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Application and validation of a 3-D calcium, chloride, and sulfate model in Lake Okeechobee

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Abstract

Introduction: The calibration, verification, and validation of calcium (Ca), chloride (Cl), and sulfate (SO_4) module of the Lake Okeechobee Environment Model (LOEM) was completed. The integrated model could simulate Ca, Cl, and SO_4 concentrations and transport due to wind driven currents and waves from 1 Oct 1999 to 30 Sept 2009 in Lake Okeechobee. The enhanced model was also used to estimate lake water quality effects resulting from different management scenarios that include discharges from planned aquifer storage and recovery (ASR) facilities.

Methods: The fate and transport processes of Ca, Cl, and SO₄ are controlled by their reactivity and their hydrodynamic transport. Reactivity includes chemical, biological, and bio-uptake processes (IJRSA 33:2233-2260, 2012). Hydrodynamic transport includes advection of water current, diffusion, and turbulent mixing within the water column. The deposition and resuspension on the water-sediment bed interface is also included. The mathematical equations for describing Ca, Cl, and SO₄ substances, including heavy metal and total organic carbon (TOC), are similar.

Results: Both the statistical results and the time series comparisons indicate that the simulation of Ca, Cl, and SO_4 are generally simulated well by the LOEM. The root mean square error over the variance rage is Cl <18%, Ca <35%, and SO_4 < 19%.

Conclusions: CI, Ca, and SO₄ concentrations in the lake were largely controlled by water temperature and lake evaporation. Inflows to the lake can also have localized effects on chloride variations. Shallow water depth and high evaporation contribute to high CI/Ca/ SO₄ concentration in the lake.

Keywords: Ca; Cl; SO₄ modeling; Lake Okeechobee; Long-term simulation; Environmental modeling

Introduction

Sorption of Ca, Cl, and SO_4 to sediments is one of the most important processes affecting their transport (Ji, 2008). An accurate description of hydrodynamic processes and sediment processes (Vermaat et al. 2000) is essential to describe the deposition and transport of Ca, Cl, and SO_4 .

Ca, Cl, and SO₄ in excess concentrations can cause adverse effects in the chemical or environmental conditions of a water body. Ca, Cl, and SO₄ are associated, at varying degrees, with suspended and deposited particles in the natural systems. Although Ca, Cl, and SO₄ can be transported into the water bodies in dissolved forms, particulate phase of the Ca, Cl, and SO₄ can be adsorbed onto fine sediment particles. Sediments are both a carrier and a possible source of Ca, Cl, and SO₄ in aquatic systems. Sorption of Ca, Cl,

and SO_4 to suspended sediment is one of the important processes affecting their dynamic balance in a water body. Ca, Cl, and SO_4 can be transported through a water body by suspended sediment, deposited to the bottom and/or resuspended from the sediment bed by chemical and hydrodynamic factors.

Due to the large variability of total suspended solid concentrations and the complicated sediment Ca, Cl, and SO_4 interaction processes, the accuracy of modeling results varied significantly in past studies. For example, Thomann et al. (1991) modeled the fate and transport of PCB in the Hudson estuary and reported that the difference between data and modeled results are up to two orders of magnitude. Thomann et al. (1993) modeled cadmium concentrations in the Hudson River and only focused on long-term (e.g. year to year) behaviors. Kuwabara et al. (1999) described the processes affecting the benthic flux of trace minerals into the water column of San Francisco Bay. Ji et al.

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(2002) simulated sediment and minerals in Blackstone River, MA.

Under a storm event, the deposited sediment, along with Ca, Cl, and SO_4 , could be resuspended into the water column. Elimination of the Ca, Cl, and SO_4 would still not remove the source on the sediment bed (Otsubo and Muraoka, 1987; Jin and Ji, 2005; Jin and Sun, 2007). The origins of Ca, Cl, and SO_4 can be divided into point and nonpoint sources (Jin and Ji, 2004). Sometimes Ca, Cl, and SO_4 are localized around the discharging location. In other cases, rivers and streams can carry the sediments and the Ca, Cl, and SO_4 downstream for a long distance. Temporal variability of nonpoint sources is directly related to watershed hydrologic variability. High runoff is usually accompanied by high loads of sediments that may contain Ca, Cl, and SO_4 .

Ca, Cl, and SO_4 in aquatic systems are removed through natural purification processes that dilute, transport, and remove Ca, Cl, and SO_4 . It is essential to understand the kinetics of reactants, the balance, and the transport of Ca, Cl, and SO_4 . It is also necessary to develop a tool to estimate the Ca, Cl, and SO_4 impact on the environment under different scenarios.

The Comprehensive Everglades Restoration Program (CERP) includes an aquifer storage and recovery (ASR) study (CERP 2014). The CERP had originally conceptualized that up to 200 ASR wells could be capable of recharging and recovering up to 1 billion gallons of water per day from and into Lake Okeechobee and its surrounding watershed. Depending on water quality characteristics of the recovered ASR water, there is a potential for various effects on flora and fauna in Lake Okeechobee (Havens and Gawlik, 2005; Havens and James, 1997; 1999; Havens et al., 1995; 1996; 2001. Evaluation of environmental effects in Lake Okeechobee (James et al., 2008; James and Havens, 2005) must be taken into consideration due to the complex nature of the ecosystem, both in terms of its distinct ecological zones (pelagic, benthic, and littoral) and the diverse array of native biota that depends on these water resources (Aldridge et al., 1995; Havens et al., 1999).

Methods

Governing equation

The fate and transport processes of Ca, Cl, and SO₄ are controlled by two factors (Hamrick, 1992; 1994; Hamrick and Wu, 1997): their reactivity and their hydrodynamic transport. Reactivity includes chemical, biological, and bio-uptake processes (Chang et al., 2012). Hydrodynamic transport includes advection of water current, diffusion, and turbulent mixing within the water column (Cerco and Cole, 1994; Cerco et al. 2002). The deposition and resuspension on the water-sediment bed interface is also included. The mathematical equations for describing Ca, Cl, and SO₄ substances, including heavy metal and total organic carbon

(TOC), are similar. The 3-D transport equation for total concentration C (dissolved plus particulate phases) is (Jin et al., 2000; Jin, et al., 2002, Jin et al., 2007):

$$\begin{split} & \partial_{t}(HC) + \partial_{x}(HuC) + \partial_{y}(HvC) + \partial_{z}(wC) - \partial_{z}\left(w_{s}f_{p}C\right) \\ & = \partial_{x}(HK_{H}\partial_{x}C) + \partial_{y}\left(HK_{H}\partial_{y}C\right) + \partial_{z}\left(\frac{K_{v}}{H}\partial_{z}C\right) + R + Q_{c} \end{split} \tag{1}$$

where H = water depth; u, v, w = velocity components, and $w_s =$ sediment settling velocity.

K vertical and horizontal mixing coefficient

R reactivity of chemical and biological processes

 Q_c = external Ca, Cl, and SO₄ sources and sinks, x and

y =cartesian coordinates in the horizontal directions

z = sigma coordinate in the vertical direction.

