Modelling Acidity Propagation in a Coastal Zone with Acid Sulphate Soils

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EXTENDED ABSTRACT

Acidic pollution caused by runoff from acid sulphate soils (ASS) can be detrimental to agriculture, aquaculture and the environment. It is difficult to quantify the amount of acid loading, how it transports and pollutes the surrounding canal networks. In a coastal zone, these phenomena are further complicated by the tidal effect on the water dynamics and the chemical reactions between saline and acid water. This paper presents a model that can simulate the propagation of acid pollution in a canal network in a coastal zone with ASS. The model was developed and coupled with a previously validated hydraulic and salinity model VRSAP (Vietnam River System And Plains).

Rain water dissolves the acid material exposed on canal embankment during excavation and dredging and drains it into canal as runoff and bypass flow. The amount of acid loading from each linear meter of canal embankment was quantified by a multiple site experiment carried out in 2005 and used as input of the model. It was calculated as function of soil types, the age (years after last dredging) of canal embankment and rainfall. The interaction between the acidic water and brackish water in the receiving canal is simulated by empirical functions. These functions, established by laboratory titration experiments, describe the change in pH of the receiving water at different salinity levels as it received increasing amount of titrant at different pH. The salinity and acidity at nodes in the canal network were calculated at each time step by solving the solute transport equation system in the VRSAP. The effect of saline water on acidity reduction is incorporated into calculations for water acidity in segments and at nodes.

Evaluation of model performance in calibration and validation steps include both statistical criteria and graphical displays for comparison. The statistical indicators of model performance are the square of linear regression coefficient (r^2) and the model efficiency (EF) (Andersen et al., 2001). For graphical comparison, the graphs showing simulated versus measured monthly pH averages of all monitored sites and monthly pH at 3 specific sites in the study area are used. The model was calibrated with pH and salinity measured monthly from December to April or bi-monthly from May to July at 63 monitored sites in 2003. During calibration, the dispersion (DISP), length of runoff path on canal embankment (ROC) and seepage across embankment (SP) were parameterized to obtain the best fit between the simulated and measured values in 2003. Subsequently, the model was validated with the measured pH in 2005.

Generally, the VRSAP with new acidity module can simulate the average pH reasonably well as reflected through the comparison of the model outputs with measured data in 2003 for calibration and in 2005 for validation. pH increased in the dry season, reached a maximum on 15 March, and gradually decreased in later months when the rainy season started. The model also describes the effect of saline water in reducing acidity in the canal network. The simulation of the acid propagation in the study area could result in evaluating the relative effectiveness of different strategies for acid load reduction in the coastal zones with ASS.

1. INTRODUCTION

Besides salt water intrusion, acid water from acid sulphate soils is a common problem in the coastal zones and limits agriculture and aquaculture. Studying the tidal buffering to neutralize the acidity in a single canal, Indraratna et al. (2002) showed that some alkalinity forms in sea water such as bicarbonate (HCO_3^-) and carbonate CO_3^{2-} could have the acid neutralizing capacity. It is possible to determine the result pH due to this capacity if mixing with acidic water occurs.

Many models were developed to simulate water quality parameters, for example the ISIS Quality (Halcrow and HR Wallingford, 1999), a fully featured water quality simulator that includes advection, diffusion of conservative, decaying pollutants, water temperature, sediment transport, interaction with quality determinants with sediment, phytoplankton and pH. However, these models do not work or apply for acid propagation in a complex canal network under tidal effect and salinity intrusion in the coastal zones.

Truong et al. (1995) presented a model for acid water transport in canal network in the Plain of Reeds of the Mekong delta. The model was based on empirical regression between pH and other toxic elements that assumed "jurbanite" equilibrium existing in the non saline, acid water environment. But the simulated pH did not agree with the measured values. The authors attributed the failure of the model to the incorrect reflection of chemical processes of acidity in the field draining into the canals.

In summary, it is difficult to quantify the amount of acid loading and how it transports and pollutes the surrounding canal networks. Furthermore, in the coastal delta the hydrodynamic model is an important platform for modelling of water quality. This study introduces a new acidity module coupled with hydrodynamic and salinity modules of an existing model to simulate the propagation of acidity in the canal network of the Camau peninsula, Mekong Delta, Vietnam.

