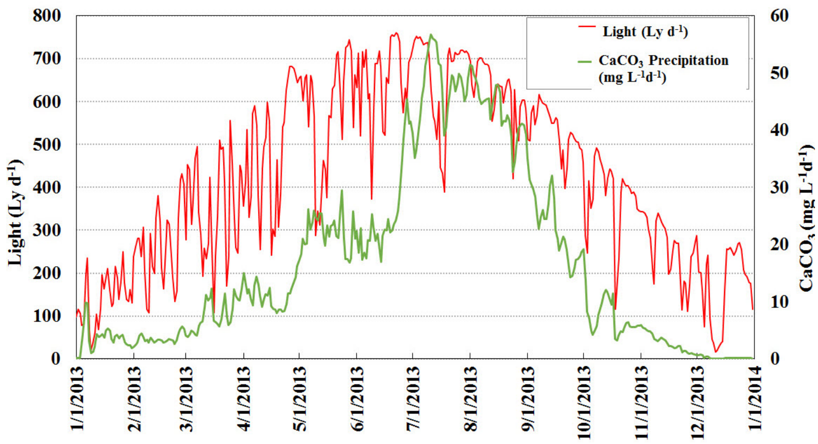
(d) Calibration of $CaCO_3$ vs water volume from TSMS in St.3

Figure B.2. Initial calibration of by modification of plant coefficients for St.3 (cont.).

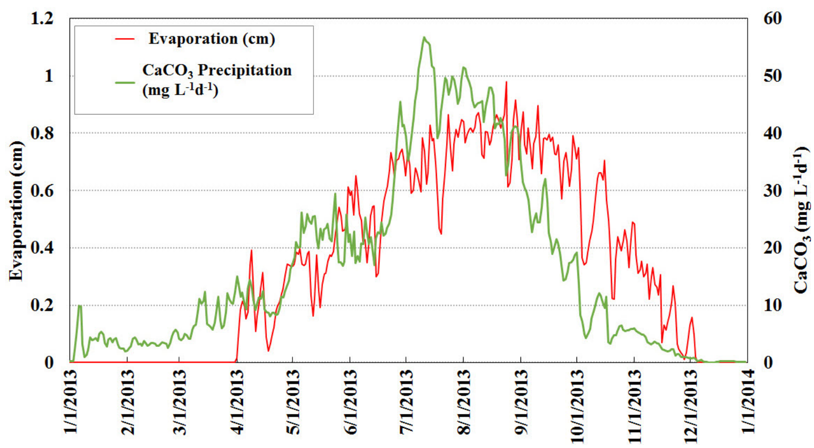


(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.4

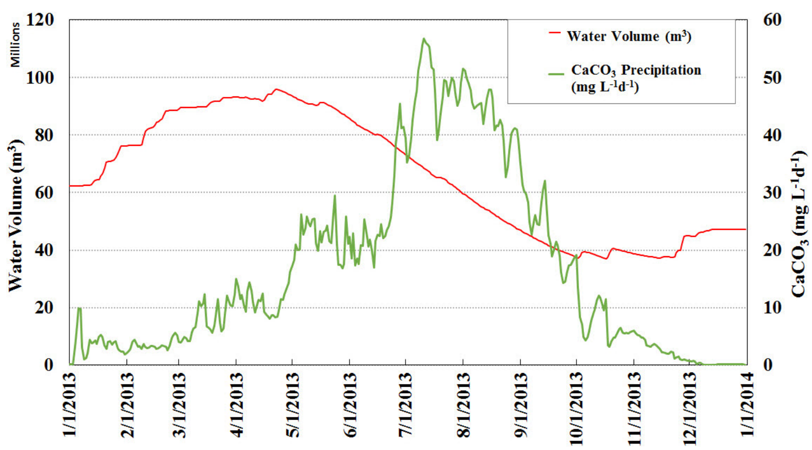
Figure B.3. Initial calibration of by modification of plant coefficients for St.4.



(d) Calibration of $CaCO_3$ vs irradiance from TSMS in St.4

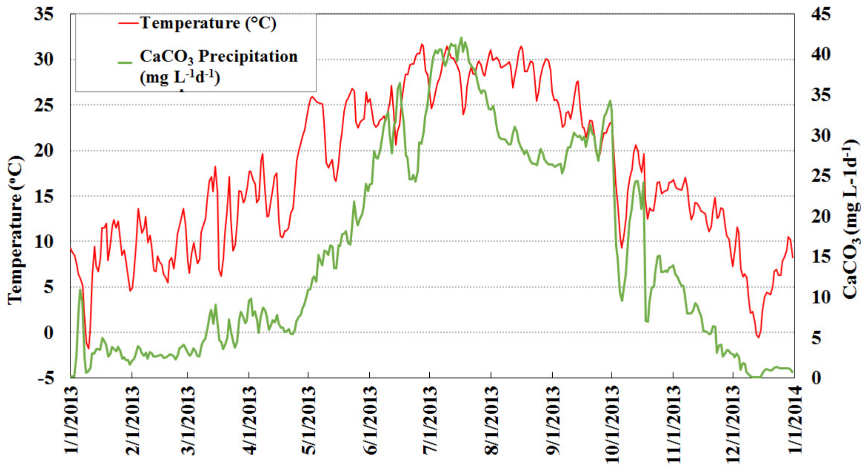


(e) Calibration of $CaCO_3$ vs evaporation from TSMS in St.4

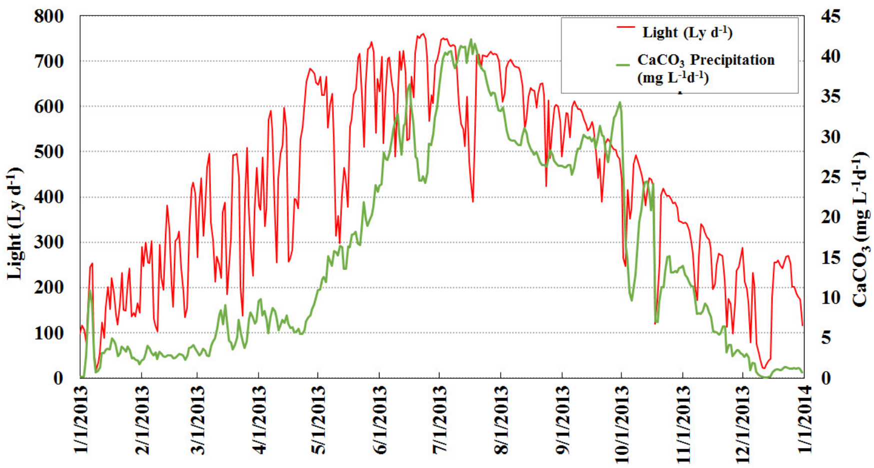


(f) Calibration of $CaCO_3$ vs water volume from TSMS in St.4

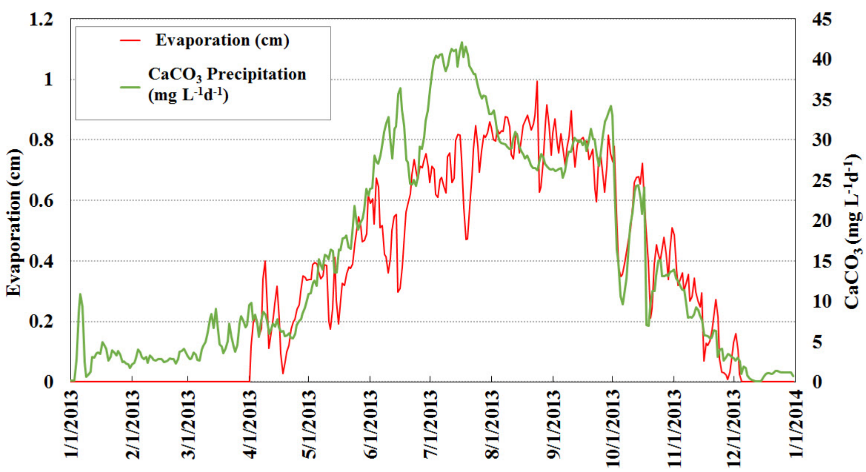
Figure B.3. Initial calibration of by modification of plant coefficients for St.4 (cont.).



(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.5

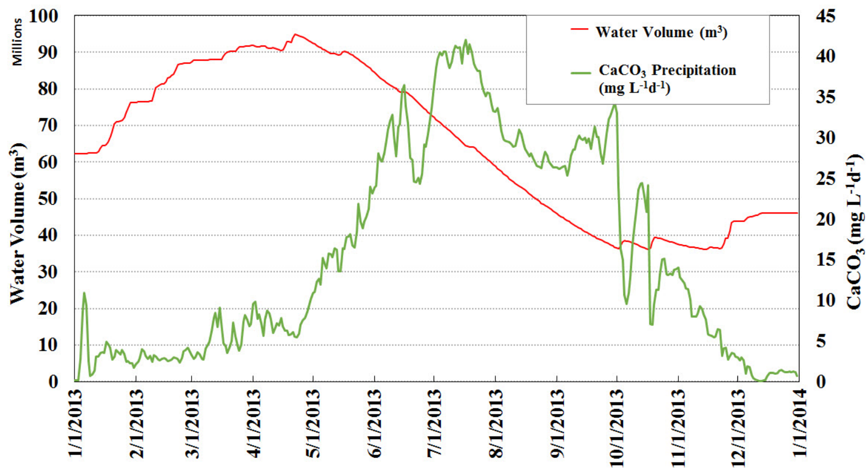


(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.5



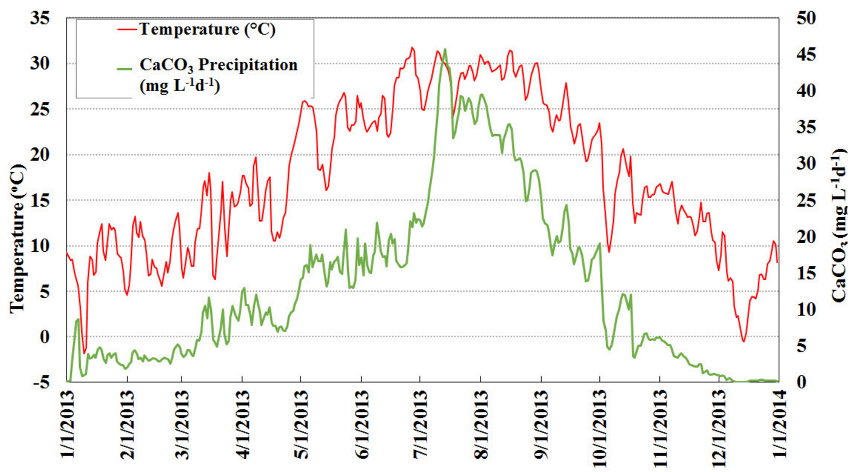
(c) Calibration of $CaCO_3$ vs evaporation from TSMS in St.5

Figure B.4. Initial calibration of by modification of plant coefficients for St.5.