As discussed before, the concentration of a Ca, Cl, and SO_4 substance is composed of a dissolved component, C_d , and a particulate component, C_p :

$$C = C_{\rm d} + C_{\rm p} \tag{2}$$

The particulate component can be expressed as a product of the Ca, Cl, and SO_4 solid phase concentration, r, and the sediment concentration, S:

$$C_n = r \times S \tag{3}$$

The Ca, Cl, and SO_4 solid phase concentration, r, is expressed in solid dry weight. For a given volume of sampled water, the Ca, Cl, and SO_4 solid phase concentration is defined as follows:

$$r = \frac{\text{Mass of toxics sorbed to sediment in } \mu \text{g or } m \text{g}}{\text{Mass of sediment in } m \text{g or } \text{g}}$$

$$\tag{4}$$

Assuming that equilibrium exists between the dissolved and particulate phases, which are usually valid in Ca, Cl, and SO_4 modeling studies, the partition coefficient, P_7 is defined as follows:

 $P = \frac{\text{Toxics sorbed to sediment (mass of toxics/mass of sediment)}}{\text{Dissolved toxics (mass of toxics/water volume)}}$

$$=\frac{r}{C_d}\tag{5}$$

Equation (5) indicates that the partition coefficient is the ratio of the Ca, Cl, and SO_4 in the particulate phase (sorbed to the sediment) to the Ca, Cl, and SO_4 in the dissolved phase. The partition coefficient is usually expressed as l/g or l/mg. The value of the partition coefficient for a given substance is affected by a number of factors. Some empirical evidence has suggested that the partition coefficient is inversely related to the sediment concentration, while in other cases, the partition coefficients are independent of sediment

concentrations (O'conner 1988; Ji et al., 2002; Ji 2008). In order to accurately calculate the dissolved and particulate phases, measured data should be used to estimate the values of *P*.

From measured data, the partition coefficient can be estimated as follows:

$$P = \frac{C_{\rm p}}{C_{\rm d}} \frac{1}{S} \tag{6}$$

The meaning of *P* becomes apparent in Equation (6); the partition coefficient is the ratio of the particulate concentration to the dissolved concentration per unit concentration of a suspended solid. For example, measured data indicate that metals in the Blackstone River, MA, have partition coefficients varying from 0.1 to 1.0 l/mg (Ji et al., 2002).

The particulate fraction of a Ca, Cl, and SO_4 (f_p) and the dissolved fraction of a Ca, Cl, and SO_4 (f_d) are defined as follows:

$$f_{\rm p} = \frac{C_{\rm p}}{C} = \frac{PS}{\theta + PS} \tag{7}$$

$$f_{\rm d} = \frac{C_{\rm d}}{C} = \frac{\theta}{\theta + PS} = 1 - f_{\rm p} \tag{8}$$

where θ is the porosity (approximately 1 for the water column). The product PS is a dimensionless parameter. The distribution of a Ca, Cl, and SO4ant between dissolved and particulate phases therefore depends on the partition coefficient and the sediment concentration. For a single metal element, there can be a variety of chemical complexes. In most measurements and simulation models, however, all dissolved metal complexes are lumped with the free ion to give the total dissolved metal concentration, and all particulate metal complexes are lumped with all sorbed species to give the total particulate metal concentration (AEE 2012).

Equation (1) includes the sediment settling term, - $\partial_z(w_s f_p C)$. In Equation (1), the total Ca, Cl, and SO4 concentration, C, is modeled, instead of calculating the dissolved and the particulate phases separately. Equations (7) and (8) specify C_d and C_p , after C and the particulate fraction, f_p , are known. It is the particulate fraction (f_p) and the sediment settling velocity (w_s) that link the Ca, Cl, and SO_4 with the suspended sediment concentration. The sediment concentration, as shown in Equation (7), affects the particulate fraction and thus affects the settling and transport of the Ca, Cl, and SO₄ described in Equation (1). In the modeling of heavy metals, the fate and decay mechanisms are usually neglected. In this sense, the modeling of metals is simpler than the modeling of some TOCs.

Vertical boundary conditions for the transport Equation (9) (Ji, 2008) are the following:

$$-\frac{K_V}{H}\partial_z C - w_\$ f_{\rm p} C = F_{\rm o}, \quad \text{at water-sediment bed interface } (z\approx 0)$$

$$-\frac{K_V}{H}\partial_z C - w_\$ f_{\rm p} C = 0, \quad \text{at the water surface } (z=1)$$
 (9)

The net flux of Ca, Cl, and SO_4 from the sediment bed to the water column, F_0 , is given by:

$$F_{o} = \max(J_{o}, 0) \left(\frac{f_{p}^{b}}{S^{b}} + \varepsilon_{r} \frac{\rho_{w}}{\rho_{s}} f_{d}^{b} \right) C^{b}$$

$$+ \min(J_{o}, 0) \left(\frac{f_{p}^{w}}{S^{w}} + \varepsilon_{d} \frac{\rho_{w}}{\rho_{s}} f_{d}^{w} \right) C^{w}$$

$$(10)$$

where the w and b superscripts define water column and sediment bed conditions at the water column-sediment bed interface, respectively, ρ_s is sediment density, ρ_w is water density, and ε_r and ε_d are the sediment bed void ratios under conditions of resuspension and deposition, respectively (Tetra Tech, 1998, 1999, 2000). J_o is the net sediment flux from the bed to the water column. This form of net flux consistently accounts for entrainment and expulsion of water and dissolved Ca, Cl, and SO_4 from and to the bed due to sediment resuspension and deposition (Jin and Wang, 1998; Jin et al., 2000; Jin and Ji, 2001; Jin et al., 2002).

Model setup

Major external forcings that are used to drive the LOEM hydrodynamic and Ca, Cl, and SO4 model include wind velocity, solar radiation, rainfall, lake inflows/outflows, inflow/outflow temperatures, air temperature, relative humidity, and Ca, Cl, and SO₄ concentrations of inflows. Rainfall, air temperature, relative humidity, and solar radiation data were collected every 15 min at four in-lake stations: LZ40, L001, L005, and L006 (Figure 1). Station LZ40 is located near the center of the lake. Hourly meteorological data at LZ40 are used in the LOEM model. Tributaries include 20 inflows and outflows (Jin et al. 2007). Their daily flow rates are measured by the USACE and SFWMD.

The measured data used for model-data comparison are water surface elevation and water temperature. Both the root mean square error (RMS) and the relative error are used to evaluate model performance. The RMS is the average of the squared differences between observed and predicted values. The RMS error is widely used to evaluate model performance. A RMS error of zero is ideal. In the hydrodynamic and water quality modeling (Havens and James, 2005; Havens et al., 2004), it is often useful to express the observation-prediction discrepancies in percentage to measure the model performance. The relative RMS error (RRE) is defined as the ratio of RMS error to the observed change:

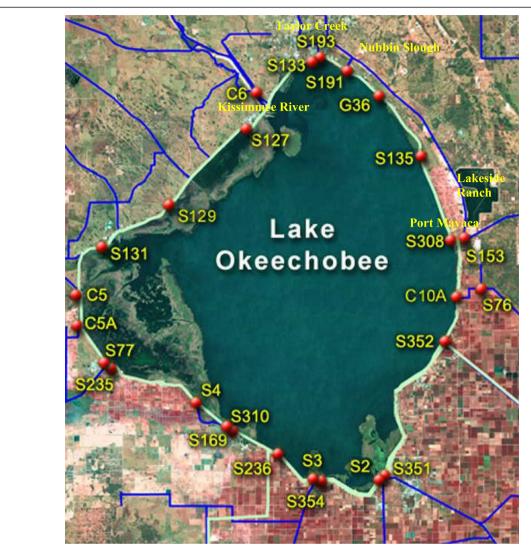


Figure 1 Lake Okeechobee data collection sites.

$$RRE = \frac{RMS \ error}{Observed \ change} \times 100$$

$$= \frac{\sqrt{\frac{1}{N} \sum_{n=1}^{N} (O^{n} - P^{n})^{2}}}{O_{max} - O_{min}} \times 100$$
(11)

where

N = number of observed-predicted pairs

 O^n = the value of the nth observed data

 P^n = the value of the nth predicted data

 O_{max} = maximum value of observations

 O_{\min} = minimum value of observations

 $O_{\rm max}$ - $O_{\rm min}$ is the range of the observation data, and N is the total number of the data points. The relative error provides an overall measurement of the model performance. The consistency between model predictions

and observations is determined qualitatively by comparison plots for the various parameters and by statistical analysis tools. The LOEM model was initialized once and run continuously through the simulation period. Boundary conditions and loads were updated on a daily basis. Integration time-step was 180 s. Output from the model was stored at 1-day increments. It takes about 40 h of CPU time to conduct a 10-year simulation on a Xeon 3.2 GHz PC.