2. ACID POLLUTION IN THE STUDY AREA

The study area is the Camau peninsula located in the southern part of the Mekong delta, Vietnam with a total area of 949,599 ha (Fig. 1). Acid sulphate soil (ASS) concentrated in the western part occupies 50% of its total area (SNIAPP, 2002). Main production systems in the area are rice in the eastern part, shrimp in the western part and shrimp-rice in the intermediate zone (Hoanh et al., 2001). There are two distinctive seasons: the rainy season from May to November with roughly 90% of the annual rainfall of 1,800 mm and the dry season from mid-November to April. The hydrological regime is governed by the flow of the Mekong river and the tide from the East and West Seas. A dense manmade canal network in the area acts as a transportation route, irrigation and drainage conduit. Since the canals are heavily silted, dredging is implemented every 5 to 10 years.

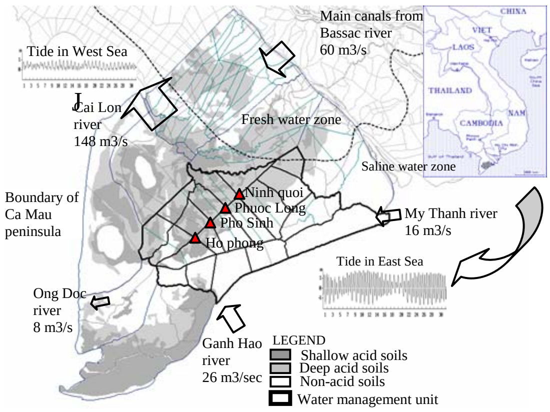


Figure 1: The Camau peninsula, Mekong Delta and its main river systems.

During excavation and dredging of canals in the ASS areas, the sulphuric and pyretic materials from subsoils were put and exposed on the canal embankments resulting in the oxidation of the pyrite (Cook et al., 2000) and forming acidity which is brought up to the soil surface by capillary rise during the dry season. Rain water dissolves the acid material from canal embankment and drains it into canal as runoff and bypass flow. Every year the acidic load propagating in the canal network results in acid pollution over a large area. During the early part of the rainy season, water pH in the canals could drop from about 7 to below 4 in a large area (the estimated pollution area in 2004 is 42,000 ha).

3. METHODOLOGY

3.1 Incorporation of acidity module into hydraulic-salinity model VRSAP

The VRSAP (Vietnam River Systems and Plains) with its hydraulics and salinity modules was calibrated and validated with data in 1996 and 1998 in the Camau peninsula (Hoanh et al., 2001). VRSAP is a numerical model using Saint-Venant equations for solving complex flow and mass transport problems in a complex network of interconnecting open channels. It is based on the continuity and the momentum equations for each canal segment:

$$\frac{\partial Q}{\partial x}+B_c\frac{\partial z}{\partial t}=q \qquad (1)$$

$$K = AC\sqrt{R} \qquad\qquad C=\frac{1}{n}R^{1/6}$$

$$\frac{\partial z}{\partial x}+\frac{\alpha_0}{g}\frac{\partial(Q/A)}{\partial t}+\frac{\alpha}{g}\frac{Q}{A}\frac{\partial(Q/A)}{\partial x}=\frac{-/Q/Q}{K^2} \qquad (2)$$

