Nutrient Sources and Dynamics in the Parafield Stormwater Harvesting Facility and Implication to Water Quality Control

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(Bachelor of Science, Master of Science in Biological Sciences)

Thesis Submitted for the Degree of

Doctor of Philosophy

In

The University of Adelaide
School of Earth and Environmental Science
Discipline of Ecology and Evolutionary Biology

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Appendix A

A-1 Total Nitrogen Analysis in Water, Sediment and Plant Samples

Digestion

- 1g of sediment and 0.25g of plant sample was digested in the presence of 4ml conc. sulfuric acid (conc. H_2SO_4) and a catalyst (Selenium pellet)
- 100ml volume of water sample was boiled down and was digested in the presence of 4ml conc. sulfuric acid (conc. H_2SO_4) and a catalyst (Selenium pellet)
- duration of the digestion process is mentioned in section 4.3.4.1 (for water), 4.4.4.2 (for sediment) and 4.5.4.1 (for plant)

Standards (0, 5, 10, 20 µg N/ml)

Standards made up in diluted (2 times) digest blank solution

Samples

- after finishing the digestion procedure the digest was diluted with 50ml of RO water
- diluted samples were diluted a second time with RO water before filled into the AA tubes, ie. 5ml samples + 5ml RO water

Reagents

Sodium Nitroprusside: Dissolve 0.4g sodium nitroprusside in 500ml RO water

Sodium Dichloroisocyanate:

a 1 % stock solution: Dissolve 1g stabilized chlorine in 100ml RO water

b Working solution: Dissolve 10g sodium hydroxide (NaOH) + 5ml of stock solution in 500ml RO water

Sodium Salicylate: 10g sodium salicylate in 1000ml RO water

Citrate Tartrate Complex: Dissolve 25g NaOH, 6g trisodium citrate, 18g sodium hydrogen tartrate in RO water and make it to 1000ml with RO water and add 0.1ml of 30% Brij

Calculation of Total Nitrogen in Water

Sample volume = 100ml   Digest volume = 50ml   Dilution = 2 times

$$\mu\text{g N in 1ml of sample} = \left[\frac{\text{standard } \mu\text{g N/ml}}{\text{peak of standard (mm)}}\right] \times \text{peak of sample (mm)} \times \left(\frac{\text{dilution}}{\text{sample volume}}\right)$$

$$= [A] \times y \times 0.02 \qquad (y = \text{sample peak in mm})$$

$$\therefore \mu\text{g N in 50 ml digest} = 0.02 \times [A] \times y \times 50$$

$$\therefore \mu\text{g N/ml of water} = 1 \times [A] \times y = [A] \times y = \text{ppm}$$

$$\therefore \text{mg N/L of water} = [A] \times y$$

Calculation of Total Nitrogen in Sediment

Digest volume = 50ml   Sediment weight = 1g   Dilution = 2 times

$$\mu\text{g N in 1ml of sample} = \left[\frac{\text{standard } \mu\text{g N/ml}}{\text{peak of standard (mm)}}\right] \times \text{peak of sample (mm)} \times \text{dilution}$$

$$= [A] \times y \times 2 \qquad (y = \text{sample peak in mm})$$

$$\therefore \mu\text{g N in 50 ml digest} = 2 \times [A] \times y \times 50$$

$$\therefore \mu\text{g N/g of sediment} = 100 \times [A] \times y = \text{ppm}$$

$$\therefore \text{mg N/kg of sediment} = 100 \times [A] \times y$$

Calculation of Total Nitrogen in Plant

Digest volume = 50ml   Plant weight = 0.25g   Dilution = 2 times

$$\mu\text{g N in 1ml of sample} = \left[\frac{\text{standard } \mu\text{g N/ml}}{\text{peak of standard (mm)}}\right] \times \text{peak of sample (mm)} \times \text{dilution}$$

$$= [A] \times y \times 2 \qquad\qquad (y = \text{sample peak in mm})$$

$$\therefore \mu\text{g N in 50 ml digest} = 2 \times [A] \times y \times 50 = 100 \times [A] \times y$$

$$\therefore \mu\text{g N/g of plant} = \frac{100 \times [A] \times y}{0.25} = 400 \times [A] \times y = \text{ ppm}$$

$$\therefore \text{mg N/kg of plant} = 400 \times [A] \times y$$

A-2 Total Phosphorus Analysis in Water and Sediment Samples

Digestion

- 0.1g of sediment and 0.5g of plant sample was digested in the presence of 7ml nitric-perchloric acid
- 100ml volume of water sample was boiled down and was digested in the presence of 7ml nitric-perchloric acid
- duration of the digestion process is mentioned in section 4.3.4.4 (for water) and 4.4.4.3 (for sediment)

Standards (0, 0.25, 0.5, 1.0 µg N/ml)

Samples

- after finishing the digestion procedure the digest was diluted with 50ml of RO water the sediment samples and 25ml of RO water for water samples

Reagents

5N Sulfuric Acid (H_2SO_4): Dilute 138.9ml conc. H_2SO_4 to 1 liter with RO water

Ammonium Molybdate: Dissolve 16g Ammonium Molybdate to 1 liter with RO water

Antimony Potassium tartrate: Dissolve 4.6g Antimony Potassium tartrate to 1 liter with RO water

Working Solution

Colour Reagent: Mix 226ml of 5N H_2SO_4 + 150ml of Ammonium Molybdate Solution + 40ml Antimony Potassium tartrate Solution and make it to 1 liter with RO water

Dilutent (contains ascorbic acid): Dissolve 4g ascorbic acid and make it to 500ml with RO water and add 30 drops of Dowfax

Calculation of Total Phosphorus in Water

Sample volume = 100ml   Digest volume = 25ml

$$\mu\text{g P in 1ml of sample} = \left[\frac{\text{standard } \mu\text{g P/ml}}{\text{peak of standard (mm)}}\right] \times \text{peak of sample (mm)}$$

$$= [A] \times y \qquad\qquad (y = \text{sample peak in mm})$$

$$\therefore\ \mu\text{g P in 25ml digest} = [A] \times y \times 25$$

$$\therefore\ \mu\text{g P/ml of water} = \frac{[A] \times y \times 25}{100} = [A] \times y \times 0.25 = \text{ ppm}$$

$$\therefore\ \mu\text{g P/ml of water} = [A] \times y \times 500 = \text{ mg/L}$$

Calculation of Total Phosphorus in Sediment

Digest volume = 50ml   Sediment weight = 0.1g

$$\mu\text{g P in 1ml of sample} = \left[\frac{\text{standard } \mu\text{g P/ml}}{\text{peak of standard (mm)}}\right] \times \text{peak of sample (mm)}$$

$$= [A] \times y \qquad\qquad (y = \text{sample peak in mm})$$

$$\therefore\ \mu\text{g P in 50ml digest} = [A] \times y \times 50$$

$$\therefore\ \mu\text{g P/g of sediment} = \frac{[A] \times y \times 50}{0.1} = [A] \times y \times 500 = \text{ ppm}$$

$$\therefore\ \mu\text{g P/g of sediment} = [A] \times y \times 500 = \text{ mg/kg}$$

A-3 Total Phosphorus Analysis in Plant Samples

Digestion

The procedure of the digestion for plant samples has been mentioned in section 4.5.4.2.