Model results

Hydrodynamics and sediment (total suspended solid)

In the hydrodynamic modeling, the water inflow and outflow are required for the mass balance in the lake. The measured daily flow rate data were used as time series boundary conditions to drive the model. Water evaporation is also an important factor for the water balance in the lake. The LOEM calculates the water evaporation rate based on measured air temperature, relative humidity, air pressure, wind speed, and the modeled water temperature. Figure 2 shows a sample comparison between the modeled and the measured water depth at LZ40. The red line represents the measured data and the black line represents the model result. The relative RMS error is 4.6%. It is evident that the model simulated the lake depth very well.

There are 25 stations in the lake that have regular monitoring of water quality data, including water temperature, TSS, Ca, Cl, and SO_4 (Phlips, et al., 1993; Murphy and Yesaki, 1983; Figure 3). Data from these stations are used for model-data comparison to evaluate the model performance. Both the statistical results (Table 1) and the time series comparisons (Figure 4) indicate that the LOEM model simulated T, TSS, Ca, Cl, and SO_4 very well with mean relative errors of 17.4%, 34.1%, and 18.9% for Cl, Ca, and SO_4 , respectively.

Results and discussion

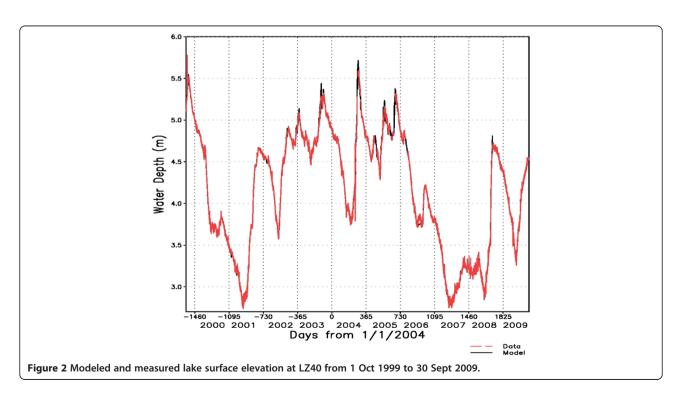
Sediment transport, deposition, and resuspension processes are important to the understanding of eutrophication; Ca, Cl, and SO_4 transport; sediment bed erosion; siltation; and waste disposal. To understand sediment transport processes, it is critical to have good knowledge of the hydrodynamic processes.

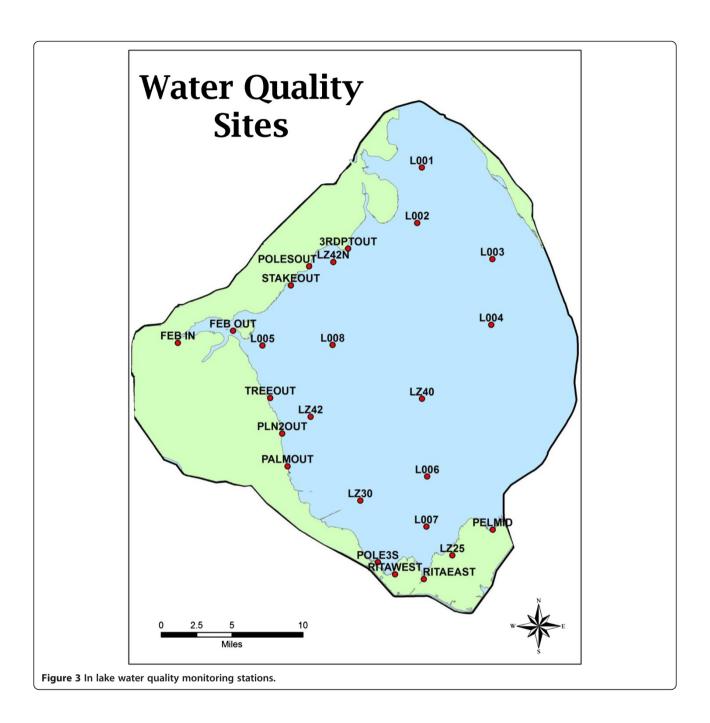
Total suspended solids (TSS) influence density, light climate, and nutrient availability in lakes. Solids also may carry other pollutants into water bodies. Nutrients and Ca, Cl, and SO₄ chemicals may attach to sediment particles on land and can be attached to the particles into surface waters where the pollutants may settle with the sediment or detach and become soluble in the water column. Increased TSS reduces light penetration in the water column affecting water temperature, which in turn affects biological and chemical reaction rates. Light climate in the water column also directly affects algae and vegetation growth. Nutrient concentrations also are affected by TSS through sorption and settling (Jin and Sun 2007).

The LOEM sediment module has been calibrated, verified, and validated using the sediment data in 2000, 2001, and 2002, respectively (Jin and Ji, 2004, 2005; Ji and Jin, 2006). The model parameter values and model sensitivity tests are also discussed in these studies. The modeled sediment concentrations from 1 Oct 1999 to 30 Sept 2009 for 3,653 days at the 25 monitoring stations were reasonable (Tables 1, 2, 3, 4, 5). For example, the relative error of modeled sediment concentration (TSS) at L006 is 14.5% (Table 2).

Modeling results

As an example, the model-data comparison of Ca, Cl, SO_4 , and TSS at LZ40 from 1 Oct 1999 to 30 Sept 2009 for 3,653 days is presented (Figure 4); the green lines are the results from the benchmark run, which is used for model calibration and verification. The panels of Ca, Cl,





and SO_4 indicate that these three constituents are generally simulated well by the LOEM.

Both the statistical results and the time series comparisons indicate that the LOEM simulated T (10%), TSS, Ca, Cl, and SO₄ well with the RMSE (T) <10%; RMSE (TSS) <27%; RMSE (Cl) <18%; RMSE (Ca) <35%; and RMSE (SO₄) <19% (Tables 2, 3, 4, 5). As an example, Figure 4 gives the model-data comparison of Ca, Cl, SO₄, and TSS at LZ40 from 1 Oct 1999 to 30 Sept 2009 for 3,653 days. In Figure 4, the green lines are the results from the benchmark run, which is the benchmark case

for model calibration and verification. The panels of Ca, Cl, and ${\rm SO_4}$ in Figure 4 indicate that these three constituents are generally simulated well by the LOEM.