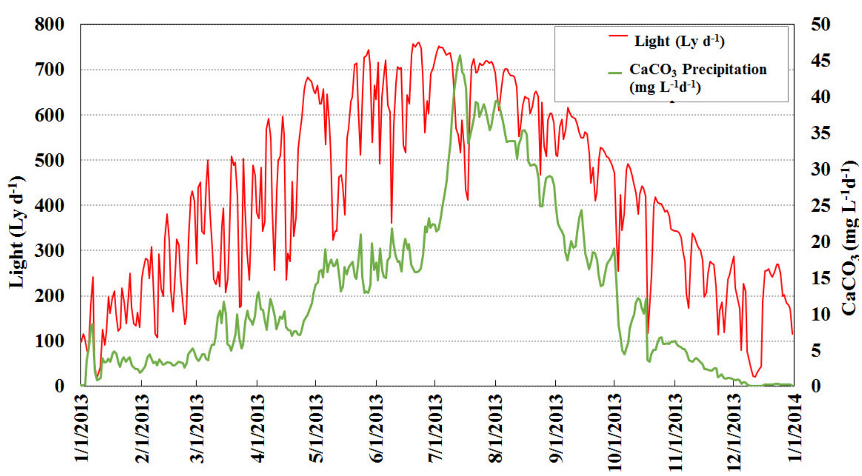


(d) Calibration of $CaCO_3$ vs water volume from TSMS in St.5

Figure B.4. Initial calibration of by modification of plant coefficients St.5 (cont.).

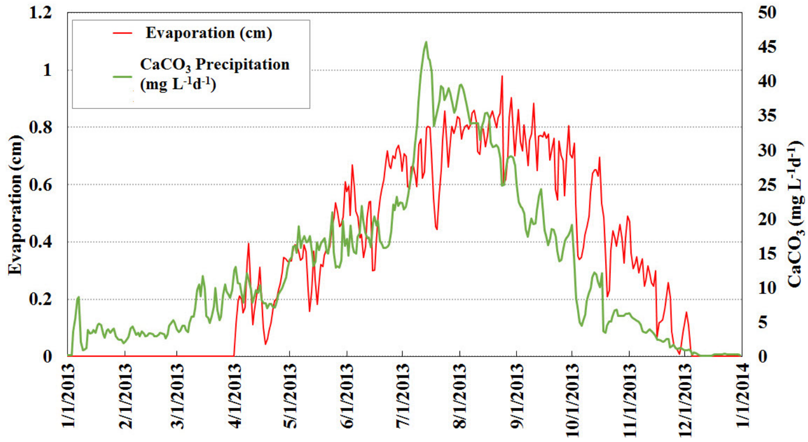


(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.6

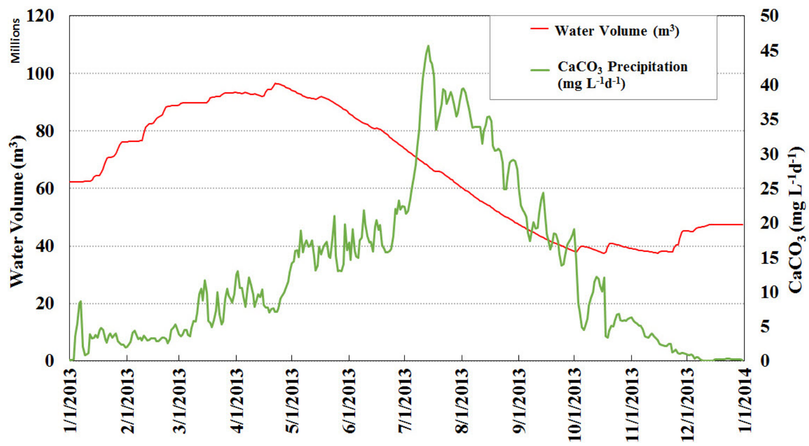


(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.6

Figure B.5. Initial calibration of by modification of plant coefficients for St.6.

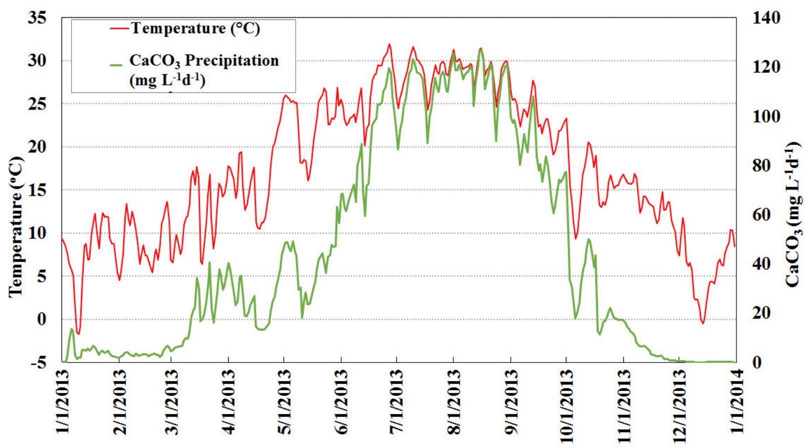


(c) Calibration of $CaCO_3$ vs evaporation from TSMS in St.6



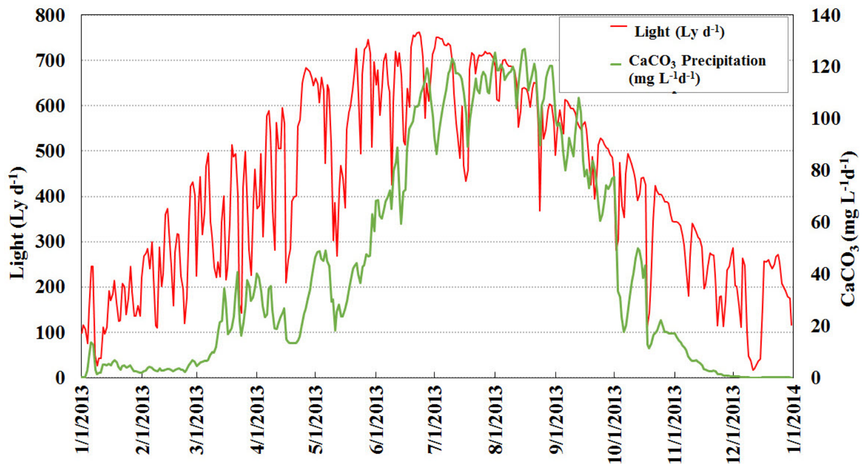
(d) Calibration of $CaCO_3$ vs water volume from TSMS in St.6

Figure B.5. Initial calibration of by modification of plant coefficients for St.6 (cont.).

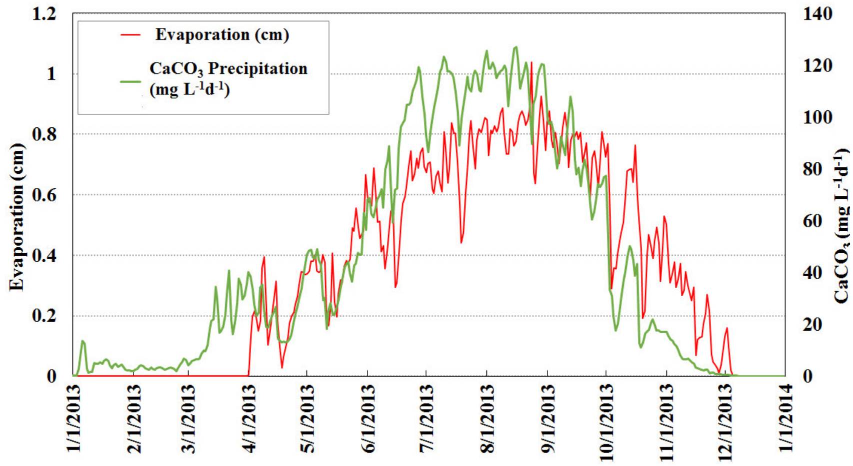


(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.7

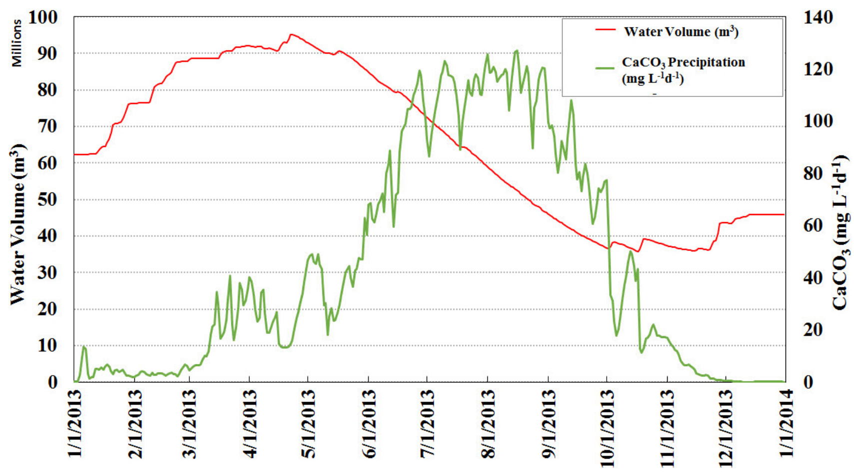
Figure B.6. Initial calibration of by modification of plant coefficients for St.7.