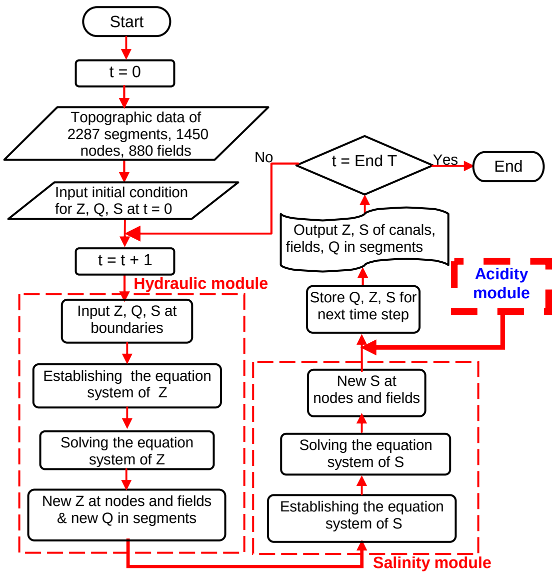
where; Q is the discharge (L^3T^{-1}), x is the distance along the segment, B_c is the canal width, including storage area, averaged over the segment (L), z is the water level (L), t is time (T), q is the lateral flow per unit length ($L^3T^{-1}L^{-1}$) into the segment, α_o and α are adjustment coefficients, varying from 1.0 to 1.1, g is the gravity acceleration (LT^{-2}), A is the cross-section area (L^2), C is the Chezy coefficient for bottom roughness ($L^{-2}T^{-1}$), R is the hydraulic radius (L), n is the Manning's coefficient.

The model applies the concept of advection and dispersion (Harleman, 1971) to simulate salinity intrusion:

$$\frac{\partial(A_cS)}{\partial t}+\frac{\partial(QS)}{\partial x}-\frac{\partial}{\partial x}(D_xA\frac{\partial S}{\partial x})=qS_v \qquad (3)$$

where; A_c is the cross section, including storage area evenly spread along the segment (L^2), S is the salt concentration (ML^{-3}), D_x is the longitudinal dispersion coefficient (L^2T^{-1}), S_v is the salt concentration of lateral flow (ML^{-3}).

The new acid module is incorporated into the VRSAP model after the hydraulic and salinity modules as shown in Figure 2.



Notes: Z, S are water level and salinity at nodes and fields, and Q is discharge in segments. t is current time step. End T is last time step.

Figure 2: Incorporation of acidity module into VRSAP model

The general equations of acidity transport including the effect of salinity on decreasing acidity are in (4):

$$\frac{\partial C}{\partial t}=\frac{\partial(QS)}{A\partial x}-\frac{\partial}{A\partial x}(AD_x\frac{\partial C}{\partial x})+\lambda(\frac{q_L}{A}C_L-C) \qquad (4)$$

where; A is the cross section of canal segment (L^2), C is the acid concentration of canal water (ML^{-3}), D_x is the longitudinal dispersion coefficient (L^2T^{-1}), C_L is the acid concentration of lateral flow (ML^{-3}), λ is the rate of decreasing acidity by effect of salinity [1/T] and q_L is lateral inflow rate [L^3/T-L].

Figure 3 explains details of the computation in acidity module. The advection and dispersion (first and second components on the right of equation (4)) are calculated in block c, the last component on the right of equation (4) dealing with the acid load into the canal network caused by runoff, bypass or seepage is calculated in blocks b and c. By using the implicit finite difference scheme to solve the acid equation system as for salinity, the acidity at all nodes is computed in block e. The last step in block f is the recalculation of acidity at nodes by taking into account the effect of salinity on acidity reduction.

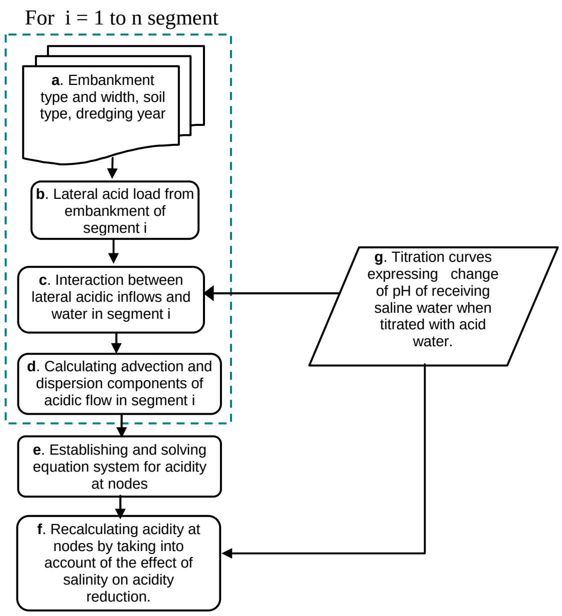


Figure 3: Flowchart of calculation in acidity module

Input data for acidity module includes parameters of canal segment that influence the acid load into the canal such as embankment type (road or no road), canal level (primary, secondary or tertiary level for determining the embankment width), soil type (severe, medium or non ASS), year of the last dredging/excavation and the fields connected to the segment. The input acid loading from the canal banks were calculated by the regression model established from results of a field experiment (Section 3.2). In addition, to calculate the change in pH of the saline receiving water caused by acidic inflow, the titration curves established from a laboratory experiment are also used in the acidity module (Section 3.3).