The lake experienced a prolonged drought in 2007 and 2008. During these two years, water levels were quite low (Figure 2). High concentrations of Ca, Cl, and SO_4 were observed, and the increased concentration was accurately captured by the LOEM (Figure 4). Model sensitivity analysis indicates that Cl (along with Ca and SO_4) concentrations in the lake were largely controlled by water temperature and lake evaporation. Higher

Table 1 Error analysis of observed and modeled water temperature at the 25 stations from 1999 to 2009

Station number	Station name	Number of data points	Observed mean (°C)	Modeled mean (°C)	RMS error (°C)	Observed change (°C)	RER (%)
1	L006	74	24.7	25.3	1.7	20.7	8.6
2	L001	70	24.9	25.5	1.9	18.7	10.5
3	LZ40	72	24.4	24.9	1.7	17.6	9.9
4	L005	72	25.4	25.5	1.7	17.2	10.1
5	3RDPTOUT	60	25.2	24.5	1.8	17.5	10.7
6	KBAROUT	43	24.2	24.0	2.1	19.3	11.0
7	L002	68	25.3	25.1	1.6	17.9	9.3
8	L003	73	24.4	24.8	1.6	19.2	8.5
9	L004	71	24.2	24.8	2.0	18.4	11.3
10	L007	63	24.6	24.3	1.4	20.7	7.1
11	L008	72	24.9	25.1	1.6	16.4	9.9
12	LZ2	63	25.4	25.3	2.3	18.8	12.2
13	LZ25	55	24.8	23.9	1.8	18.8	9.6
14	LZ30	73	24.9	24.9	1.5	19.3	7.9
15	LZ42	72	24.8	25.1	1.5	19.7	7.8
16	LZ42N	65	25.3	24.6	1.7	18.0	9.4
17	PALMOUT	61	24.9	24.7	1.6	16.9	9.7
18	PELMID	61	24.9	24.1	1.5	19.1	8.1
19	PLN2OUT	70	25.2	25.3	1.7	17.5	9.9
20	POLE3S	65	25.2	24.6	1.5	17.7	8.8
21	POLESOUT	61	25.6	24.7	2.0	18.9	10.7
22	RITAEAST	69	25.6	25.0	1.7	18.2	9.3
23	RITAWEST	65	25.3	24.6	1.6	18.6	8.9
24	STAKEOUT	62	25.4	24.6	1.8	18.3	10.0
25	TREEOUT	63	24.6	24.6	1.4	20.5	7.0
	Total Mean		25.0	24.8	1.7	18.5	9.5

chloride concentrations in the summer and fall seasons were largely due to stronger water evaporation from the lake surface. Inflows to the lake can also have localized effects on chloride variations. Shallow water depth and high evaporation contribute to high Cl concentration in the lake (Figures 5, 6, 7).

In the fall of 2002, large fluctuations of Ca, Cl, and SO_4 were observed in the measured data showed at L004. The concentrations were lowered dramatically due to large inflows into the lake (Figure 4). The large amount of inflow diluted the in-lake concentration of Ca, Cl, and SO_4 .

Water depth (EL) and measured chloride concentration (Cl) at LZ40 from 1 Oct 1999 to 30 Sept 2009 are inversely related (Figure 5). The chloride values shown in the figure are calculated in this way: $\text{Cl}' = \text{Cl} \times 0.05 + 1.5$. This is done in order to allow Cl' and the water depth to be shown together. For example, a Cl value of 80 mg/l

leads to a Cl' value of 5.5. Because the variation of chloride concentration lags behind the water depth variation, the time of chloride concentration is subtracted by 51 days to better align the spikes of Cl and EL. This time, shift moves the spikes of the Cl leftward by 51 days.

When the lake is shallow and its volume is small, the Cl concentration is high. When the lake water depth is large, the Cl concentration is low. Thus, the lake volume is a critical factor to the Cl concentration.

The factor that dominates lake water budget is water evaporation. About 70% of the lake's water leaves the lake by evaporation (James and McCormick 2012). High evaporation reduces lake volume (water depth) and increases the Cl concentration. This mechanism explains why low lake volume leads to high Cl concentration.

Because of the dilution and concentration effects of water volume on ions in Lake Okeechobee, water depth and Cl, Ca, and SO₄ concentrations are strongly

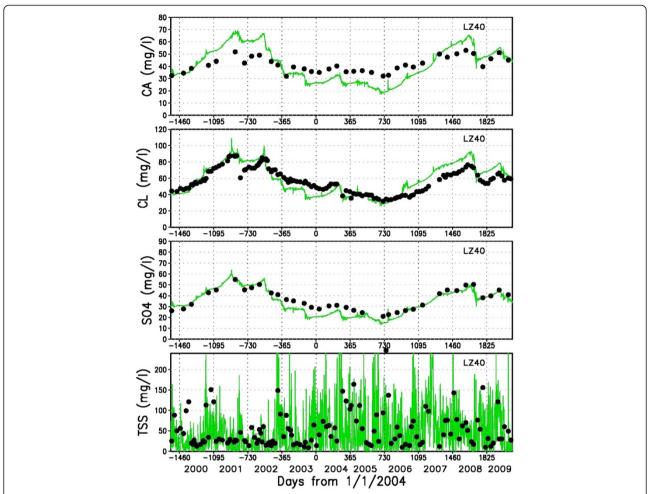


Figure 4 Model-data comparisons. Model-data comparisons of Ca, Cl, SO4, and TSS at LZ40 from 1 Oct 1999 to 30 Sept 2009. The black dots are measured data. The green lines are modeled results from the benchmark run.

correlated (Table 6: LZ40). When the Cl concentration lags behind the water depth by 51 days, the correlation coefficient is a maximum of -0.70, clearly indicating a strong correlational lag between the two. When there is no time lagging between the two, the correlation coefficient is only -0.60. This finding is also consistent with the one concluded in Figures 6 and 7.

Similar strong correlations between the water depth and the Ca and SO_4 concentrations exist (Table 6). This suggests that variations of Ca and SO_4 concentrations are also strongly controlled by lake evaporation. When the Ca concentration lags behind the water depth by 51 days; the correlation coefficient is a maximum of -0.83. There are also negative correlations between water depth and Cl and water depth and SO_4 concentrations. This suggests that variations of Cl and SO_4 concentrations are also strongly controlled by lake evaporation.

To study the long-term variations of chloride, calcium, and sulfate concentrations in the lake, more than 30 years of measured data (SFWMD, 2011) was analyzed. Figure 8 gives the measured chloride concentration at L002 for 37 years, from 1972 to 2009. Figure 8 shows that in the past 4 decades, the lake's Cl concentration generally exhibited a downward trend. The mean values were reduced by about one half, from approximately 90 mg/l in the early 1970s to approximately 40 mg/l in the 2000s. Figure 8 gives the measured sulfate concentration at L002 for 35 years, from 1974 to 2009. It shows a downward trend similar to the one in Figure 8 for Cl. The mean SO₄ values were reduced by about half, from around 55 mg/l to about 22 mg/l, in the past 4 decades. The measured calcium concentration at L002 for 37 years (1992 to 2009) is also presented in Figure 8. Ca's mean values were also reduced in the past 4 decades (James and McCormick, 2012).