(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.7

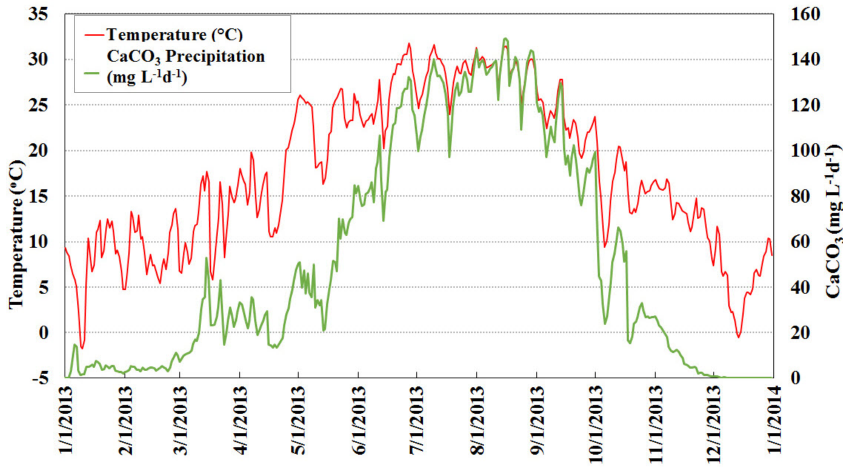


(c) Calibration of $CaCO_3$ vs evaporation from TSMS in St.7

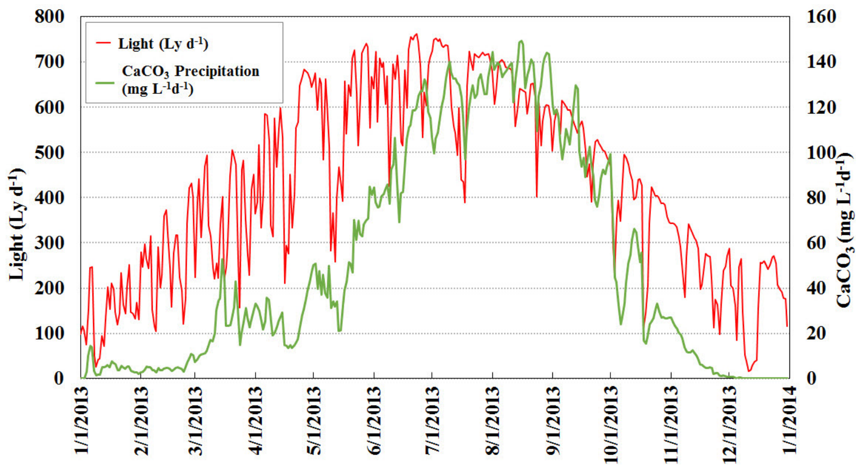


(d) Calibration of $CaCO_3$ vs water volume from TSMS in St.7

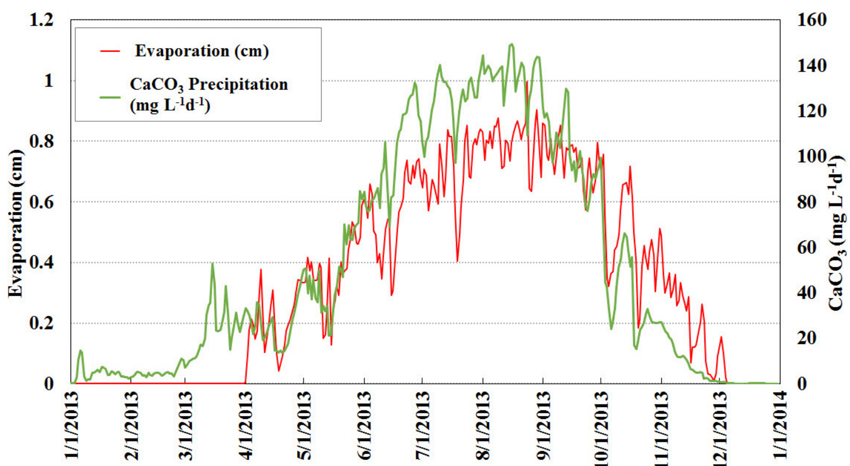
Figure B.6. Initial calibration of by modification of plant coefficients for St.7 (cont.).



(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.8

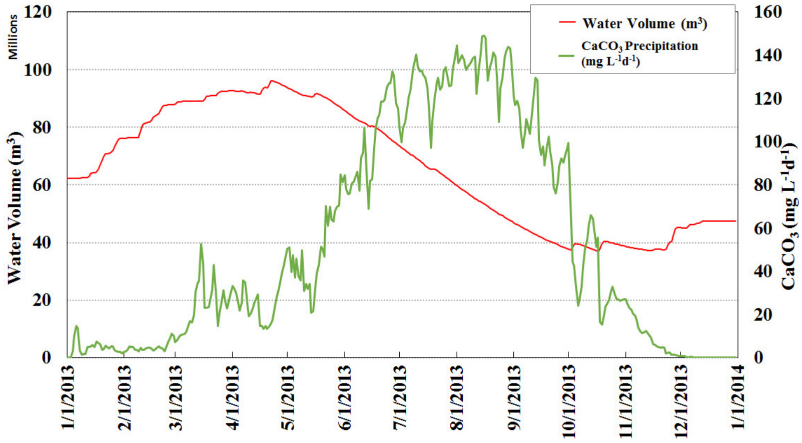


(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.8



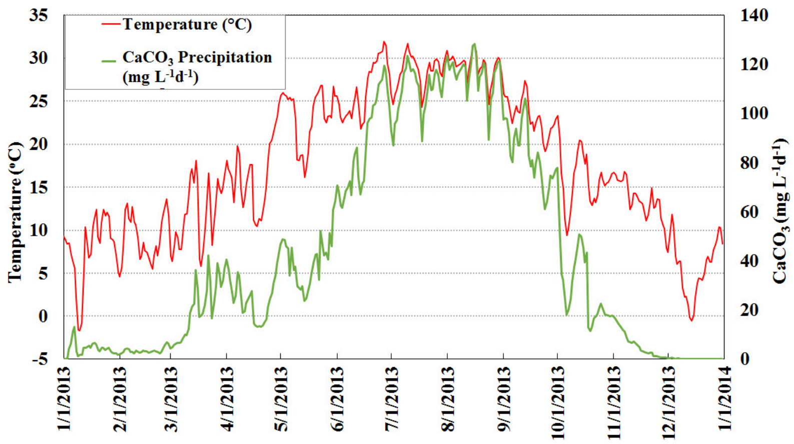
(c) Calibration of $CaCO_3$ vs evaporation from TSMS in St.8

Figure B.7. Initial calibration of by modification of plant coefficients for St.8.

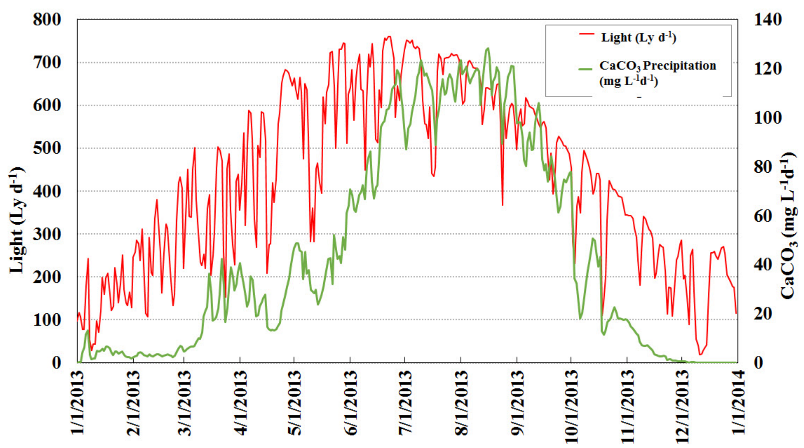


(d) Calibration of $CaCO_3$ vs water volume from TSMS in St.8

Figure B.7. Initial calibration of by modification of plant coefficients for St.8 (cont.).

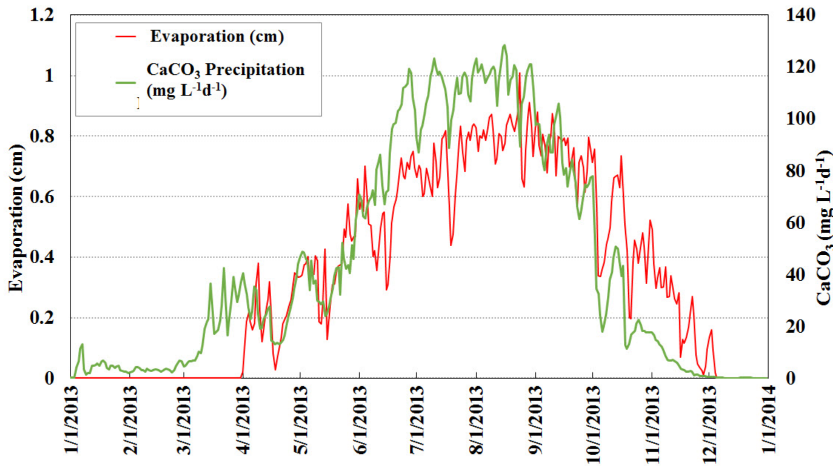


(a) Calibration of $CaCO_3$ vs temperature from TSMS in St.9

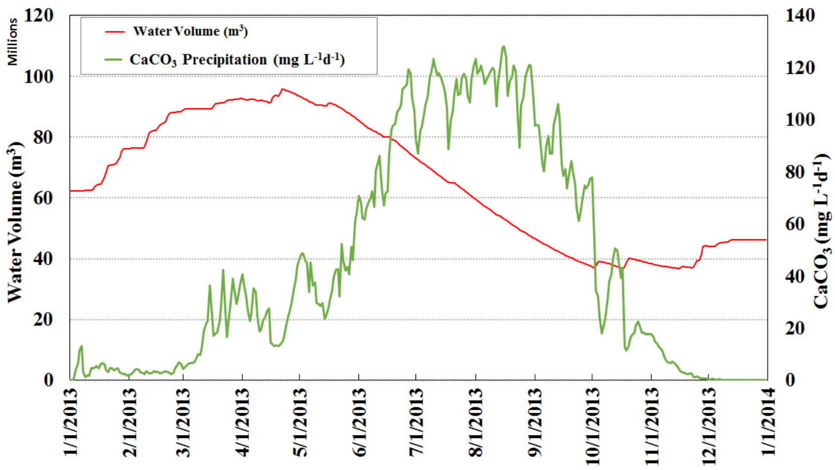


(b) Calibration of $CaCO_3$ vs irradiance from TSMS in St.9

Figure B.8. Initial calibration of by modification of plant coefficients for St.9.



(c) Calibration of $CaCO_3$ vs evaporation from TSMS in St.9



(d) Calibration of $CaCO_3$ vs water volume from TSMS in St.9

Figure B.8. Initial calibration of by modification of plant coefficients for St.9 (cont.).