Standards (0, 2, 4, 6, 8, 10 µg P/ml)

Samples

- after finishing the digestion procedure the digest was diluted with 50ml of RO water

Reagents

Concentrated nitric acid

0.25% Ammonium vanadate: Dissolve 2.5g NH_4VO_3 in 1 liter RO water

5.0% Ammonium molybdate: Dissolve 50g $(NH_4)_6Mo_7O_{24}$ in 1 liter RO water

Mixed Reagent: add conc. Nitric acid to ammonium vanadate solution, mix thoroughly, then add ammonium molybdate, mix well and allow to cool

Standard Solution

Stock Solution (1000µg P/ml): Dissolve 4.3937g KH2PO4 in RO water and dilute to 1 liter

Working Solution (100µg P/ml): Dilute 100ml stock solution to 1 liter with RO water

Procedures

- take an aliquot of 0.1ml of the sample
- dilute it with 2.75ml water
- add 0.25ml of the mixed reagent to get a total volume of 3.1ml
- wait an hour before taking readings on the spectrophotometer at a wavelength of 390nm

Calculation of Total Phosphorus in Plant

Plant weight = 0.5g Digest volume = 50ml Dilution = 15ml

$$\text{curve readings } \mu\text{g/ml for sample} = \frac{\text{standard}}{\text{abs of standard}} \times y \qquad (y = \text{absorbance of sample})$$

$$= [A] \times y$$

$$\therefore \mu\text{g P in 50ml digest} = [A] \times y \times a \times b \qquad (a = \text{dilution}, b = \text{digest volume})$$

$$\therefore \mu\text{g P in 0.5g of plant} = [A] \times y \times a \times b$$

$$\therefore \mu\text{g P/g of plant} = \frac{[A] \times y \times a \times b}{0.5} = \text{mg P/kg}$$

A-4 Nitrate and Phosphate Analysis in Water Samples

Nitrate and phosphate concentration in the water samples were measured using the DR/2000

Measuring Nitrate in water samples:

- Enter the stored program number (950) for nitrate and rotate the wavelength dial until the display shows 400nm
- Fill a sample cell with 25ml of sample (the prepared sample) and another cell with 25ml of de-ionized water (the blank)
- Add the contents of one NitraVer5 Nitrate reagent powder pillow to each cell
- Press SHIFT + TIMER, which will begin a one minute reaction period; shake the cells until the end of the period
- Press SHIFT + TIMER again, which will begin a second reaction period lasting five minutes
- When the timer beeps, place the blank into the cell hold and close the light shield
- Press ZERO. When the display shows 0.00 mg/L, replace the blank with the prepared sample. Press READ
- The display will show the results in mg/L

Measuring Phosphate in water samples:

- Enter the stored program ,number (951) for phosphate and rotate the wavelength dial until the display shows 890nm
- Fill the 25ml cell with sample, and add one PhosVer3 powder pillow. Swirl immediately to mix (the prepared sample) and fill a second cell with sample (the blank)
- Allow 2 minutes reaction period by pressing SHIFT + TIMER
- When the timer beeps, place the blank into the cell hold and close the light shield
- Press ZERO. When the display shows 0.00mg/L, replace the blank with the prepared sample. Press READ
- The display will show the result in mg/L

Appendix B

B-1 Time-series data for all measured parameters for water quality, sediment and plant

Water Quality parameters

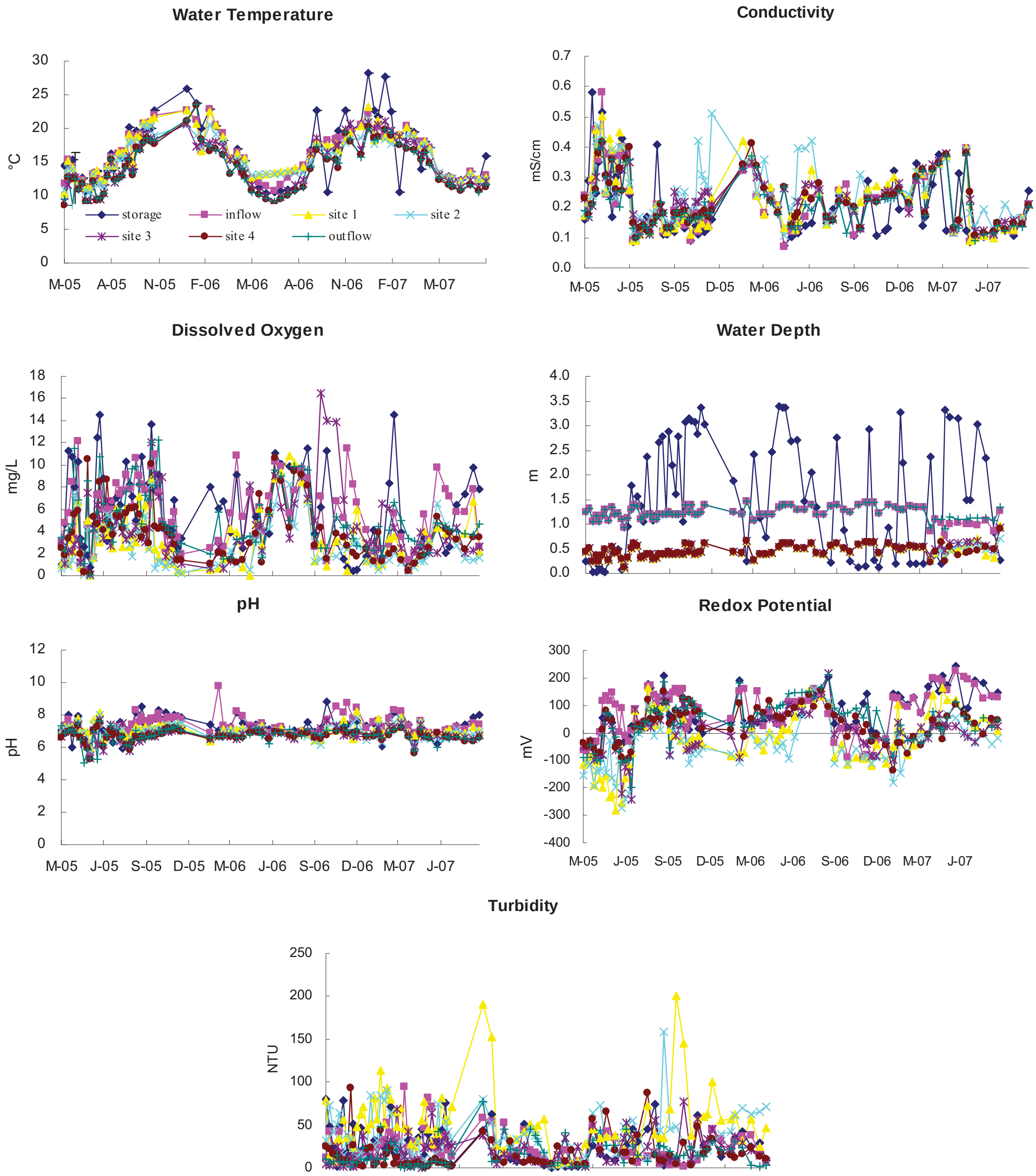


Figure B-1: Time-series of physical water quality parameters over the study period (2005-2007)