Table 2 Error analysis of observed and modeled total suspended solid (TSS) at the 25 stations from 1999 to 2009

Station number	Station name	Number of data points	Observed mean (mg/l)	Modeled mean (mg/l)	RMS error (mg/l)	Observed change (mg/l)	RER (%)
1	L006	74	30.8	15.5	33.0	226.5	14.5
2	L001	71	27.1	10.2	31.7	154.0	20.6
3	LZ40	73	44.9	14.1	42.9	142.0	30.2
4	L005	73	18.2	15.1	20.4	67.2	30.4
5	3RDPTOUT	62	18.5	21.9	34.3	68.0	50.5
6	KBAROUT	44	12.4	47.9	71.2	100.6	70.8
7	L002	69	26.3	17.5	28.9	152.0	19.0
8	L003	73	38.3	15.7	33.9	177.3	19.1
9	L004	70	40.2	15.4	52.2	391.4	13.3
10	L007	63	21.6	20.9	22.6	173.2	13.0
11	L008	73	40.6	18.4	41.2	207.4	19.8
12	LZ2	63	15.2	9.5	24.6	147.5	16.7
13	LZ25	55	19.8	11.6	23.7	123.7	19.1
14	LZ30	73	22.2	19.4	23.6	170.5	13.8
15	LZ42	73	34.1	19.4	46.2	336.5	13.7
16	LZ42N	66	17.8	18.8	24.4	65.0	37.5
17	PALMOUT	61	16.9	16.7	21.0	93.8	22.4
18	PELMID	61	12.8	10.0	13.7	64.5	21.3
19	PLN2OUT	71	15.8	17.4	23.3	82.8	28.1
20	POLE3S	66	13.9	13.7	18.0	84.5	21.3
21	POLESOUT	62	14.6	17.7	28.3	46.0	61.7
22	RITAEAST	69	13.7	5.9	18.3	96.5	18.9
23	RITAWEST	65	15.0	14.2	19.7	122.5	16.1
24	STAKEOUT	64	15.9	18.3	26.2	63.2	41.5
25	TREEOUT	64	18.3	18.7	26.6	95.0	28.0
	Total Mean		22.6	17.0	30.0	138.0	26.5

Aquifer storage and recovery application

Aquifer storage and recovery is a water management technology/strategy that uses groundwater aquifers to store wet season surface water and then recovers this water later to augment dry season surface water supplies. The Comprehensive Everglades Restoration Plan (USACE 1999) included the hypothetical construction of up to 330 ASR storage wells throughout south Florida, of which 200 were conceptualized for the Lake Okeechobee basin (USACE, 1999). Each well was estimated to have a capacity of 5 million gallons per day. The existing LOEM model was modified to incorporate SO₄ predictions specifically to evaluate potential impacts from SO₄ loads resulting from a wide scale implementation of ASR technology within the Lake Okeechobee basin. Sulfate water column concentrations play a role in regulating the rate at which mercury becomes methylated in the environment. The results of this LOEM modeling effort will be incorporated into downstream models to predict changes to sulfate concentrations and mercury methylation potential downstream of Lake Okeechobee in the Everglades protection area.

After the LOEM was calibrated and verified for the period of 10 years (3,653 days), from 1 Oct 1999 to 30 Sept 2009 (Ji and Jin 2006; Jin et al. 2007), the model was applied for the same time period to evaluate a variety of hypothetical ASR management scenarios. The proposed ASR inflows/outflows enter or exit the lake at five locations: Kissimmee River, Nubbin Slough, Taylor Creek, Lakeside Ranch, and Port Mayaca (Figure 1). The following ASR scenarios were evaluated: 200 ASR wells in operation from 1 Oct 1999 to 30 Sept 2009, 100 ASR wells in operation from 1 Oct 999 to 30 Sept 2009, and 50 ASR wells in operation from 1 Oct 1999 to 30 Sept 2009. Recent groundwater modeling conducted

Table 3 Error analysis of observed and modeled chloride (CI) at the 25 stations from 1999 to 2009

Station number	Station name	Number of data points	Observed mean (mg/l)	Modeled mean (mg/l)	RMS error (mg/l)	Observed change (mg/l)	RER (%)
1	L006	74	62.8	65.2	9.0	51.5	17.4
2	L001	71	56.7	63.6	15.6	92.7	16.8
3	LZ40	73	62.8	64.8	8.7	49.1	17.8
4	L005	73	60.7	64.1	10.8	63.9	16.9
5	3RDPTOUT	62	56.2	57.5	12.4	67.3	18.4
6	KBAROUT	44	47.8	38.8	19.2	79.4	24.2
7	L002	69	61.0	63.4	10.4	66.0	15.8
8	L003	73	61.5	64.4	9.9	70.7	14.0
9	L004	70	63.1	65.1	8.0	56.5	14.2
10	L007	63	59.3	61.6	14.9	92.7	16.1
11	L008	73	62.8	65.0	8.4	53.6	15.8
12	LZ2	63	51.2	65.7	23.9	82.3	29.1
13	LZ25	55	63.3	62.9	10.9	42.9	25.5
14	LZ30	73	63.0	64.7	8.5	59.9	14.2
15	LZ42	73	62.8	64.8	8.5	56.2	15.2
16	LZ42N	66	56.5	60.7	12.3	75.7	16.2
17	PALMOUT	61	59.5	59.9	9.3	49.4	18.8
18	PELMID	61	65.3	64.3	9.7	69.8	13.9
19	PLN2OUT	71	62.3	64.3	10.6	65.2	16.2
20	POLE3S	66	64.4	63.2	10.6	54.1	19.7
21	POLESOUT	62	55.2	57.7	13.0	73.0	17.9
22	RITAEAST	69	67.5	66.8	10.8	62.3	17.3
23	RITAWEST	65	66.1	63.1	9.9	59.6	16.7
24	STAKEOUT	64	55.8	59.6	12.3	76.7	16.0
25	TREEOUT	64	60.4	60.3	11.6	118.0	9.8
	Total Mean		60.3	62.1	11.6	67.5	17.4

by the USACE has indicated that the 50-well scenario may be most realistic (in terms of effects on the regional hydrogeology, groundwater movement, and impacts to existing users); however, for purposes viewing the comparative LOEM model results, the 200, 100 and 50-well scenarios will be presented herein.

The time series of ASR inflow/outflow rate boundary conditions under these three scenarios were created based on the lake stage and lake management rules and general ASR operating scheme as outlined in the Comprehensive Everglades Restoration Plan study (USACE 1999).

Water quality boundary conditions for ASR discharges are also required for the LOEM model. The concentration of chemical constituents in the discharged ASR water depends upon the volume of surface water stored in the aquifer, the percent of stored water recovered, and the quality of the groundwater in the storage zone and

the surface water. During recovery, the quality of water recovered from an ASR well changes as more of the stored water is extracted. Essentially, during extended recovery, the water quality begins to reflect less of the original stored surface water and more like the ambient concentrations of constituents in the Floridan aquifer. The most conservative assumption from the perspective of predicting worse case impacts from ASR discharges is to assume that the quality of the recovered water will always be equivalent to an original groundwater quality within the Floridan aquifer, since for critical water quality constituents such as CL and SO₄, the ambient groundwater concentrations significantly exceed the ambient surface water concentrations. For this reason, the water quality boundary conditions for ASR discharges were conservatively estimated as equal to ambient groundwater concentrations for the upper Floridian aquifer in the vicinity of the five ASR locations. It should be noted that during actual

Table 4 Error analysis of observed and modeled calcium (Ca) at the 25 stations from 1999 to 2009