APPENDIX C: Results of Validation

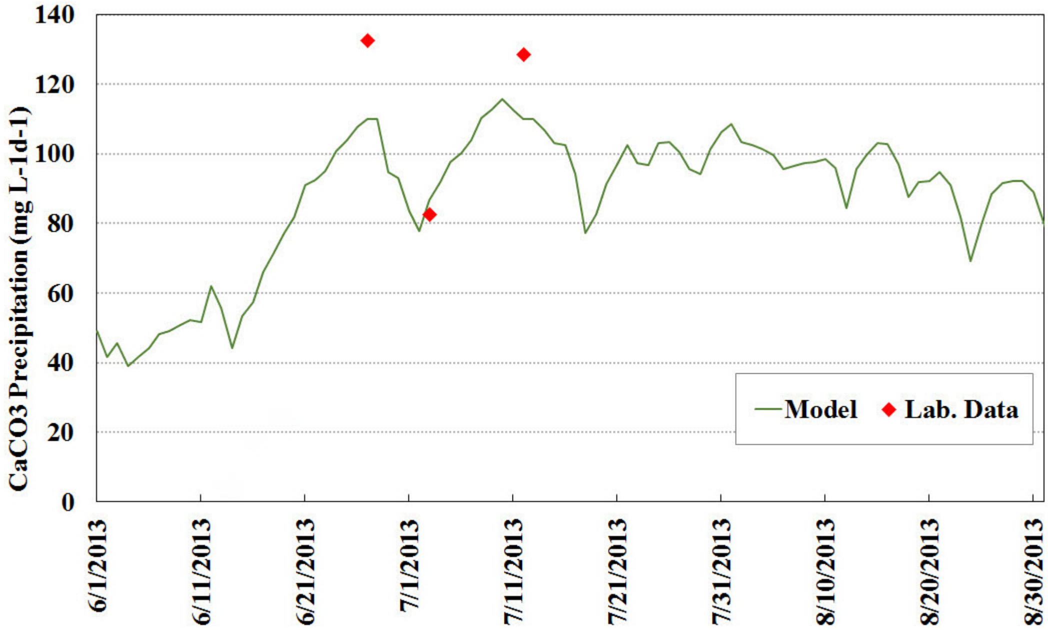


Figure C.1. Validation of $CaCO_3$ by laboratory measurements in St.2.

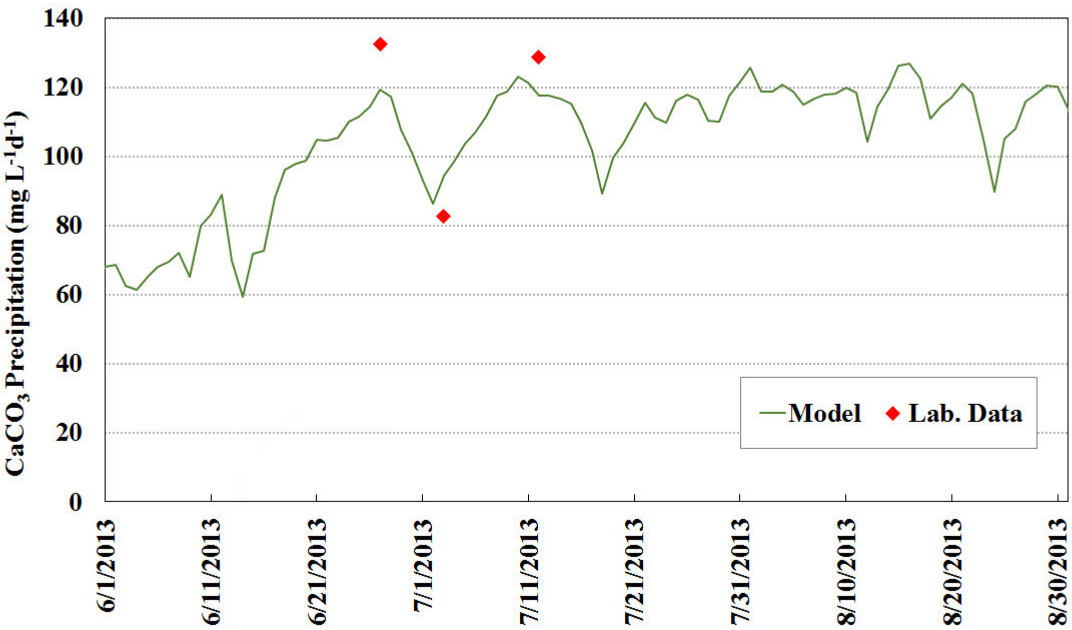


Figure C.2. Validation of $CaCO_3$ by laboratory measurements in St.7.

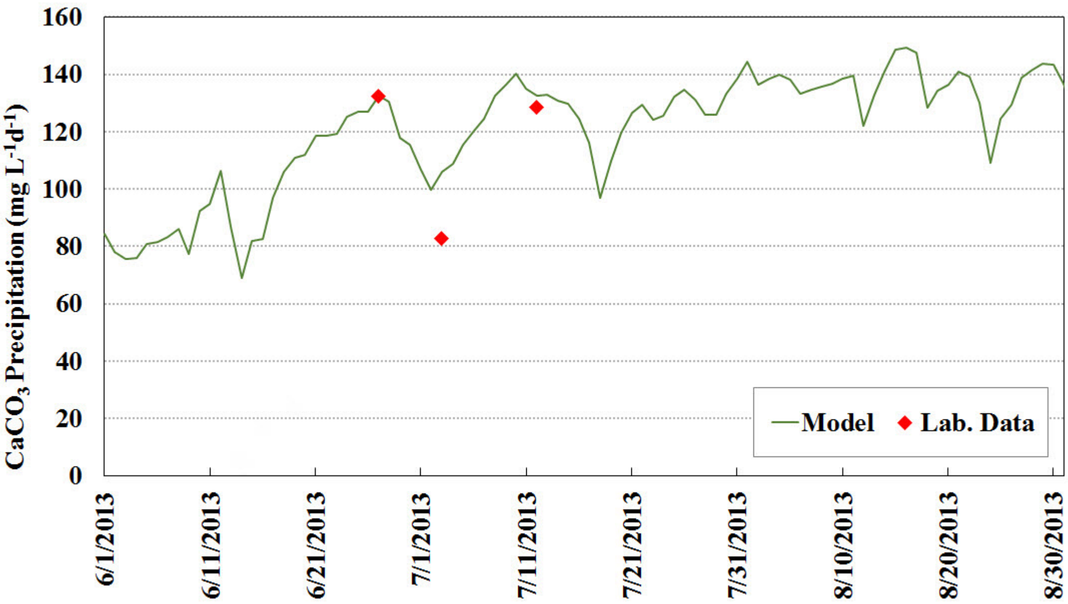


Figure C.3. Validation of $CaCO_3$ by laboratory measurements in St.8.

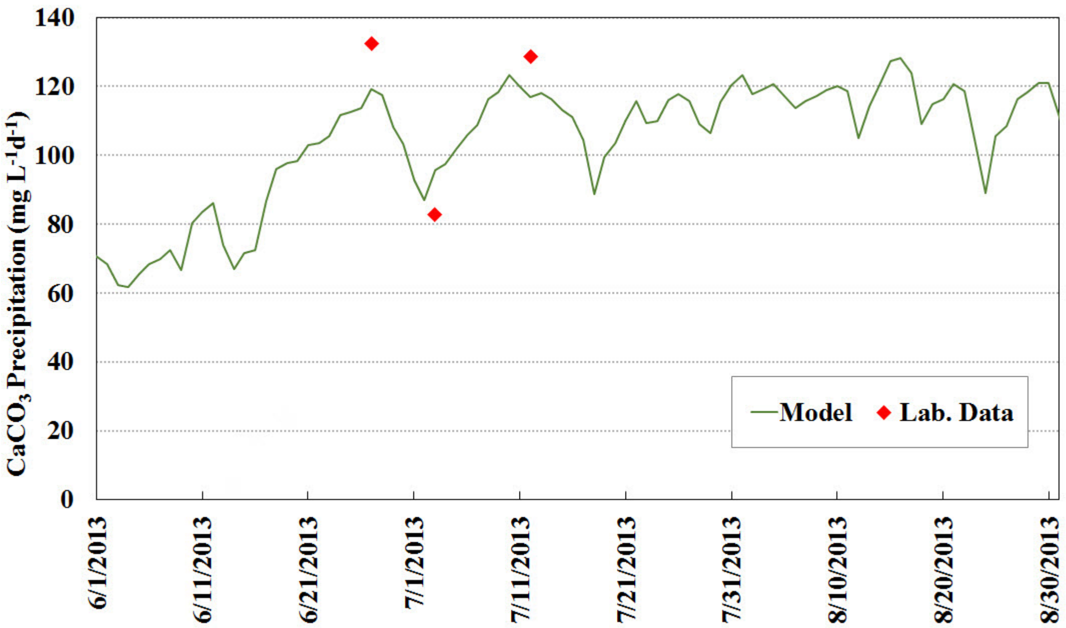


Figure C.4. Validation of $CaCO_3$ by laboratory measurements in St.9.

APPENDIX D: Results of Sensitivity Analysis

Table D.1. Initial condition and input parameters applied in plants sensitivity analysis.

Tested Plant Coefficients for Sensitivity Analysis		
Phyto, Navicula: Saturating Light	Phyt, Blue-Greens JC: Optimal Temperature	Ostracode: Optimal Temperature
Phyto, Hi-Nut Diatom: Saturating Light	Hydrilla: Optimal Temperature	Daphnia: Optimal Temperature
Phyto, Green: Saturating Light	Phyt, Blue-Green max: Optimal Temperature	Gastropod: Optimal Temperature
Greens: Saturating Light	Phyt, Blue-Greens DR: Optimal Temperature	Shrimp: Optimal Temperature
Phyto, Green, Marine: Saturating Light	Phyto, Navicula: Max Photosynthetic Rate	Phyto, Navicula: Initial Condition
Phyt Blue-Green HiLt: Saturating Light	Phyto, Hi-Nut Diatom: Max Photosynthetic Rate	Phyto, Hi-Nut Diatom: Initial Condition
Phyt, Bl-Greens, Mar: Saturating Light	Phyto, Green: Max Photosynthetic Rate	Phyto, Green: Initial Condition
Phyt, Blue-Greens CR: Saturating Light	Greens: Max Photosynthetic Rate	Greens: Initial Condition
Phyt, Blue-Greens JC: Saturating Light	Phyt Blue-Green HiLt: Max Photosynthetic Rate	Phyto, Green, Marine: Initial Condition
Hydrilla: Saturating Light	Phyt, Bl-Greens, Mar: Max Photosynthetic Rate	Phyt Blue-Green HiLt: Initial Condition
Phyt, Blue-Green max: Saturating Light	Phyt, Blue-Greens CR: Max Photosynthetic Rate	Phyt, Bl-Greens, Mar: Initial Condition
Phyt, Blue-Greens DR: Saturating Light	Phyt, Blue-Greens JC: Max Photosynthetic Rate	Phyt, Blue-Greens CR: Initial Condition
Phyt, Blue-Green max: P Half-saturation	Hydrilla: Max Photosynthetic Rate	Phyt, Blue-Greens JC: Initial Condition
Phyt, Blue-Greens DR: P Half-saturation	Phyt, Blue-Green max: Max Photosynthetic Rate	Hydrilla: Initial Condition
Phyt, Blue-Green max: N Half-saturation	Phyt, Blue-Greens DR: Max Photosynthetic Rate	Ostracode: Initial Condition
Phyt, Blue-Greens DR: N Half-saturation	Phyt, Blue-Green max: Photorespiration Coefficient	Daphnia: Initial Condition
Phyt, Blue-Green max: Inorg. C Half-saturation	Phyt, Blue-Greens DR: Photorespiration Coefficient	Gastropod: Initial Condition
Phyt, Blue-Greens DR: Inorg. C Half-saturation	Phyt, Blue-Green max: Mortality Coefficient:	Shrimp: Initial Condition
Phyto, Navicula: Optimal Temperature	Phyt, Blue-Greens DR: Mortality Coefficient:	Phyt, Blue-Green max: Initial Condition
Phyto, Hi-Nut Diatom: Optimal Temperature	Phyt, Blue-Green max: Light Extinction	Phyt, Blue-Greens DR: Initial Condition
Phyto, Green: Optimal Temperature	Phyt, Blue-Greens DR: Light Extinction	Phyt, Blue-Green max Min. Salinity Tolerance, Photo.
Greens: Optimal Temperature	Phyt, Blue-Green max: Sedimentation Rate	Phyt, Blue-Greens DR Min. Salinity Tolerance, Photo.
Phyto, Green, Marine: Optimal Temperature	Phyt, Blue-Greens DR: Sedimentation Rate	Phyt, Blue-Green max Max. Salinity Tolerance, Photo.
Phyt Blue-Green HiLt: Optimal Temperature	Daphnia: Half Sat Feeding	Phyt, Blue-Greens DR Max. Salinity Tolerance, Photo.
Phyt, Bl-Greens, Mar: Optimal Temperature	Gastropod: Half Sat Feeding	Phyt, Blue-Green max Min. Salinity Tolerance, Mortality
Phyt, Blue-Greens CR: Optimal Temperature	Shrimp: Half Sat Feeding	Phyt, Blue-Greens DR Min. Salinity Tolerance, Mortality