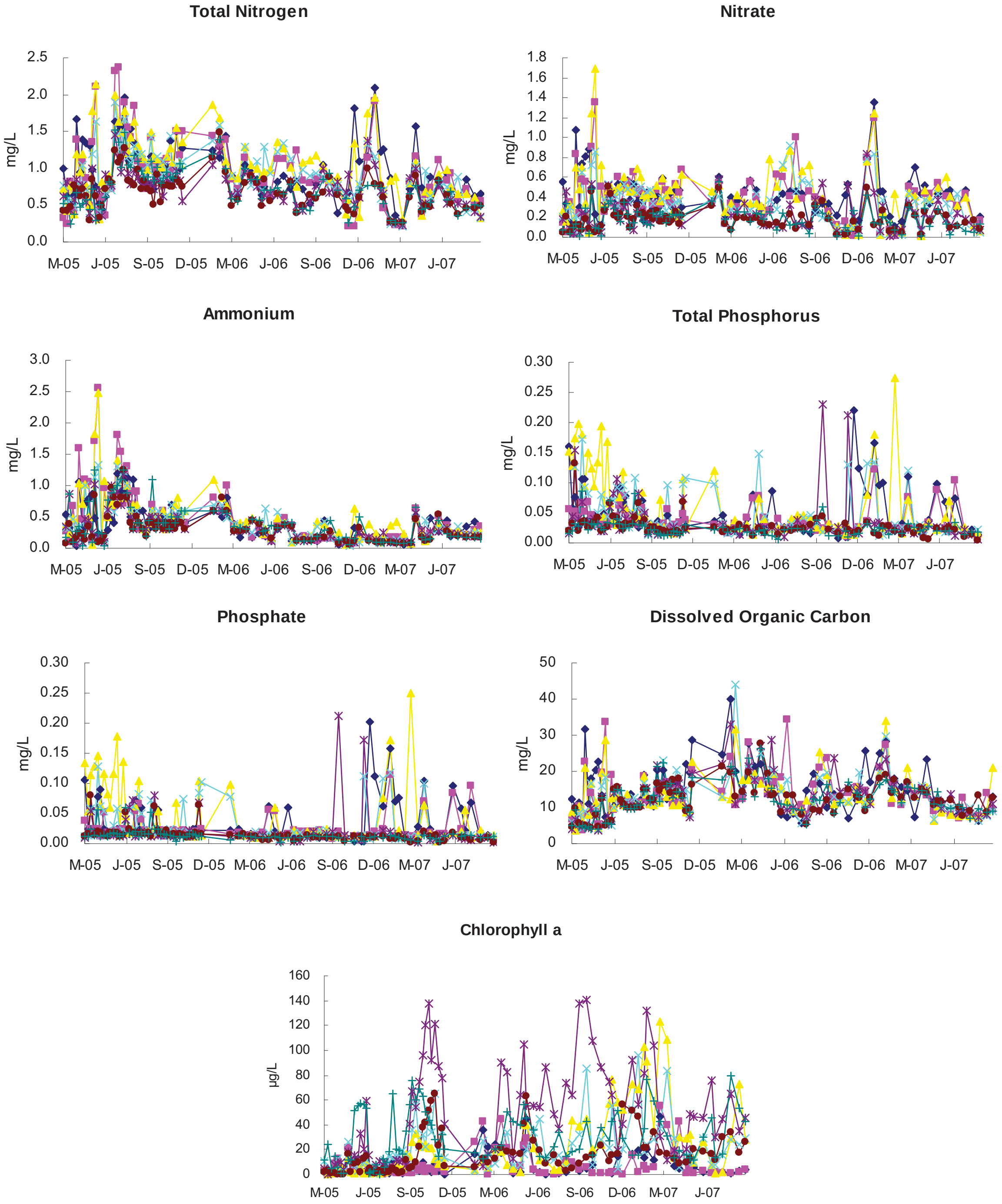


Figure B-2: Time-series of chemical and biological water quality parameters over the study period (2005-2007)