3.2 Quantifying acidity inflows from canal embankment into canal network

A field experiment was carried out in the study area from 1 April 2005 to 15 July 2005 to verify that acidity released from the canal embankment depend on its soil type and its age. The experiment included 7 sites along different secondary canals in the study area. The site selection was based on two factors: ASS type (distinguished by the existing and depth of the sulphuric horizon along soil profile, i.e. at 0-50 cm depth: severe ASS, 50-100 cm depth: medium ASS, and without sulphuric horizon: non ASS) and age of the embankment (number of years after the last dredging: either <2, 2 to 3 or >3 years). Data from the field experiment were used to generate the regression equations that simulate runoff and its acidity for every combination of soil type and age of the embankment.

Experiment setup

Daily rainfall, runoff and bypass volume were measured by using a collection system at each experimental site that comprised of a standard rain gauge (8" diameter and 24" tall), a runoff collector box and a bypass collector box (Fig. 4). Rainwater, runoff and bypass water were stored in an ice box and transported right after sampling to a mobile laboratory located at a farmer's house nearby these experimental sites for measurement of pH and acidity. Seepage water across canal embankment was also sampled once a week by using a vacuum sampling technique with suction cups (Phong, 2001). Acidity of all runoff, bypass and seepage water samples was analysed using the titration method (APHA, 1989).

The Darcy's equation was applied for calculating seepage flow where the hydraulic gradient is the different between water levels in fields and canals. The saturated hydraulic conductivity Ks were measured at 3 locations in each of 4 canals with different soil types. However, the variation of Ks does not cause a significant variation in seepage flow, therefore we use an average value of $0.0001 m.s^{-1}$ for all combinations of soil type and age of the embankment.

Computation of acid loading

Acidity is expressed in term of $[H^+]$ per volume unit or pH = 1/log (H^+). The daily total acidity of runoff per unit of canal length (TA) is defined as:

$TA = [H^+] \times RO$ $\quad$ ($mmol\ H^+.m^{-1}.day^{-1}$)

where: RO is runoff ($l.m^{-1}.day^{-1}$). In the acidity module, TA at day i is calculated from the cumulative total acidity at day i (Ts_i) and previous day i-1 (Ts_{i-1}):

$TA = Ts_i - Ts_{i-1}$

Ts_i and Ts_{i-1} are looked up from the empirical regression model between the cumulative acidity and daily rainfall established for each combination of soil type and age of the embankment.

The experiment results that the bypass acid load was very low compared with runoff and seepage components, therefore it was negligible in the acid module. The monitored acidity of seepage across canal embankment did not vary much during the experiment, hence average values obtained from experimental data for each soil type were used and assumed unchanged during dry season and beginning of rainy season.

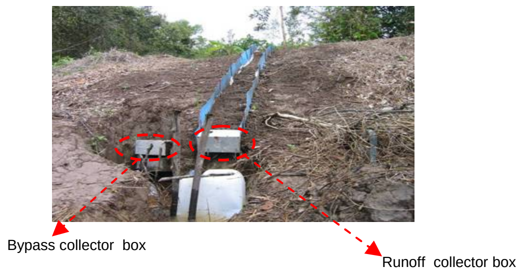


Figure 4: Runoff and bypass water collection on canal embankment

3.3 Interaction between acidic inflow and receiving water body

When acidic water from the banks drains into a canal, the pH of canal water will be lower because of the addition of H^+ into the water body. The change in pH of the receiving water body depends on (i) the ratio between the receiving water volume and the acidic inflow and (ii) the salinity concentration of the receiving water, because sea water contains bicarbonate that has a neutralization capacity.