Table D.2. Initial condition and input parameters applied in sensitivity analysis.

Tested General Parameters for Sensitivity Analysis	
Site: Mean Depth	Initial Condition: Susp&Diss Detr
Initial Condition: R detr sed	Initial Condition: Water Vol
Initial Condition: L detr sed	Initial Condition: Temp
Initial Condition: L detr diss	Initial Condition: Light
Initial Condition: R detr part	pH: Initial Condition
Initial Condition: L detr part	Remin: Optimum Temperature
Initial Condition: NH_3 & NH_4	Remin: Min. pH for degradation
Initial Condition: NO_3	Remin: Max. pH for degradation
Initial Condition: Tot. Sol. P:	Remin: Detrital Sed. Rate
Initial Condition: CO_2	Remin: Temp. of Obs. KSed
Initial Condition: O_2	Remin: Salinity of Obs. KSed
Initial Condition: TSS	Setup: N to P Ratio

APPENDIX E: Results of Scenario Analysis

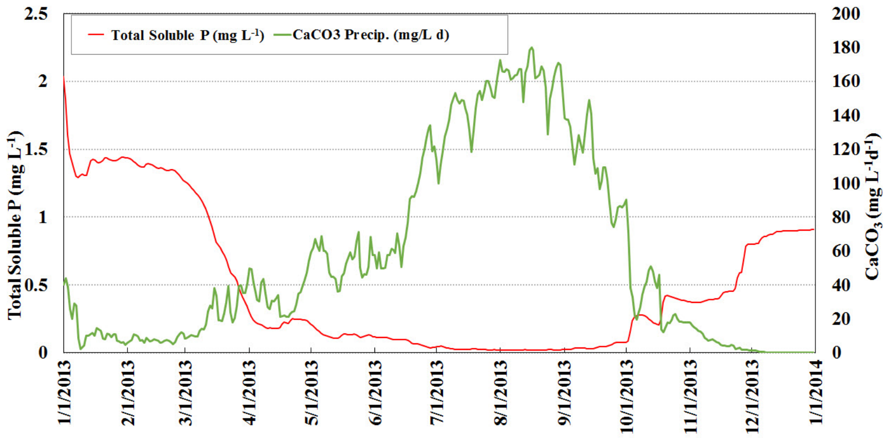


Figure E.1. Simulated $CaCO_3$ vs. total soluble phosphorus in St.2

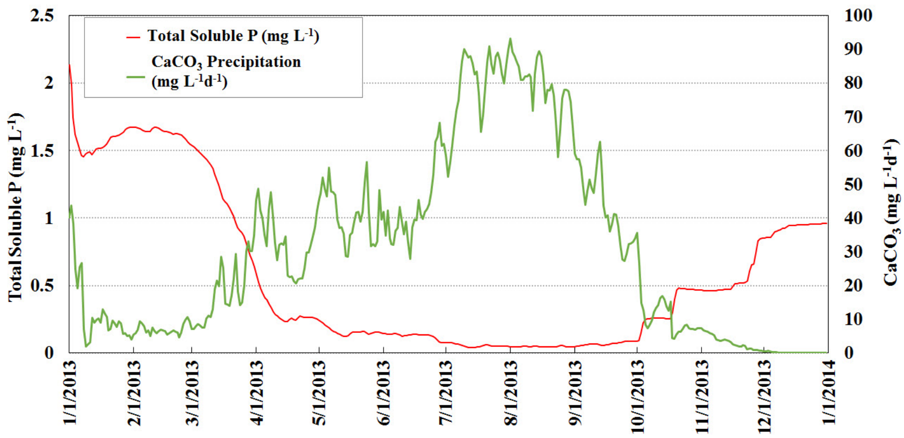


Figure E.2. Simulated $CaCO_3$ vs. total soluble phosphorus in St.3

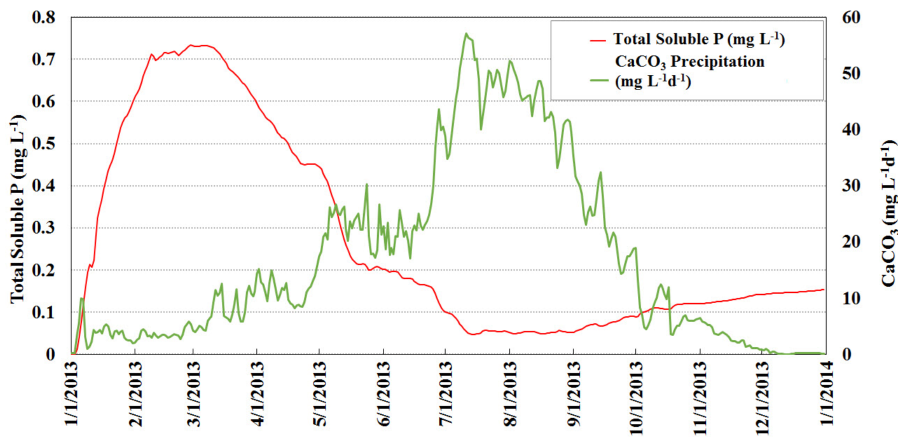


Figure E.3. Simulated $CaCO_3$ vs. total soluble phosphorus in St.4

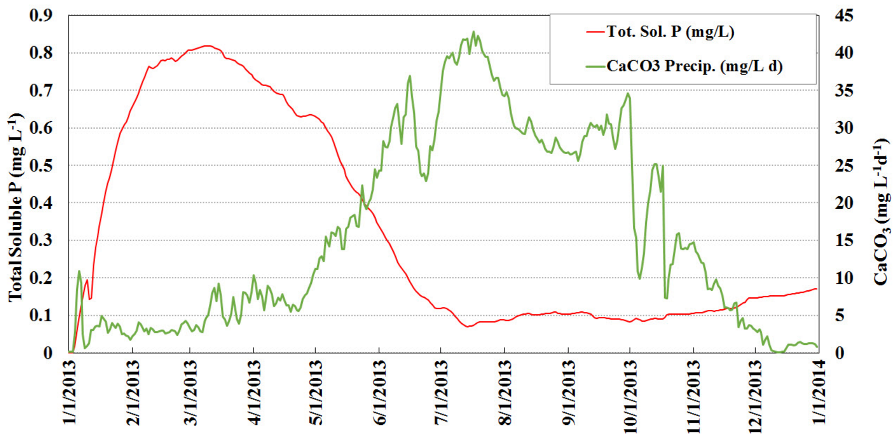