Station number	Station name	Number of data points	Observed mean (mg/l)	Modeled mean (mg/l)	RMS error (mg/l)	Observed change (mg/l)	RER (%)
1	L006	74	41.5	39.8	8.7	30.7	28.4
2	L001	71	34.2	38.5	12.8	40.5	31.6
3	LZ40	73	40.0	43.7	8.6	19.8	43.6
4	L005	73	38.5	39.3	7.6	41.6	18.3
5	3RDPTOUT	62	36.1	37.6	10.3	28.1	36.6
6	KBAROUT	44	30.6	29.4	11.4	27.5	41.5
7	L002	69	37.0	38.5	8.8	25.7	34.2
8	L003	73	39.3	39.2	9.7	41.7	23.3
9	L004	70	41.2	39.5	9.8	44.9	21.8
10	L007	63	40.6	38.8	8.2	19.5	42.4
11	L008	73	41.1	39.6	8.9	36.3	24.7
12	LZ2	63	30.8	42.8	17.2	24.3	71.1
13	LZ25	55	42.8	43.7	8.5	20.6	41.6
14	LZ30	73	41.5	43.4	8.6	23.8	36.2
15	LZ42	73	40.7	39.9	9.1	41.2	22.1
16	LZ42N	66	35.0	37.5	9.3	33.8	27.6
17	PALMOUT	61	38.0	42.0	10.2	25.3	40.4
18	PELMID	61	42.3	43.7	7.9	19.9	39.9
19	PLN2OUT	71	39.5	43.3	10.6	52.0	20.5
20	POLE3S	66	42.9	42.8	9.0	31.3	28.8
21	POLESOUT	62	36.8	39.2	9.6	21.0	45.8
22	RITAEAST	69	42.9	46.4	10.0	41.3	24.2
23	RITAWEST	65	41.2	43.4	9.6	33.0	29.3
24	STAKEOUT	64	36.7	40.2	9.8	25.6	38.3
25	TREEOUT	64	37.6	41.5	9.6	24.6	39.0
	Total Mean		38.8	40.6	9.8	30.9	34.1

operation, recovery from the ASR wells can be terminated when pre-determined constituent concentrations are observed, based on ecological or lake level considerations. For instance, ASR recovery can be terminated when the recovered water exhibits a chloride concentration of 100 mg/L, or the sulfate concentration reaches 60 mg/L.

After 10 years of ASR operation, the LOEM predicts no significant increase in Ca concentration (Figure 9). This is primarily because the ASR inflow Ca concentrations are similar to ambient concentrations in the lake, so that the added ASR inflow load does not change the Ca concentration significantly. In contrast, Cl and SO_4 results for the ASR scenarios are significantly different from the base condition. With 200 ASR wells, the LOEM projects Cl concentrations more than 100 mg/l higher than the base condition in the summer of 2008 dry period (increase from 50 mg/L

to a range of 150 to 200 mg/L; Figure 9). For the same scenario, the LOEM predicted increases of SO₄ concentrations to about 50 mg/l more than the base condition in the summer of 2008. The primary reason for the Cl and SO₄ increases are that the assumed concentrations of SO₄ and Cl from the ASR wells are directly from the Floridan aquifer and therefore are much higher than the in the Lake, and water levels are lower for these drought periods. In contrast to these increases, after 10 years of ASR operation, the Lake TSS concentration has not changed significantly (Figure 9). This is because ASR discharges have very limited impact on the lake TSS concentration. Figure 9 gives model-data comparisons of Ca, Cl, SO₄, and TSS at LZ40. The black dots are measured data. The green lines are model results from the benchmark/historical run, which are also presented in Figure 9. The blue lines are the results of the 200 ASR well scenarios,

Table 5 Error analysis of observed and modeled sulfate (SO4) at the 25 stations from 1999 to 2009

Station number	Station name	Number of data points	Observed mean (mg/l)	Modeled mean (mg/l)	RMS error (mg/l)	Observed change (mg/l)	RER (%)
1	L006	74	38.0	35.7	4.0	27.2	14.8
2	L001	71	31.9	35.4	10.5	44.7	23.6
3	LZ40	73	37.2	35.6	3.8	28.7	13.5
4	L005	73	34.6	35.2	4.2	40.6	10.4
5	3RDPTOUT	62	32.0	30.2	9.1	39.3	23.1
6	KBAROUT	44	34.5	35.1	6.5	38.2	17.2
7	L002	69	35.6	34.9	4.4	28.4	15.4
8	L003	73	36.8	34.9	5.5	31.8	17.5
9	L004	70	36.8	34.3	4.8	23.8	20.2
10	L007	63	36.5	35.7	4.0	29.1	13.9
11	L008	73	26.0	34.3	12.7	31.3	40.5
12	LZ2	63	41.7	36.2	8.7	31.7	27.4
13	LZ25	55	38.0	35.5	5.2	36.7	14.1
14	LZ30	73	37.2	35.8	4.7	33.8	13.9
15	LZ42	73	32.6	33.2	6.9	39.5	17.6
16	LZ42N	66	35.3	34.1	4.6	26.4	17.5
17	PALMOUT	61	39.8	36.8	4.9	24.2	20.4
18	PELMID	61	36.1	35.3	4.6	37.1	12.4
19	PLN2OUT	71	40.6	35.2	9.7	41.8	23.2
20	POLE3S	66	33.2	31.5	7.6	37.2	20.6
21	POLESOUT	62	45.7	38.5	18.6	111.0	16.8
22	RITAEAST	69	39.6	35.8	5.6	25.1	22.2
23	RITAWEST	65	32.1	32.4	6.9	38.5	17.9
24	STAKEOUT	64	34.0	33.7	4.2	22.5	18.9
25	TREEOUT	64	38.0	35.7	4.0	27.2	14.8
	Total Mean		36.1	34.8	6.7	36.2	18.9

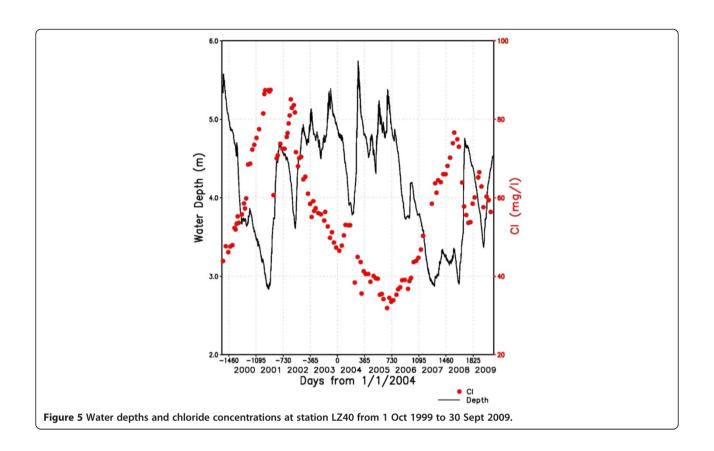
the cyan lines are the results of the 100 ASR well scenarios, and the red lines are the results of the 50 ASR well scenario.

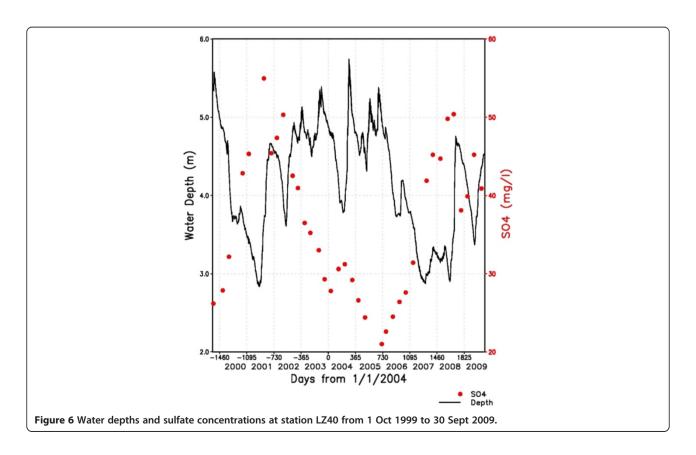
Modeled water depth at a nearshore location PALM-OUT (location shown in Figure 3) is typically between 1 and 2 m (Figure 10a). Modeled and lake averaged submerged aquatic vegetation (SAV) biomass (Jin and Ji 2013) indicate good correspondence (Figure 10b) On an aerial basis, the model and observed lake SAV distribution are very similar (Figure 10c).