A titration experiment was carried out to simulate the interaction between the acidic inflow and the canal water. The titrants represented the acidic inflow with different acidity levels (pH 3 to 7); and the receiving water (recipient) samples represented the canal water with different salinity levels (0, 10, 20, 30 or 55 dSm^{-1}). The titrants were prepared by diluting extracted soil solution of a severe ASS sample (pH =3.21 at soil water ratio 1:5) taken from the study area. The receiving water samples were prepared by using the sea water (salinity 70 dSm^{-1}, pH 7.8) taken at Ganh Hao near the East Sea side and the fresh water (salinity 0 dSm^{-1} and pH = 6.9) taken at upstream of the Quan Lo Phung Hiep canal (QLPH). To establish a titration curve, the titrant was dropped continuously into 50 ml recipient sample. The titrant volume and pH of the sample are recorded during titration. The input was stopped when the pH of the water sample was almost unchanged or the volume of titrant was approximately more than 10 times that of the recipient sample. The pH and volume of titrant were plotted to draw the titration curves (or pH curves) for the recipient samples with different salinity levels.

3.4 Large scale monitoring of pH and salinity

The available data in 2003 and 2005 include salinity and pH measured during the dry and the beginning of rainy season on 10 days (15/12 of previous year, 15/1, 15/2, 15/3, 15/4, 30/4, 15/5, 30/5, 15/6 and 30/6 of 2003 and 2005) at 63 monitored sites in the study area. The acidity situation in 2003 was more serious than in 2005 because more canals were dredged in 2002-2003 than in 2004-2005. The 2003 and 2005 measured data were used for calibration and validation of the acid module, respectively.

3.5 Model calibration and validation

The calibration was carried out by adjusting the coefficients used in the acidity module that could not be measured easily or accurately in the fields: the dispersion coefficient DISP, the length of runoff path on canal embankment ROC and the seepage across embankment SP. The adjusted coefficients in calibration stage were remained unchanged in validation stage. To evaluate the model performance, two statistical indicators and two illustrators were used:

a. Two statistical indicators: the square of linear regression coefficient (r^2) and the model efficiency (EF). EF was calculated as:

$$EF = \left(\sum_{i=1}^{n} (M_i - \overline{M})^2 - \sum_{i=1}^{n} (S_i - M_i)^2 \right) \Big/ \sum_{i=1}^{n} (M_i - \overline{M})^2$$

where n is number of pairs of simulated and measured data; S_i is simulated value i; $\overline{M}$ is average value of n measured data; and M_i is measured value i.

These indicators were calculated from 10 pairs of simulated and measured monthly pH averages of 63 monitored sites. Ranking of model performance is given in Table 1 (Andersen et al., 2002).

Table 1: Ranking of model performance by r^2, EF

Performance level	r^2	EF
1. Very good	> 0.8	> 0.95
2. Good	0.7-0.8	0.85-0.95
3. Fair	0.5-0.6	0.7-0.85
4. Poor	< 0.5	< 0.7

b. Two illustrators: the simulated versus measured monthly pH averages of all 63 monitored sites (Fig. 6) and monthly pH at 3 specific locations Ninh Quoi (NQ), Pho Sinh (PS) and Phuoc Long (PL) (locations in Fig.1 and results in Fig.7) along the QLPH canal where salinity was referred for decision of the operation of sluice gates.

4. RESULTS AND DISCUSSIONS

4.1 Acid load from canal embankment

All the regression models of runoff versus daily rainfall and cumulative total acidity versus cumulative rainfall at 7 experimental sites (Tables 3 and 4) are valuable (r^2 >0.9) and significant, except at site 7 (non-ASS). These models are applied for other canals with same combinations of soil type and age of the embankment as those sites. However, the released acidity is assumed to be zero if embankment is road or non-ASS type or along a primary canal.