Figure E.4. Simulated $CaCO_3$ vs. total soluble phosphorus in St.5

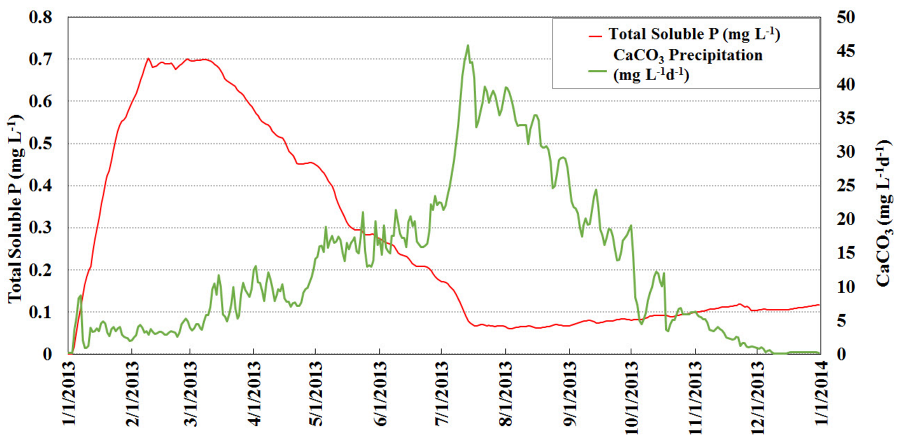


Figure E.5. Simulated $CaCO_3$ vs. total soluble phosphorus in St.6

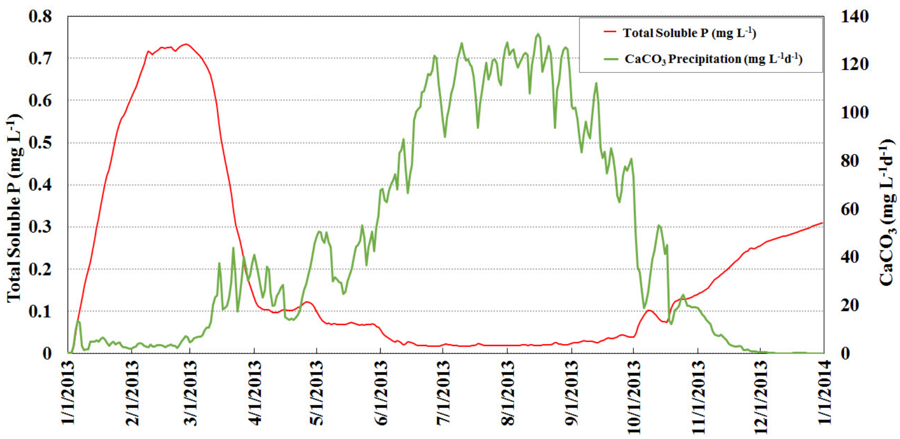


Figure E.6. Simulated $CaCO_3$ vs. total soluble phosphorus in St.7

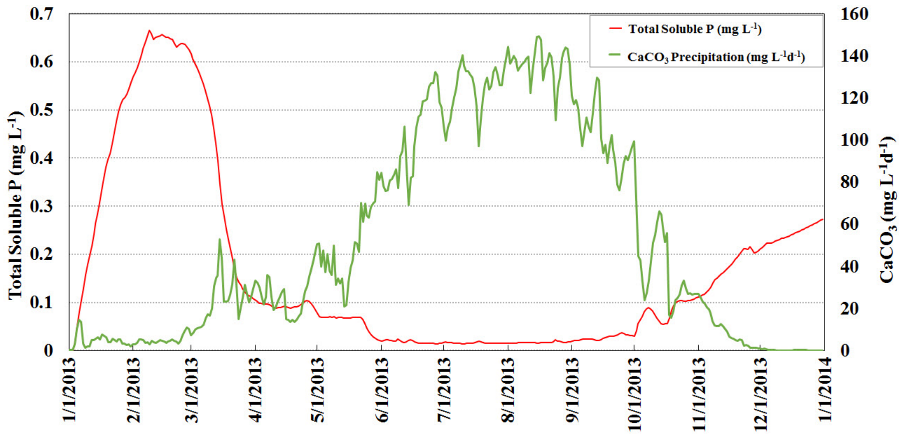


Figure E.7. Simulated $CaCO_3$ vs. total soluble phosphorus in St.8

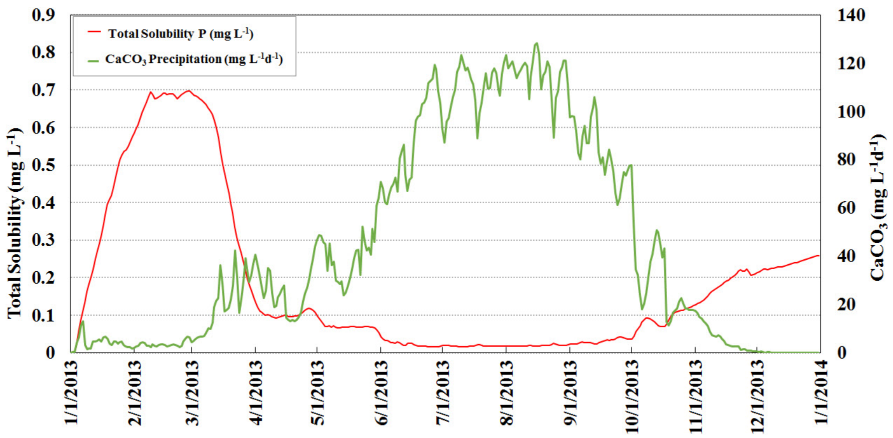


Figure E.8. Simulated $CaCO_3$ vs. total soluble phosphorus in St.9

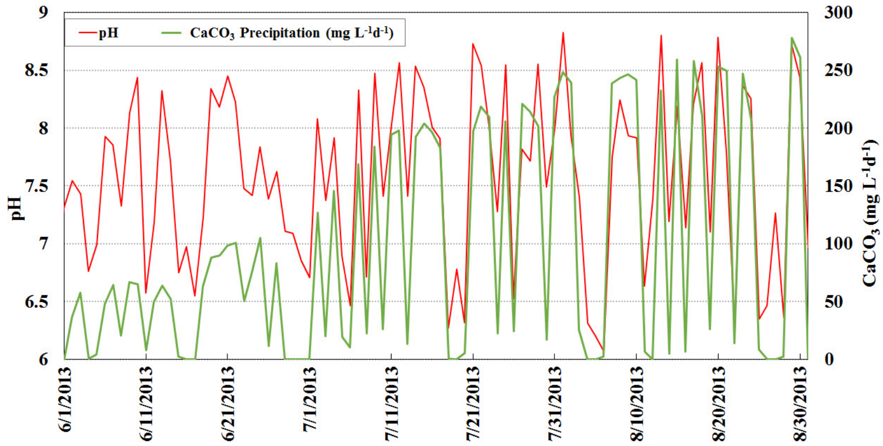


Figure E.9. Modeled $CaCO_3$ vs time series pH in AQUATOX in St.2.

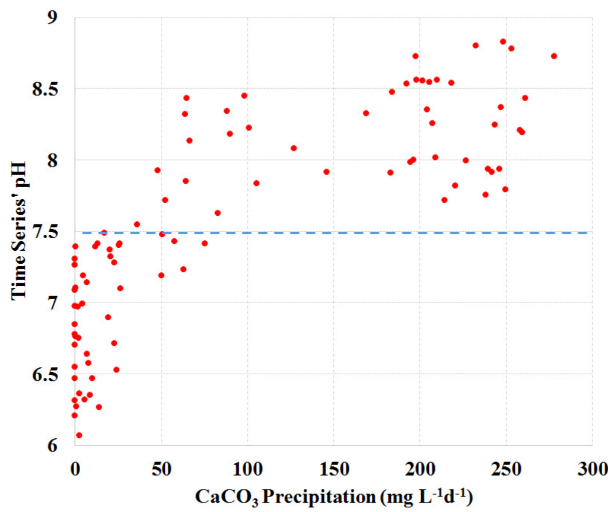


Figure E.10. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.2

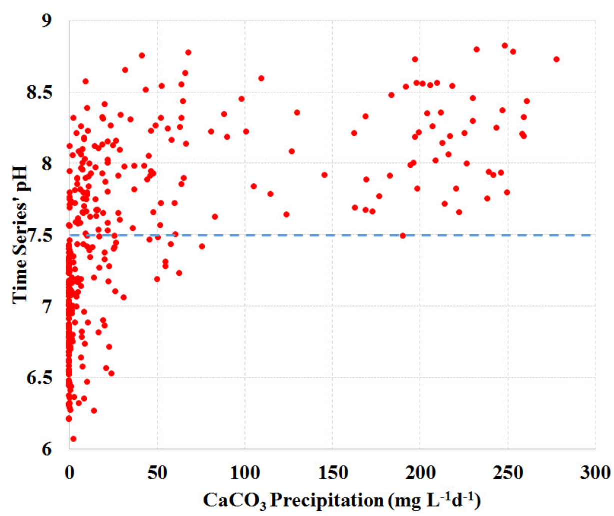


Figure E.11. Modeled $CaCO_3$ vs. time series pH to check threshold in St.2.

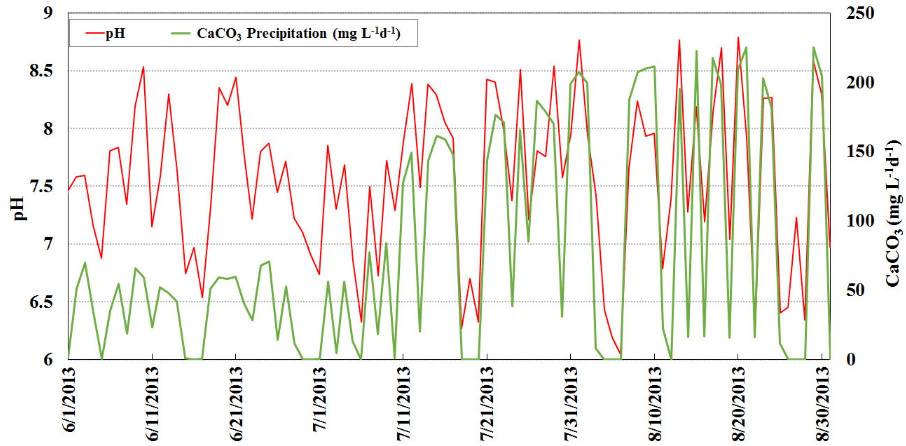


Figure E.12. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.3.

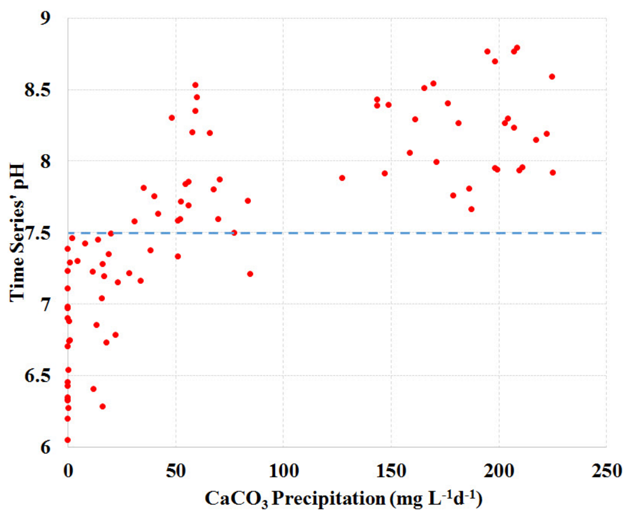


Figure E.13. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.3

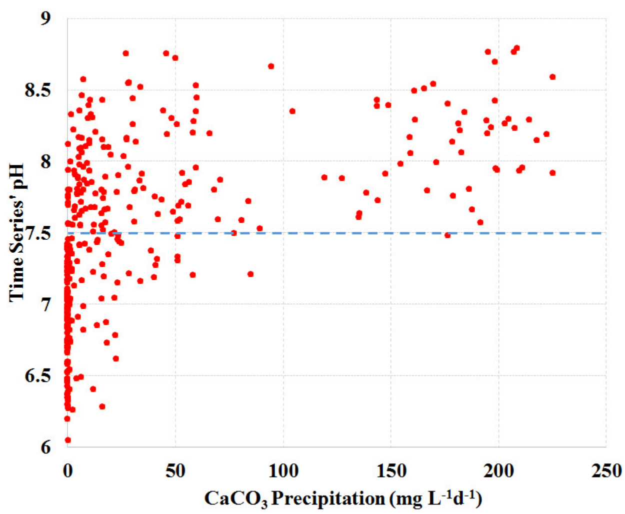


Figure E.14. Modeled $CaCO_3$ vs. time series pH to check threshold in St.3.