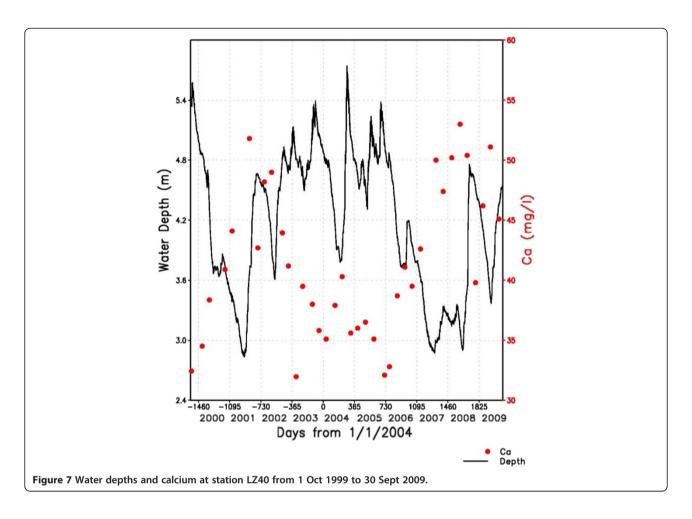
During the summer of 2001, the 200 ASR well scenario increased water depth by about 0.3 m. The increase resulted in an increased SAV biomass (Figure 10b) and SAV area (Figure 10c). The total area of SAV was 39,531 acres on 4 July 2001, an increase of 60% from the base condition. Similar patterns are observed in the summers of 2007 and 2008. The 100 ASR and 50 ASR well scenarios produced similar patterns but

with smaller variation amplitudes (data not shown). Therefore, it is believed that ASR wells can help SAV growth by maintaining higher water depth, when the lake stage is too low for optimum SAV growth (Jin et al., 2011). The beneficial effects of increased SAV biomass resulting from ASR operation needs to be strongly considered when evaluating any perceived negative water quality effects of the recovered water.

The water quality modeling results from the three hypothetical ASR management scenarios are also examined and compared with the historical observed results. Over the period of 10 years (1 Oct 1999 to 30 Sept 2009) at LZ40, the total number of measured data varied from 127 for TP to 36 for SO4 (Table 7). For the purpose of model-data comparison and for consistency, the modeled results at the corresponding data measurement time were also used in calculating the modeled means. The average simulated values for







DO, Chl-a, TP, SRP, TKN, NOx, TSS, and T do not vary dramatically under the four different scenarios. Statistical analysis and graphical comparison at the other stations lead to similar conclusions (data not shown). Based on these results and given the assumptions inherent in the LOEM model, these water quality parameters should not be altered significantly by the ASR operation. Two factors contributed to this result:

 Concentrations of the water quality variables from the ASR inflows for nutrients and TSS concentrations are similar to ambient lake concentrations. ASR inflows do not appear to add significant amount of nutrient loadings

Table 6 Correlation coefficients between water depth and Cl, Ca, and SO4 at LZ40 from 1999 to 2009

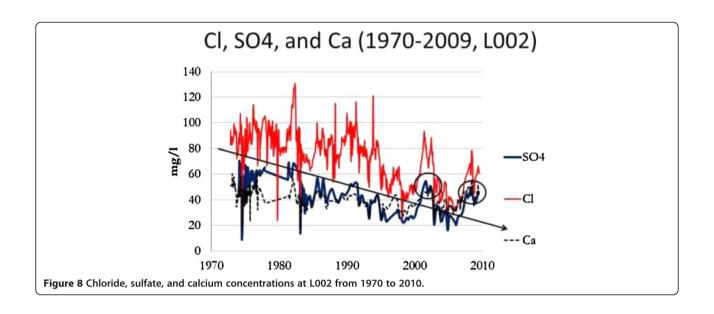
Variable	Lagging days	Correlation coefficient
Cl	51	-0.7/-0.57
Ca	51	-0.72/-0.83
SO4	51	-0.7/-0.66

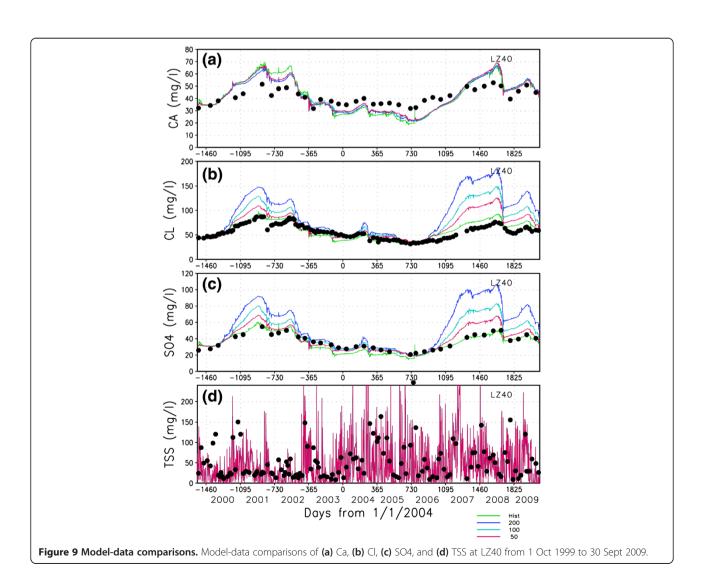
- into the lake. Recent data from the ASR pilot project at the Kissimmee River has indicated that significant reduction in *P* concentrations may take place via storage in the Floridan aquifer (USACE and SFWMD, 2013).
- 2. The lake has strong internal cycling of nutrients between the water column and the sediment bed. The nutrients recycled from the bed into the lake water column can often be larger than the amount from the external inflows and become the most important source of nutrient, especially during major hurricane seasons.

The results at station PALMOUT, which is located at the outside edge of the littoral zone, are similar to those at LZ40 (Tables 7 and 8).

A mass balance of CL for the lake under the 200 ASR well scenario was developed (Table 9) which included the following:

Cl mass at the beginning of the calendar year (CL_{ti}).
 For example, at the beginning of 2000, the lake had a total of 2,343,994 metric tons (t) of Cl.





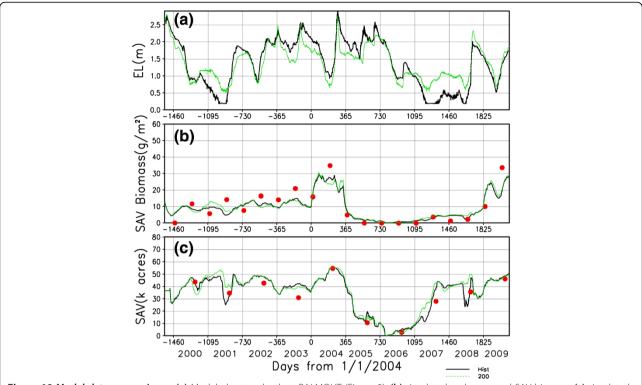


Figure 10 Model-data comparisons. (a) Modeled water depth at PALMOUT (Figure 3), (b) simulated and measured SAV biomass, (c) simulated and measured SAV area. The period is from 1 Oct 1999 to 30 Sept 2009 for 10 years.