Sediment parameters

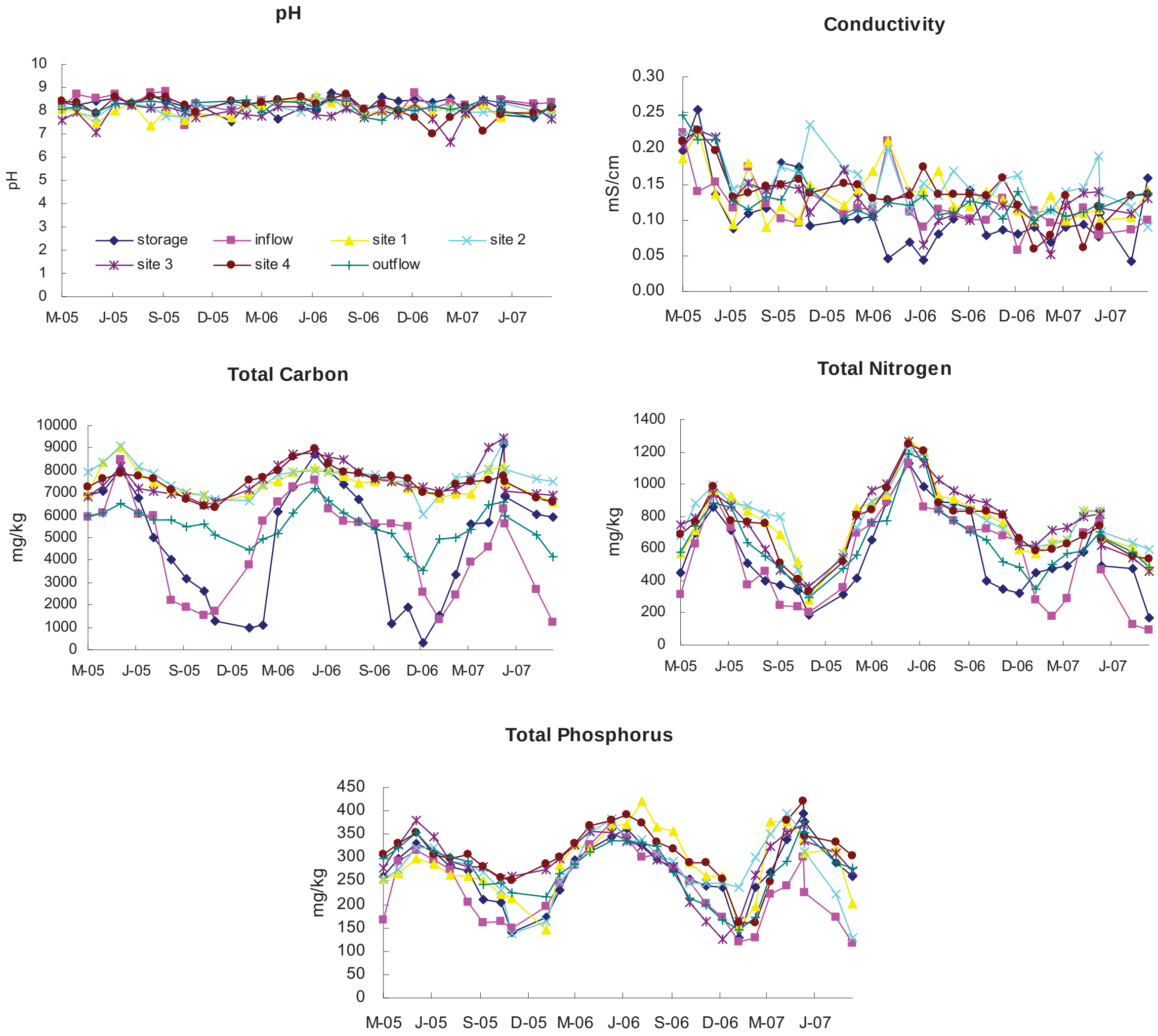


Figure B-3: Time-series of physical and chemical sediment parameters over the study period (2005-2007)

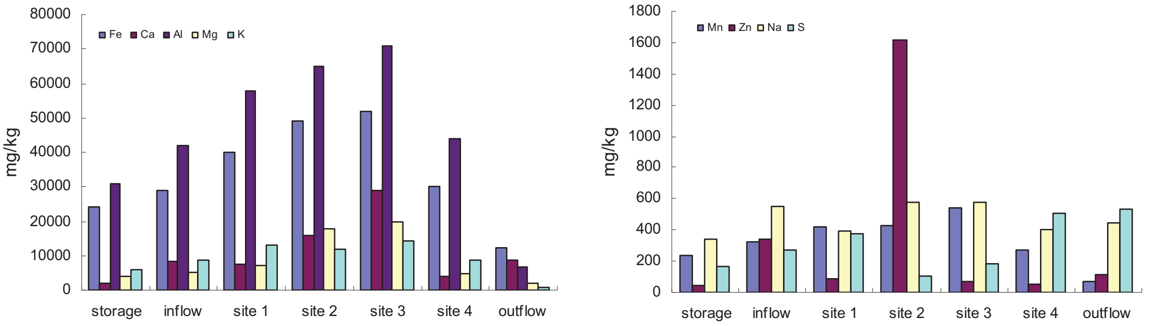


Figure B-4: Wetland sediment ICP results for the major minerals and metals for the different collection sites

Plant parameters

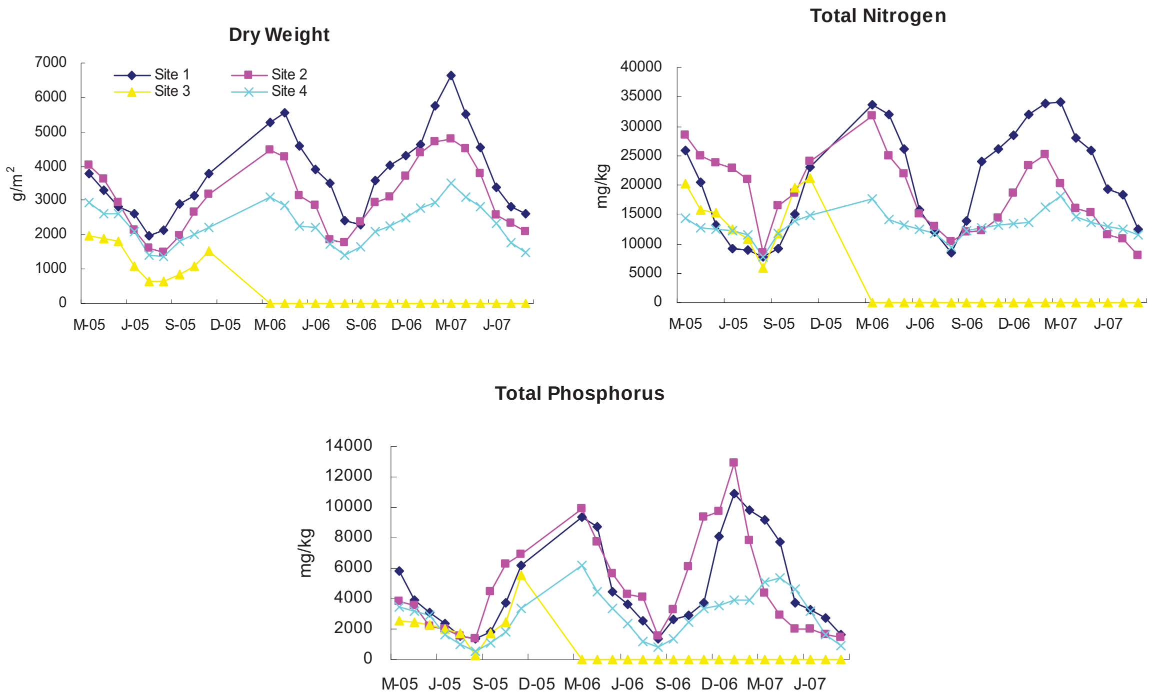


Figure B-5: Time-series of physical and chemical plant parameters over the study period (2005-2007)