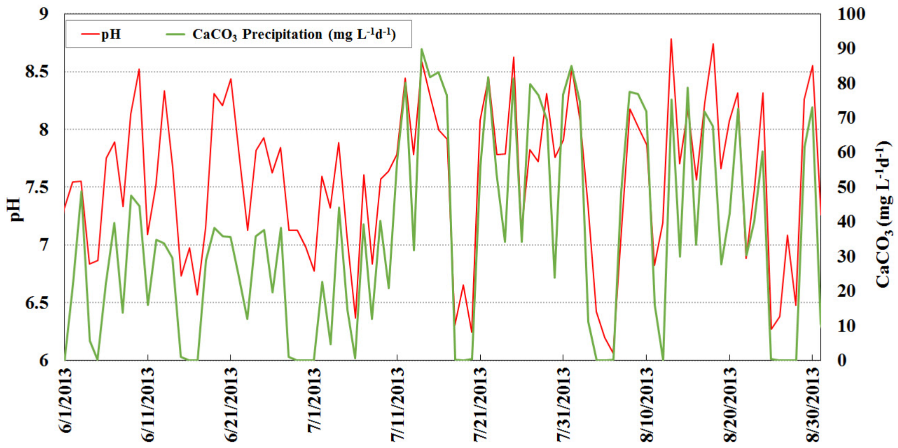


Figure E.15. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.4.

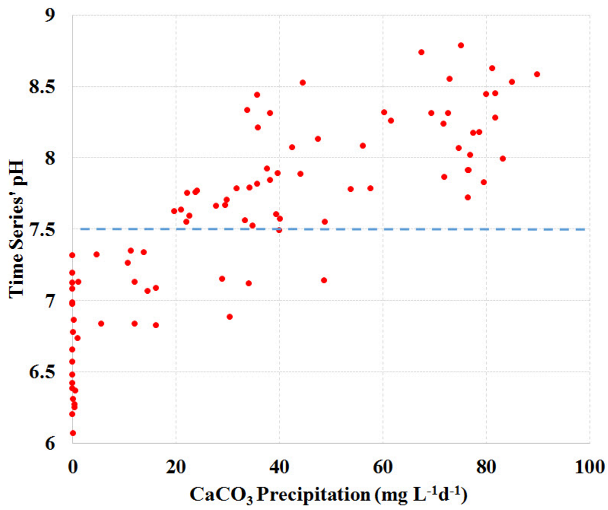


Figure E.16. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.4.

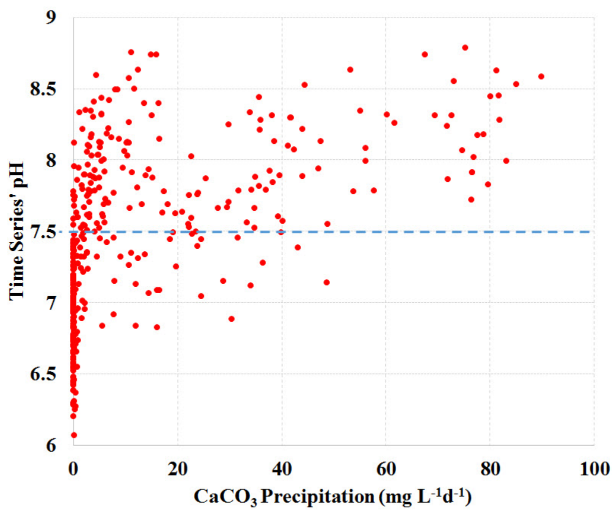


Figure E.17. Modeled $CaCO_3$ vs. time series pH to check threshold in St.4.

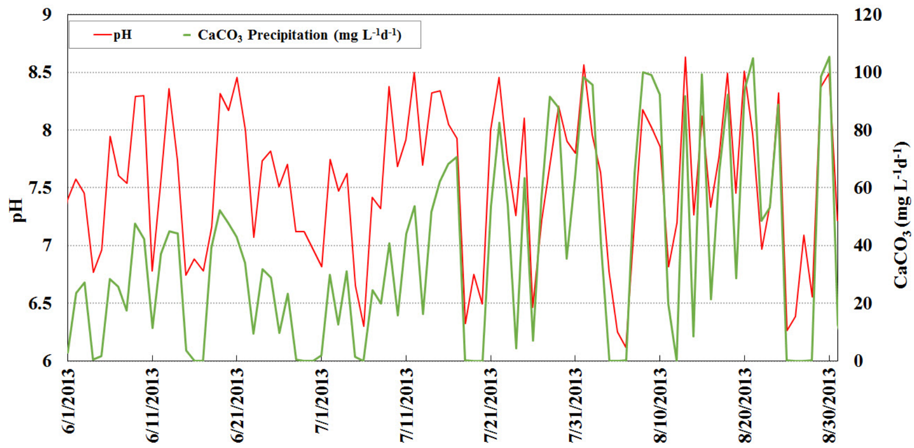


Figure E.18. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.5.

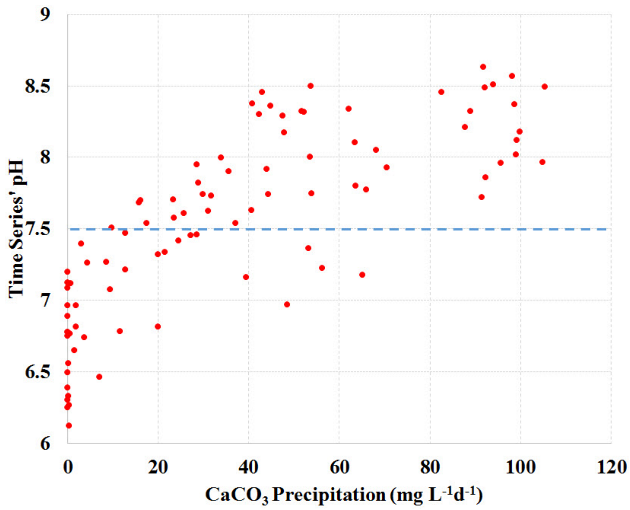


Figure E.19. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.5.

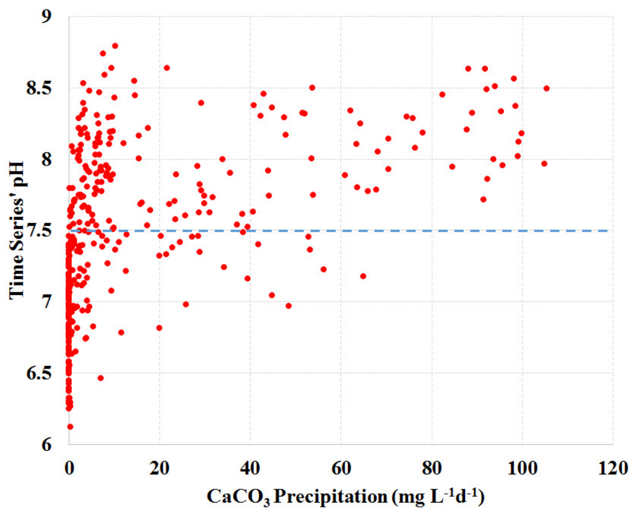


Figure E.20. Modeled $CaCO_3$ vs. time series pH to check threshold in St.5.

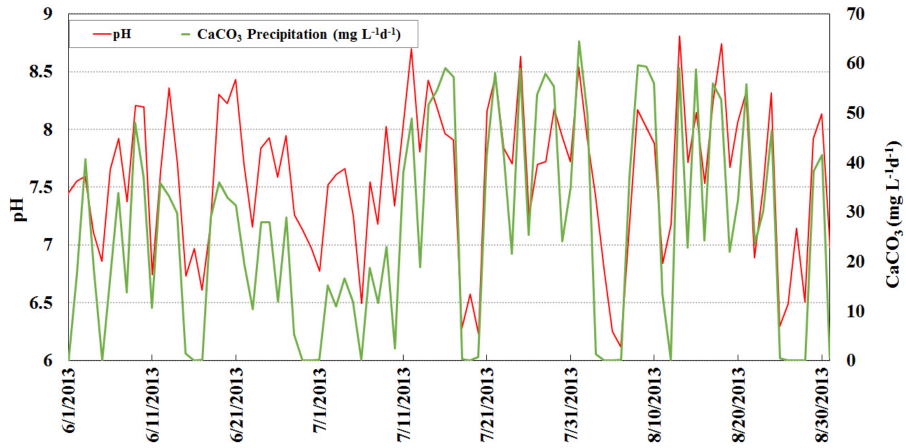


Figure E.21. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.6.

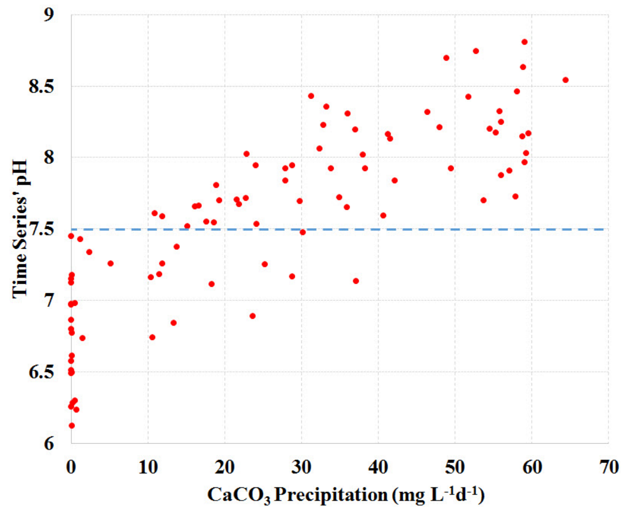


Figure E.22. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.6.

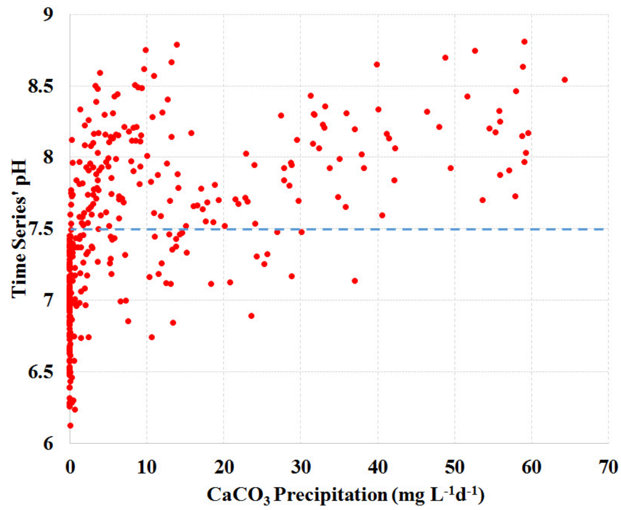


Figure E.23. Modeled $CaCO_3$ vs. time series pH to check threshold in St.6.