Table 2: Regression models of runoff (RO - $m3.s^{-1}.m^{-1}$) versus daily rainfall (R - mm)

Site	ASS type	Age	Regression equation	r^2
1	Medium	> 3yrs	RO = 0.25 R – 0.25	0.77**
6	Severe	> 3yrs	RO= 1.03 R – 1.29	0.96**
2	Medium	2-3 yrs	RO= 0.84 R – 1.66	0.63**
5	Severe	2-3 yrs	RO= 1.10 R – 3.40	0.91**
3	Severe	1 yrs	RO= 0.94 R - 2.12	0.93**
4	Medium	1 yrs	RO= 0.11 R - 0.43	0.61**
7	Non ASS	> 3yrs	RO= 0.25 R – 3.67	0.26^{ns}

*Note: ** : the regression equation is very significant at 0.01 probability. ^{ns} : the equation has no significance.*

Table 3: Regression models of cumulative total acidity (Ts - mmol H^+) versus cumulative rainfall (Rs - mm)

Site	ASS type	Age	Regression equation	r^2
1	Medium	> 3yrs	Ts = 1.24 Rs + 83.3	0.99**
6	Severe	> 3yrs	Ts = 1.82 Rs + 17.9	0.97**
2	Medium	2-3 yrs	Ts = 102.6 Rs – 3488	0.99**
5	Severe	2-3 yrs	Ts = 92.9 Rs + 11851	0.99**
3	Severe	1 yrs	ln Ts = 2.85ln Rs - 9.45	0.99**
4	Medium	1 yrs	ln Ts = 3.22 lnRs - 14.1	0.98**
7	Non ASS	> 3yrs	0	

4.2 Titration curves of saline water

Titration curves are given in Figures 5a, 5b and 5c for recipient with different salinity (S = 0, 10, 20, 30, 55 dSm^{-1}) titrated by titrants with pH = 3, 5 and 7, respectively. These curves are used to determine the reduction of acidity corresponding to salinity in a canal segment. The initial pH of recipient ranges from 7.5 to 7.8 depending on its alkalinity. When titrant with low pH (= 3) is added into recipient sample, the pH of recipient will decrease sharply because a lot of base (alkalinity) was consumed to neutralize the acid concentration. Near the equivalence point which is at pH 4.3 to 4.9 depending on the alkalinity of recipient (APHA, 1989), the change occurs very quickly, therefore the graphs in Figure 5a is extremely steep around this point.

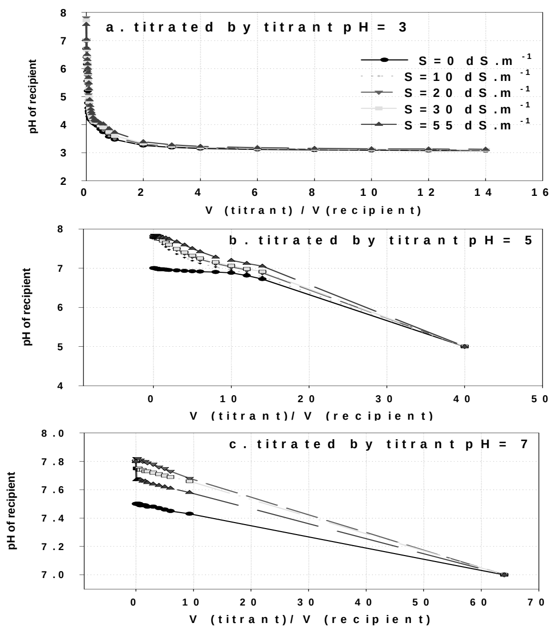


Figure 5: Titration curves showing the change in pH of the recipient due to addition of titrant with pH = 3 (a), 5 (b) and 7 (c). *Note: Values in x-axes and y-axes are not same in three cases.*

On the other hand, when the titrant with high pH (= 7) is added, a large volume of titrant is needed to decrease significantly the pH of recipient as shown in Figure 5c. Figure 5b presents the transitional case between two cases 5a and 5c when titration is done with titrant of pH = 5.

4.3 Calibration and validation

Generally, the acidity module can simulate the average pH reasonably well as shown by the comparison of the model outputs with measured data in 2003 for calibration and in 2005 for validation (Figures 6a and 6b). pH increased in the dry season, reached a maximum on 15 March, and gradually decreased in later months when the rainy season started. From January to March without rainfall, pH in the canal network often remained stable (7.5 to 7.7) but lower than pH of sea water (7.8) possibly due to the permanent acidity load by seepage along canals. In 2005, although the amount of rainfall was similar to that in 2003, both simulated and measured pH values at most sites were remained higher than 7 until 30 June. These high pH values were explained by less dredging activities in 2004-2005 that caused less acidity release in 2005 compared to 2003.