B-2 Annual Pattern

Water quality parameters

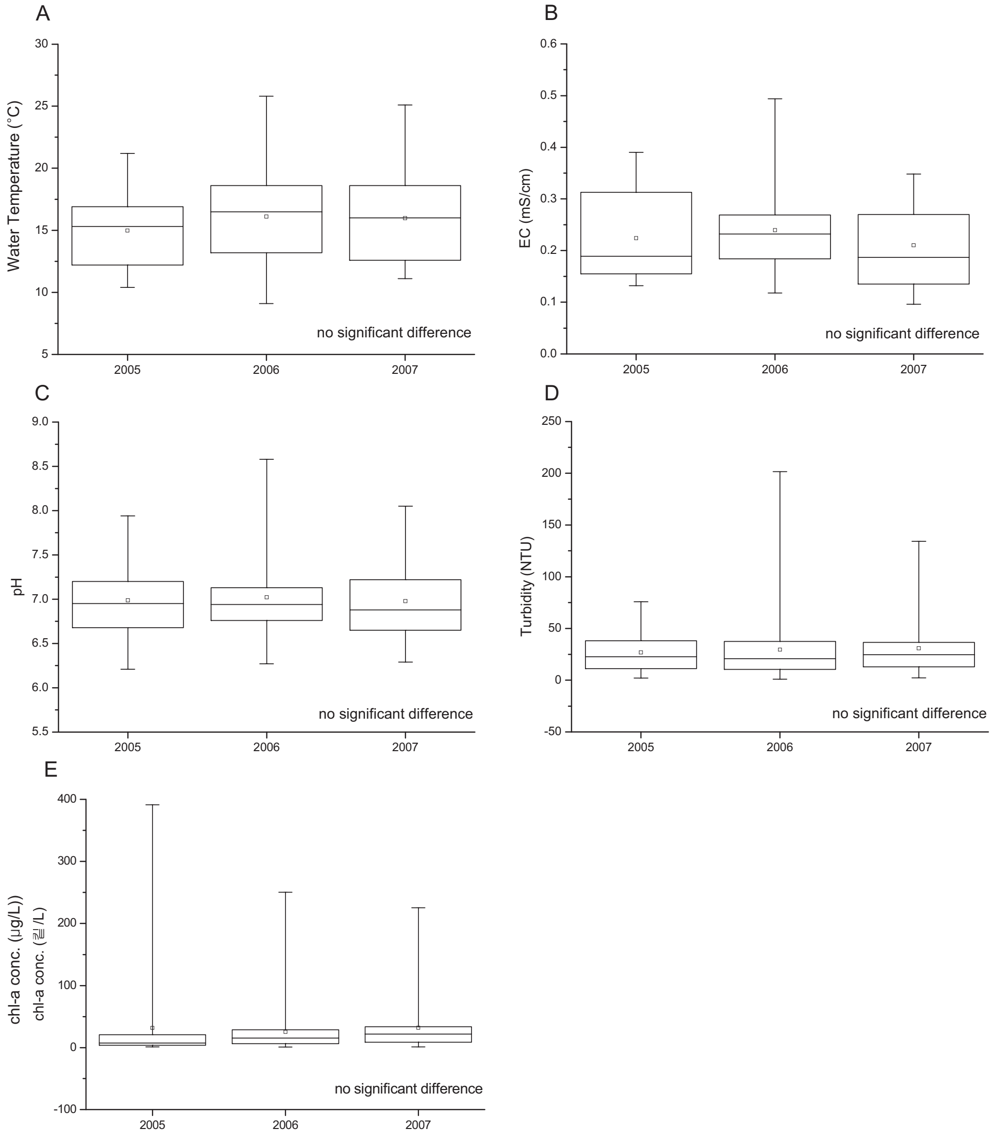


Figure B-6: Annual pattern of water quality parameters, which showed no significant differences between the years. A. water temperature, B. conductivity, C. pH, D. turbidity and E. chlorophyll a ($\alpha = 0.05$; 2005 n= 63, 2006 n = 84 and 2007 n = 56)

B-3 Flow and Flow rate

Flow rate

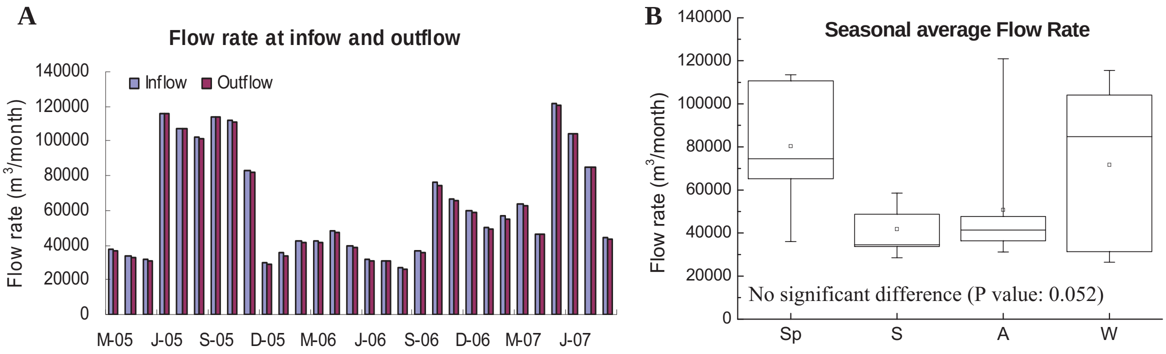


Figure B-7: A. Monthly inflow and outflow rates; B. Bar and whisker graph comparing the average flow during the different seasons. (Sp = Spring, S = Summer, A = Autumn, W = Winter) The columns marked with the same letter indicate no significant difference according to Tukey's test (α = 0.05, n= 11)

ANOVA performed including all seasons showed no significant difference, but the ANOVA performed between the flow rates during the summer and winter seasons showed a significant difference in the flow rate, where the level of flow rate was higher during the winter than summer (P value: 0.4867<0.05).

The flow data were provided by the City of Salisbury.

Appendix C

C-1 N removal efficiency

Table C-1: Results of Tukey's multiple comparisons for the performance for: A. NO_3^- removal efficiency; B. NO_3^- removal rate

A	**site 1**	**site 2**	**site 3**	**site 4**	**outflow**
site 1					
site 2	N.S.				
site 3	N.S.	N.S.			
site 4	N.S.	N.S.	N.S.		
outflow	N.S.	N.S.	N.S.	N.S.	

B	**site 1**	**site 2**	**site 3**	**site 4**	**outflow**
site 1					
site 2	***				
site 3	***	N.S.			
site 4	N.S.	N.S.	N.S.		
outflow	N.S.	**	**	N.S.	