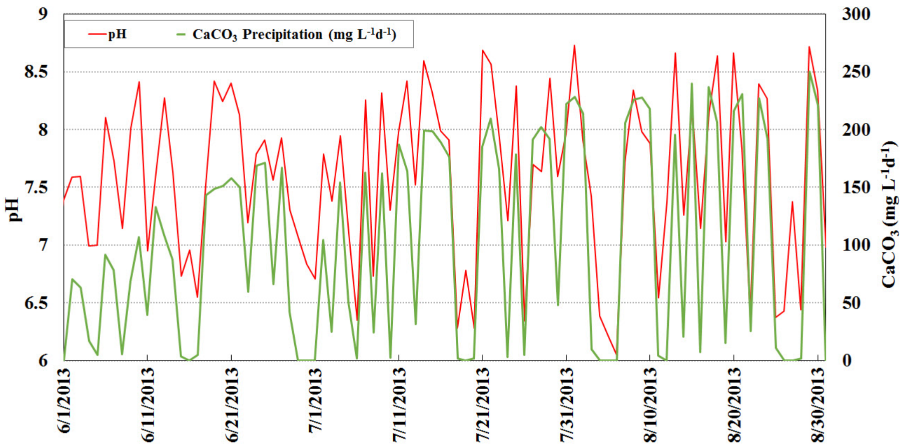


Figure E.24. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.7.

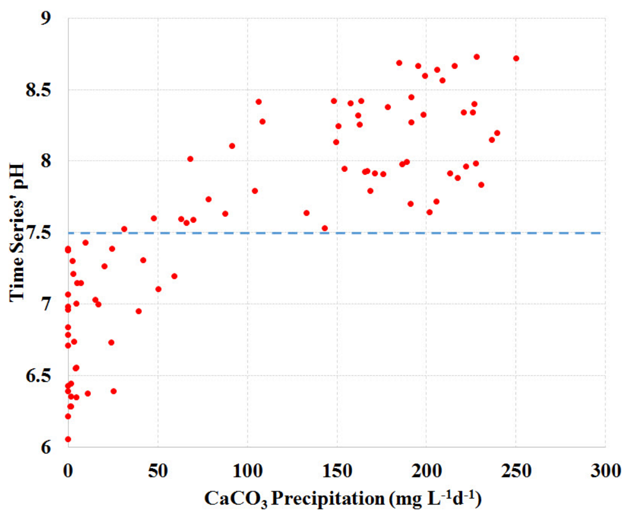


Figure E.25. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.7.

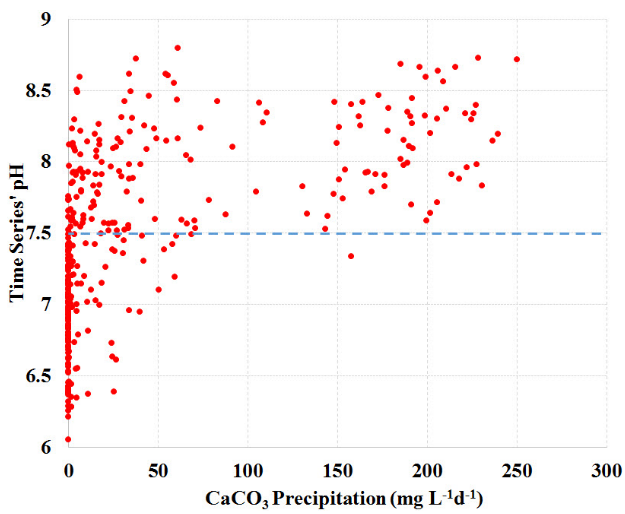


Figure E.26. Modeled $CaCO_3$ vs. time series pH to check threshold in St.7.

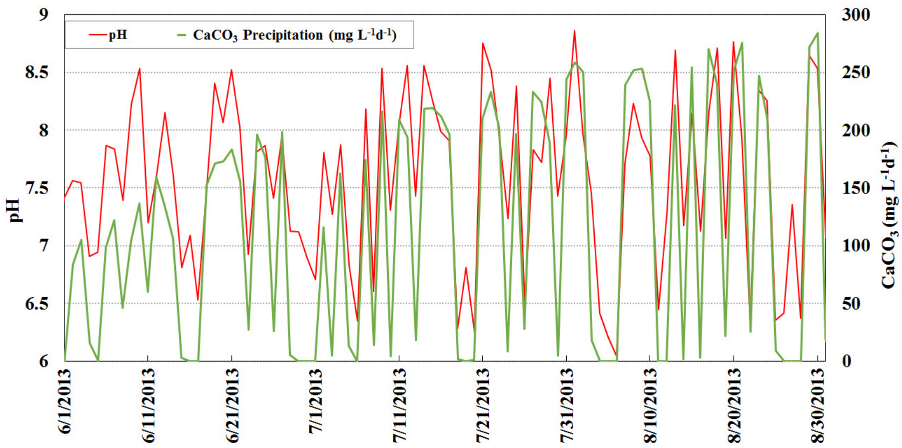


Figure E.27. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.8.

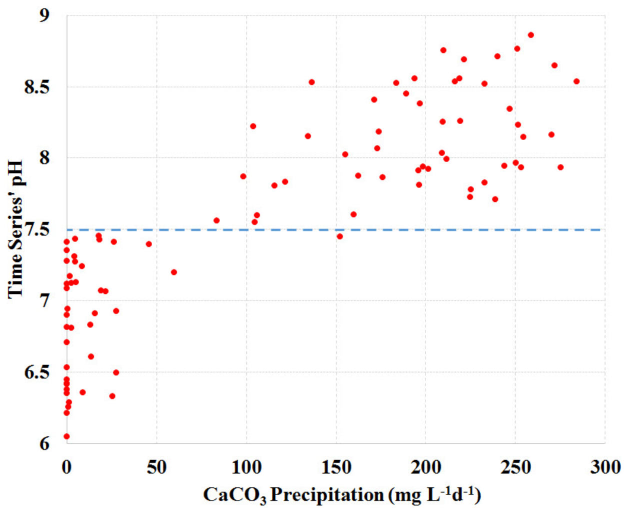


Figure E.28. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.8.

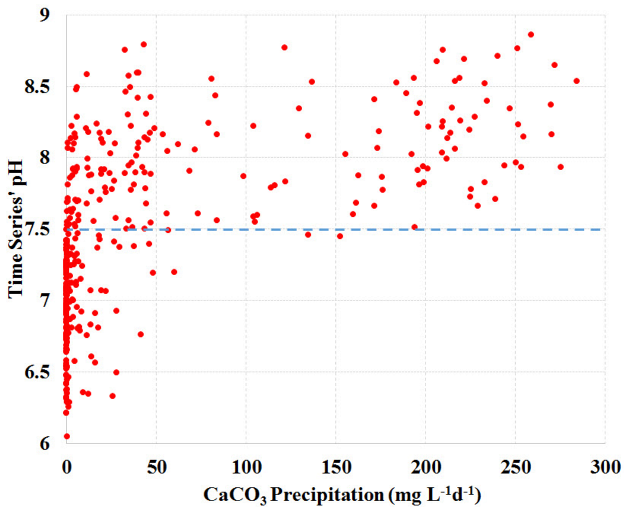


Figure E.29. Modeled $CaCO_3$ vs. time series pH to check threshold in St.8.

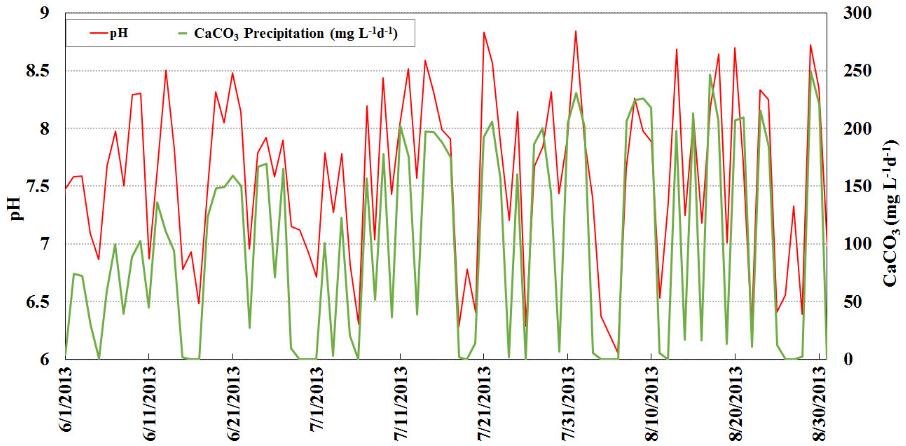


Figure E.30. Modeled $CaCO_3$ vs. time series pH in AQUATOX in St.9.

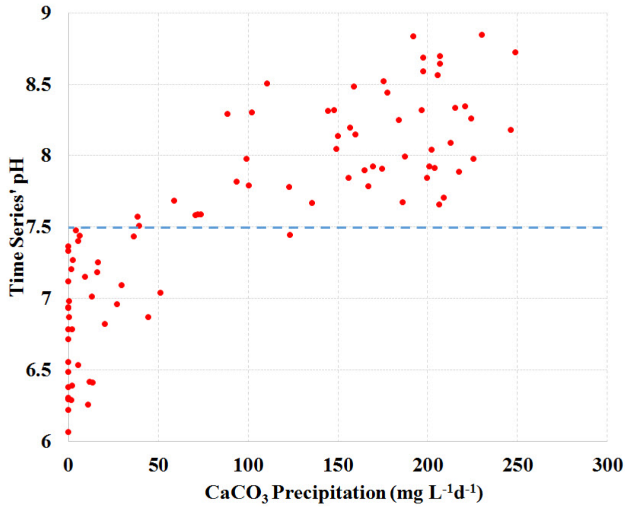


Figure E.31. Modeled $CaCO_3$ vs. time series pH during summer 2013 in St.9.

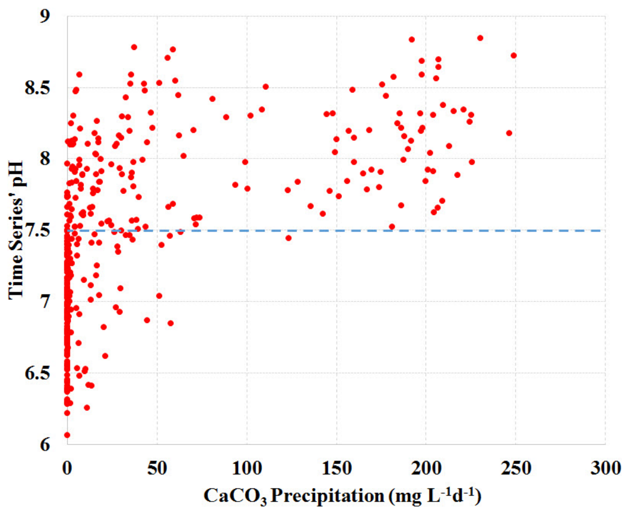


Figure E.32. Modeled $CaCO_3$ vs. time series pH to check threshold in St.9.