- Net load (I_t O_t) of Cl input (I_t) minus output (O_t) added through regular the inflows/outflows and ASR wells during the year. For example, during 2000, 171,057 t of Cl was added into the lake.
- The end of year result based on input/output calculation was $C_{\rm te} = C_{\rm ti} + I_{\rm t} O_{\rm t}$, which is the total estimated Cl mass at the end of year based on the conservation of mass. For example, in 2000, the estimated Cl mass at the end of the year should be 405,051 t.
- C_{tem} Model calculated Cl mass at the end of the year. For example, at the end of 2000, the lake had a total of 411,722 t CL_{ti}. For example, at the beginning of 2000, the lake had a total of 2,343,994 t of Cl.
- Net load $(I_t O_t)$ of Cl input (I_t) minus output (O_t) added through regular the inflows/outflows and ASR wells during the year. For example, during 2000, 171,057 t of Cl was added into the lake.
- The end of year result based on input/output calculation was $C_{te} = C_{ti} + I_t O_t$ of Cl.
- Bias of the LOEM calculation is calculated as bias = $C_{\rm tem} C_{\rm te}/C_{\rm tem} \times 100$. For example, the LOEM has a bias of 2.8% in Cl calculation for the 2000 measured data.

Conclusions

This manuscript presents the results from the LOEM simulation from 1 Oct 1999 to 30 Sept 2009 with 3,653 days of ASR operations (Jin and Ji 2004, 2005; Jin et al. 2011). The refined, calibrated, and verified LOEM was applied to study water quality and SAV growth (Scheffer, 1989; Scheffer et al. 1994) under three different ASR management scenarios 50, 100, and 200 ASR wells. Major conclusions from this study include the following:

- During the 10 years of hypothetical ASR operations (1999 to 2009), and assuming that the water recovered from the ASR wells is identical to the ambient water in the Floridan aquifer, the Lake Ca concentration is not altered significantly compared to the base condition. Also, Cl concentration can increase by more than 100 mg/l in the summer; and SO₄ concentration can increase by approximately 50 mg/l in the summer.
- The variations of the concentrations of Ca, Cl, and SO₄ in the lake from ASR return flows are strongly affected by the ASR well return flow rate and lake volume. Lower water depth and smaller lake volume generally lead to higher

Table 7 Mean values of observed data and modeled results at LZ40 from 1999 to 2009

Parameter name	Number of data points	Observed mean	Modeled mean (history)	Modeled mean (200-well)	Modeled mean (100-well)	Modeled mean (50-well)
DO (mg/l)	121	8.081	8.663	8.665	8.658	8.649
Chl-a (µg/l)	122	16.179	17.321	19.231	19.004	18.894
TP (mg/l)	127	0.188	0.130	0.129	0.131	0.131
SRP (mg/l)	126	0.056	0.070	0.065	0.065	0.065
TKN (mg/l)	127	1.486	1.298	1.419	1.432	1.438
NO2 + NO3 (mg/l)	117	0.292	0.047	0.038	0.042	0.044
TSS (mg/l)	127	51.324	39.315	29.302	31.012	32.694
T (°C)	126	24.263	24.592	24.650	24.655	24.640
CI (mg/l)	125	57.577	59.104	88.888	76.528	68.430
Ca (mg/l)	37	41.322	40.951	40.994	41.668	41.859
SO4 (mg/l)	36	36.369	33.880	52.482	44.249	39.265

The scenarios include historic run, 200-well ASR, 100-well ASR, and 50-well ASR.

Table 8 Mean values of observed data and modeled results at PALMOUT from 1999 to 2009

Parameter name	Number of data points	Observed mean	Modeled mean (hist.)	Modeled mean (200-well)	Modeled mean (100-well)	Modeled mean (50-well)
DO (mg/l)	107	8.387	8.353	8.575	8.524	8.465
Chl-a (µg/l)	105	21.432	16.775	18.703	18.828	18.919
TP (mg/l)	109	0.101	0.123	0.128	0.129	0.128
SRP (mg/l)	83	0.037	0.064	0.063	0.063	0.063
TKN (mg/l)	110	1.347	1.236	1.417	1.426	1.427
NO2 + NO3 (mg/l)	58	0.287	0.014	0.014	0.015	0.014
TSS (mg/l)	95	23.094	22.454	19.795	21.628	21.224
T (°C)	109	24.643	24.692	24.735	24.589	24.576
CI (mg/l)	110	55.238	56.811	81.165	70.751	64.072
Ca (mg/l)	31	37.445	38.473	37.984	38.695	38.688
SO4 (mg/l)	31	32.586	31.971	43.493	38.077	34.957

The scenarios include historic run, 200-well ASR, 100-well ASR, and 50-well ASR.

Table 9 Mass balance analysis for CI under the condition of 200 ASR wells (all units except bias are in metric tons)

	•			•	•
Year	Initial lake mass C _{ti}	Net load I _t – O _t	Final lake mass C _{te}	LOEM end mass C _{tem}	Percent bias
2000	0.233994E + 6	0.171057E + 6	0.405051E + 6	0.411722E + 6	2.8
2001	0.411722E + 6	0.132059E + 6	0.543781E + 6	0.543693E + 6	-0.02
2002	0.543693E + 6	-0.116765E + 6	0.426928E + 6	0.410099E + 6	-3.1
2003	0.410099E + 6	-0.123002E + 6	0.287097E + 6	0.272714E + 6	-3.5
2004	0.272714E + 6	0.215026E + 11	0.294217E + 6	0.290415E + 6	-1.4
2005	0.290415E+6	-0.428658E + 11	0.247549E + 6	0.239610E + 6	-2.7
2006	0.239610E + 6	0.114265E + 6	0.353875E + 6	0.357096E + 6	1.3
2007	0.357096E + 6	0.276897E + 6	0.633993E + 6	0.642641E+6	2.4
2008	0.642641E+6	-0.432782E + 11	0.599363E + 6	0.584568E + 6	-2.3
2009	0.584568E + 6	-0.383576E + 11	0.546210E + 6	0.536096E + 6	-1.7

- concentrations. The correlation coefficients between the water depth and the Cl, Ca, and SO_4 concentrations can be up to -0.57, -0.83, and -0.66, respectively. The variations of these concentrations lag the variations of the water depth by about 51 days.
- 3. The ASR wells provide water to the lake when the lake stage is low relative to the desired lake management and help maintain higher lake stage (more than 1 foot during dry season). The elevated water depth during the dry season is beneficial to SAV growth in the lake (Jin and Ji 2013).
- 4. The model results indicate that eutrophication-related parameters, such as Chl-a, TP, TKN, and DO will not be significantly affected by ASR operations, although recent findings indicate that ASR may reduce TP via bio-geochemical reactions that take place during storage within the aquifer.
- 5. The model simulation of ASR well scenarios show increased Cl and SO₄ concentrations in the lake, due to the higher Cl and SO₄ concentrations from the ASR wells. During the dry years, as observed in 2007 and 2008, the 200-well ASR scenario can increase the Cl concentrations from around 50 mg/l to a range of 150 to 200 mg/l. This is largely due to the assumed high ASR inflow concentration and significantly reduced lake volume during these drought periods. Recent groundwater modeling by the CERP ASR team has indicated that the 200-well ASR scenario is not achievable due to unacceptable hydrogeologic impacts, and that a 50-well ASR scenario is probably more realistic for future evaluations. An SAV module update for chloride effects on SAV growth might be needed in the future.

The possible interactions between Ca, Cl, and SO_4 with water quality variables are not included in the LOEM. Additional studies are needed to better understand the linkages among these variables.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

KRJ carried out the data analysis and drafted the manuscript. MDS prepared ASR scenarios and boundary condition inputs. ZGJ performed the model runs and statistical analysis. All authors read and approved the final manuscript.

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