*****, Extremely significant difference ($P<0.001$); **, moderately significant difference ($P<0.01$); *, significant difference ($P<0.05$); N.S., no significant ($P>0.05$); n = 29**

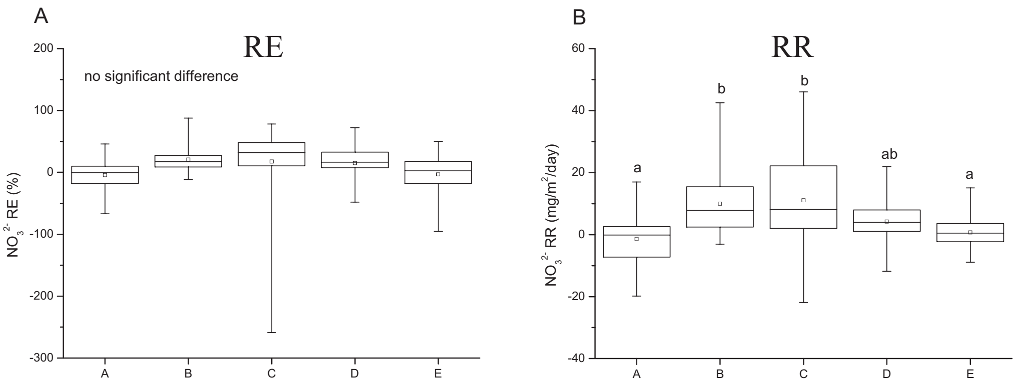


Figure C-1: A. NO_3^- removal efficiency (RE); B. NO_3^- removal rate (RR). The columns marked with different letters indicate significant difference according to Tukey's test (α = 0.05, n= 29). A. site1, B. site2, C. site3, D. site4 and E. outflow.

The performance in regards the efficiency showed no significant differences between the sites, however site 1 seems to show the least efficient performance, with site 3 the most efficient. The removal rate revealed a slightly different pattern, with site 1 having a significantly lower removal rate than the other sites. Site 2 and site 3 had significantly higher removal rates.

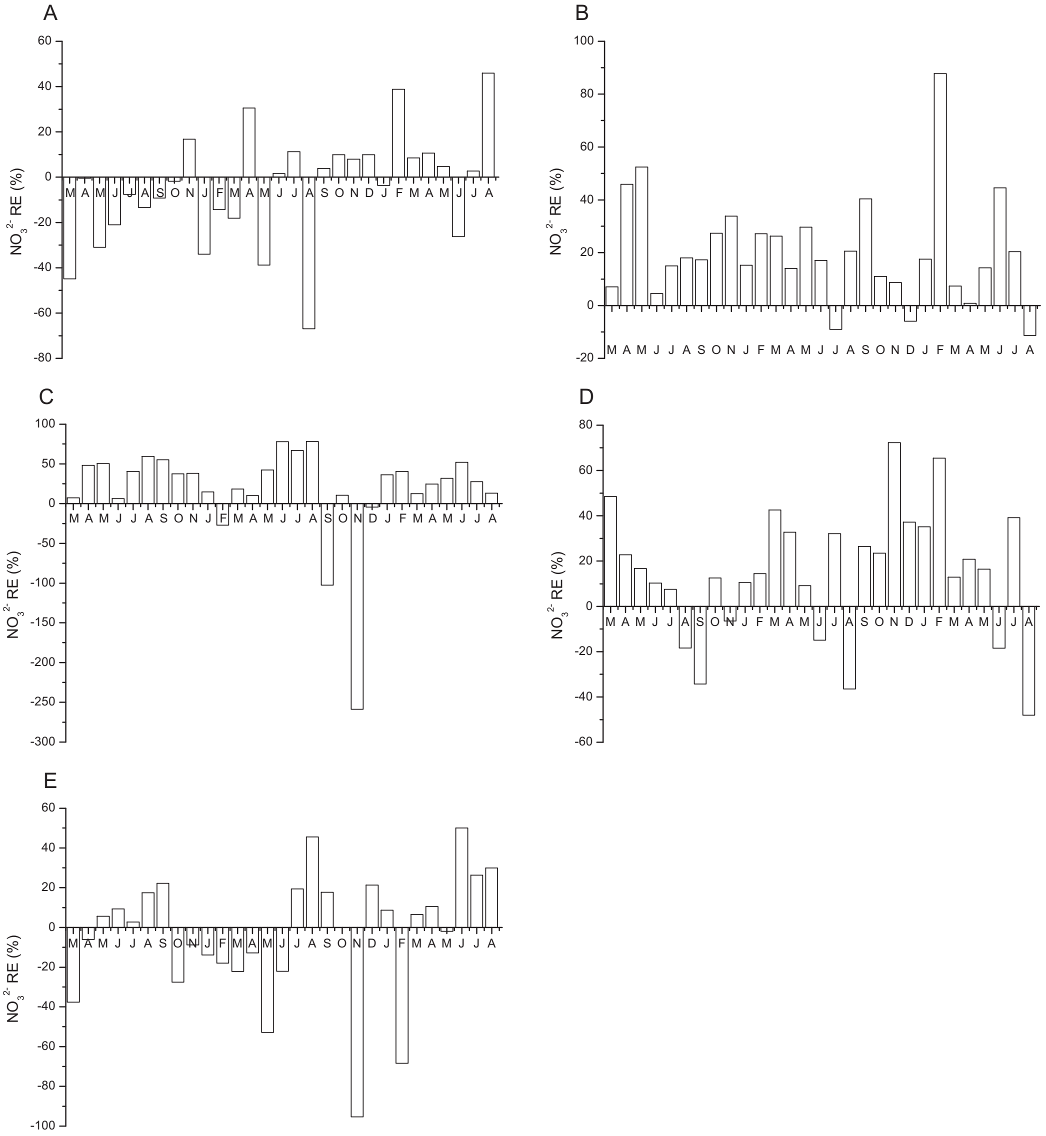


Figure C-2: Nitrate (NO_3^-) Removal Efficiency (%) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent NO_3^- release. n = 29

The seasonal pattern for nitrate removal performance showed that site 1 and outflow had for the majority of the study negative efficiencies with positive performance occurring during the winter seasons. Whereas the other sites showed positive performances during the growing seasons and showing a decline in performance in the winter seasons.

Table C-2: Results of Tukey's multiple comparisons for the performance for: A. NH_4^{+-} removal efficiency; B. NH_4^+ removal rate

A	site 1	site 2	site 3	site 4	outflow
site 1					
site 2	***				
site 3	**	N.S.			
site 4	**	N.S.	N.S.		
outflow	N.S.	*	*	N.S.	

B	site 1	site 2	site 3	site 4	outflow
site 1					
site 2	N.S.				
site 3	N.S.	N.S.			
site 4	N.S.	N.S.	N.S.		
outflow	N.S.	***	***	N.S.	