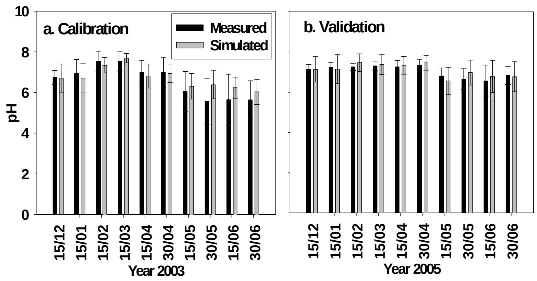


Figure 6: The simulated and measured monthly pH averages of 63 sites from 15 December to 30 June in 2003 and 2005.

The measured and simulated pH in 2003 and 2005 at three specific locations, NQ, PL and PS are shown in Figures 7a to 7f. At PL and PS located in the saline area, a quite good fit is found in comparison between simulated and measured pH in 2003 and 2005 (Figures 7c, 7d, 7e and 7f), especially in the dry season from 15 December to 30 April. In the rainy season (after 30 April), the simulated pH was over estimated, either slightly as at PL (Figures 7c and 7d) and highly as at NQ (Figure 7a and 7b). The reasons could be the non-uniform rainfall distribution (but only data from some meteorological stations in the study area were used in the model) and the operation of small sluice gates (that was not taken into consideration in the model). As NQ is located in the transitional area between fresh water and saline water, larger variation of salinity at this location causes higher simulated pH than the measured pH (Figure 7a and 7b).

Table 4 shows that the model performance indicators of calibration with 2003 data are very good and good (levels 1 and 2). On the other hand, those of validation are only good and fair (levels 2 and 3), possibly because acidity did not vary much in 2005.

However, these results show that with the methods applied in estimation of acidity from embankments and calculation of acidity reduction with saline water, the acidity module can simulate the acid propagation in the study area.

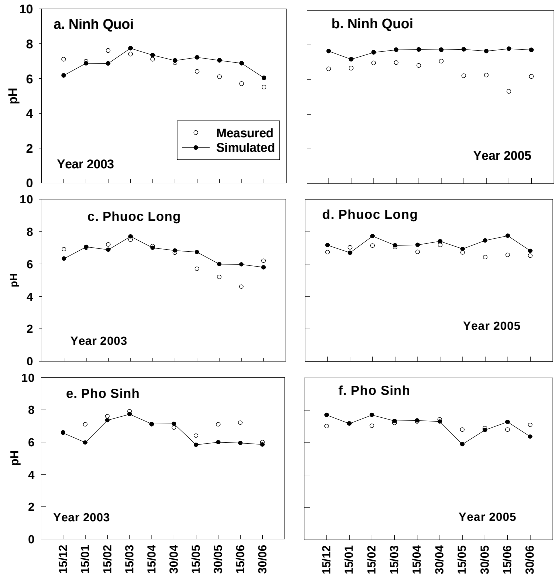


Figure 7: Simulated and measured pH at Ninh Quoi (a & b), Phuoc Long (c & d) and Pho Sinh (e & f) for 2003 (left graphs) & for 2005 (right graphs).

Table 4: Model performance results by using the average monthly pH

Model run	Data set	r^2	EF
Calibration	2003	0.87** (1)[+]	0.74 (2)[+]
Validation	2005	0.73** (2)[+]	0.62 (3)[+]

*Note: ** significant at 0.01 probability.*
[+] value inside bracket is the performance level as classified in Table 1.

5. CONCLUSIONS

The VRSAP model with new acidity module could be applied for simulation of acid propagation in the study area. The locations and the number of dredged canals in each year in ASS areas are the main factors that determine the acid load by runoff drained from canal embankments and propagating in the canal network. In addition, the model also simulates the effect of salinity on reducing acidity. The simulation of the acid propagation indicates that with suitable canal dredging plan in ASS areas and salinity control such as isolating newly dredged canals and using saline water for reducing acidity, areas influenced by acid water can be eliminated in the coastal zones with acid sulphate soils.

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