*****, Extremely significant difference ($P<0.001$); **, moderately significant difference ($P<0.01$); *, significant difference ($P<0.05$); N.S., no significant ($P>0.05$); n = 29**

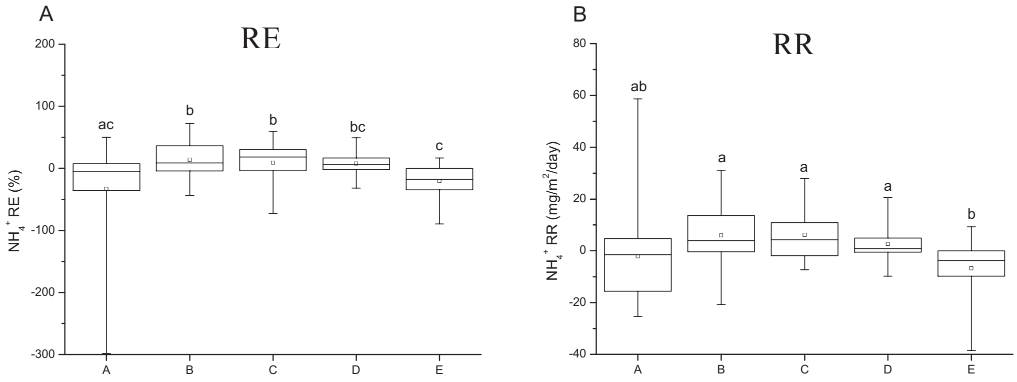


Figure C-3: A. NH_4^+ removal efficiency (RE); B. NH_4^+ removal rate (RR). The columns marked with different letters indicate significant difference according to Tukey's test ($\alpha = 0.05$, n= 29). A. site1, B. site2, C. site3, D. site4 and E. outflow.

The Tukey's test revealed that significant differences exist within the reed bed. The removal efficiency showed that site 1 and outflow were significantly different from the rest ($P<0.05$). In both performances the removal efficiency and removal rate showed that site 1 and outflow had significantly lower efficiencies and rates.

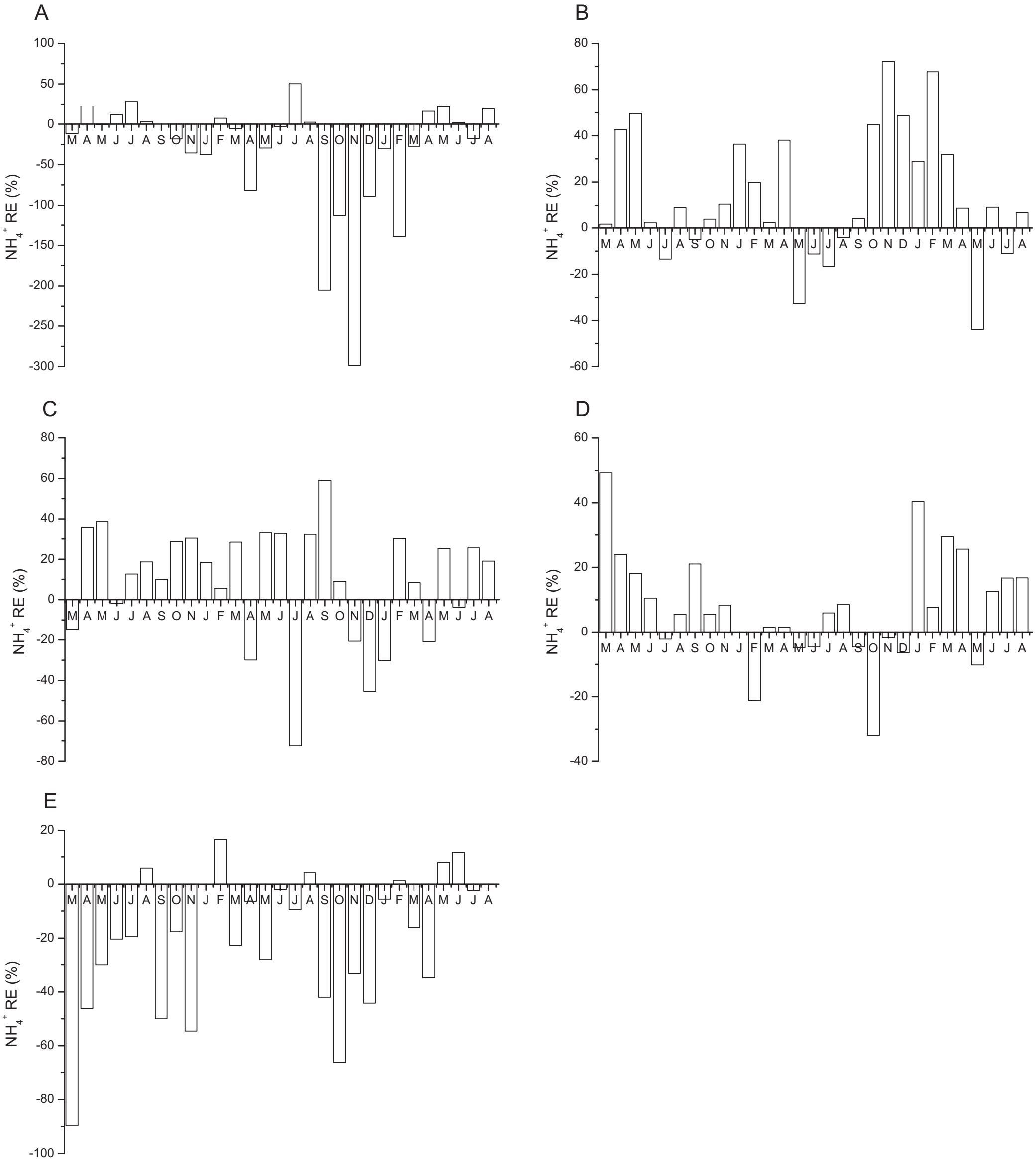


Figure C-4: Ammonium (NH$_4^+$) Removal Efficiency (%) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent NH$_4^+$ release. n = 29

The seasonal pattern for ammonium removal performance showed similar to nitrate, that site 1 and outflow showed positive performances during the non-growing seasons, with having low performance during the rest of the seasons, which show more or less a negative performance. For the rest of the sites the performance showed efficiently during the growing seasons with lower efficiencies during the non-growing season.

C-2 N removal rate

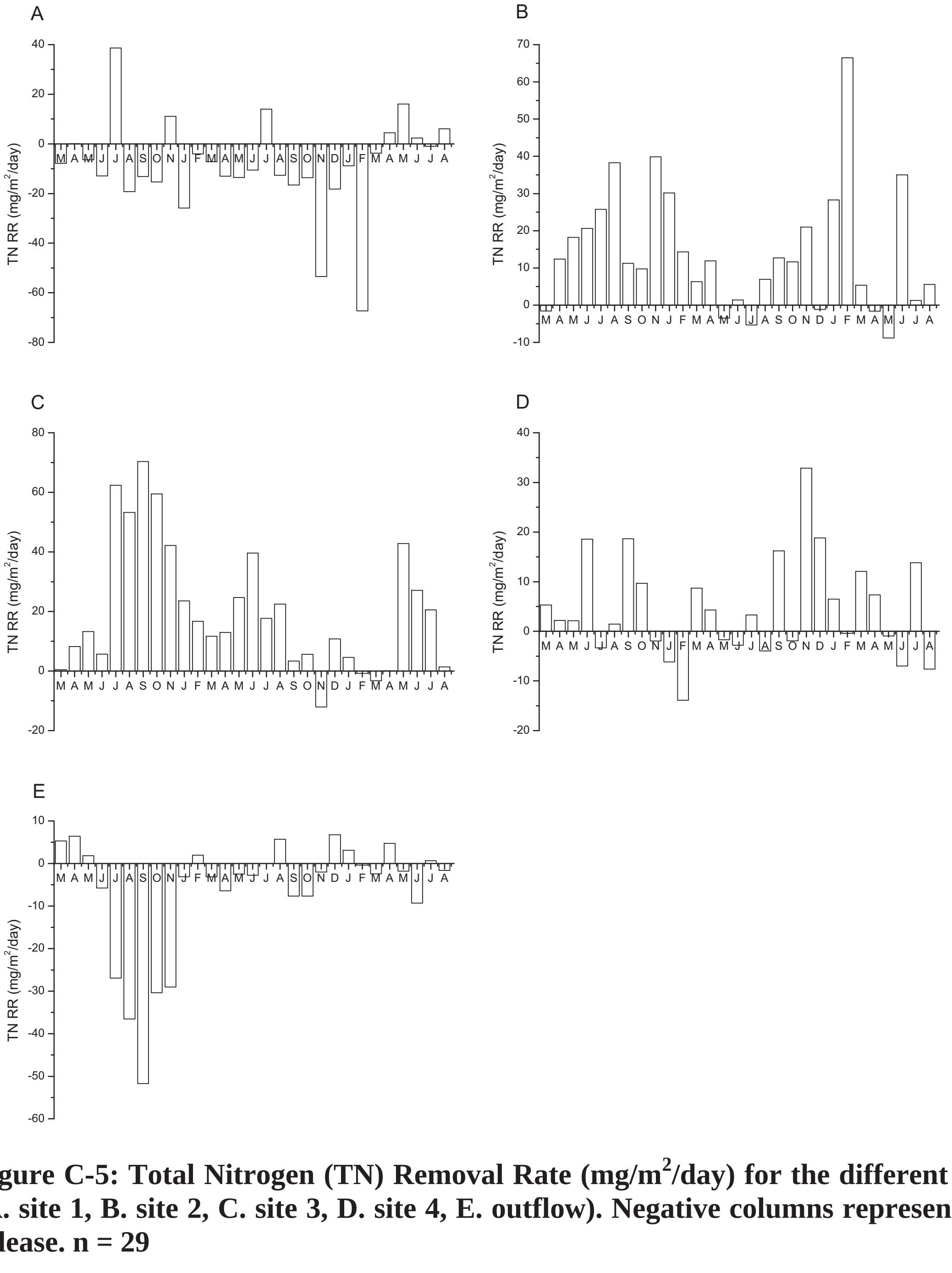


Figure C-5: Total Nitrogen (TN) Removal Rate (mg/m^2/day) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent TN release. n = 29

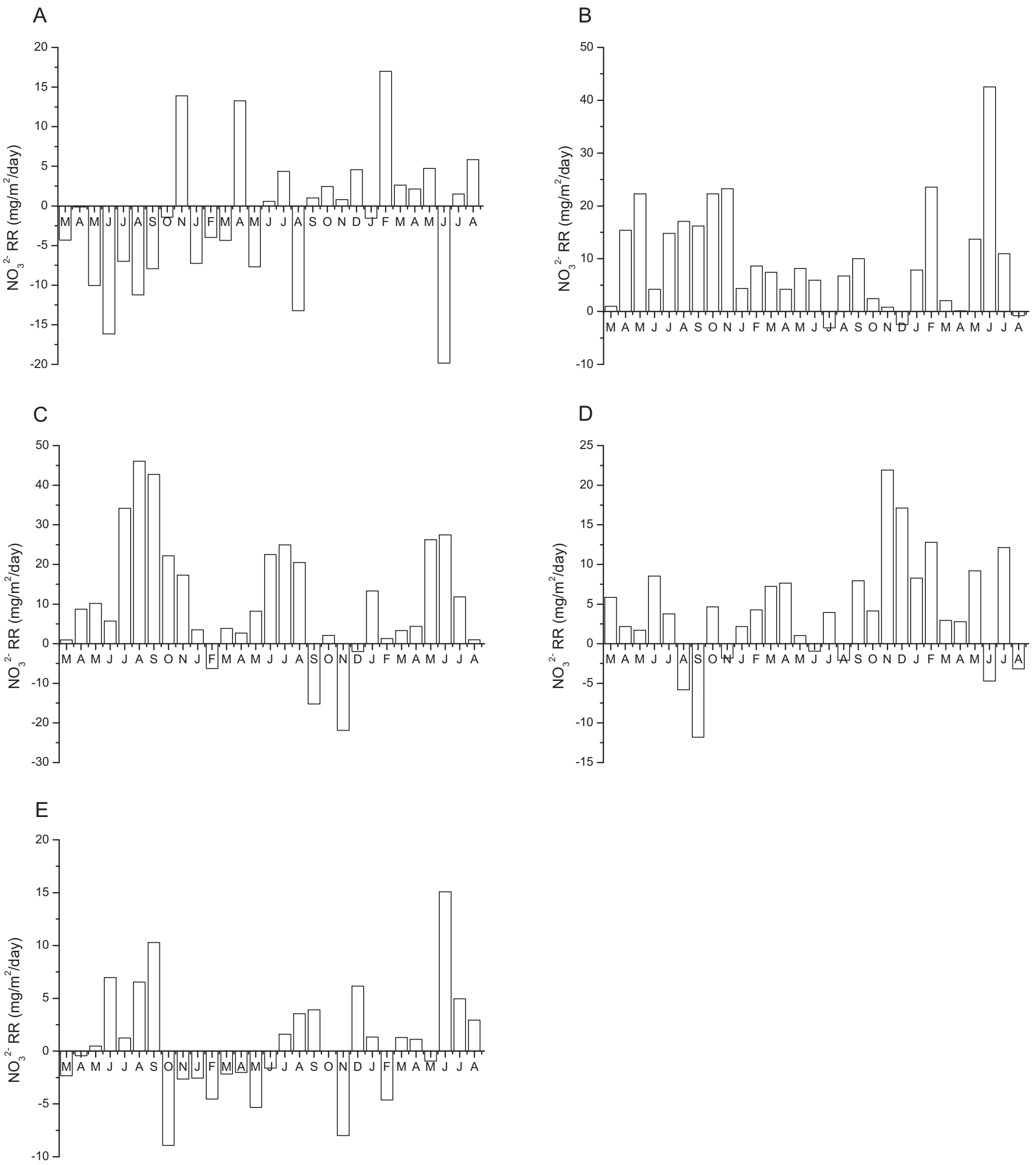


Figure C-6: Nitrate (NO_3^-) Removal Rate ($mg/m^2/day$) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent NO_3^- release. n = 29

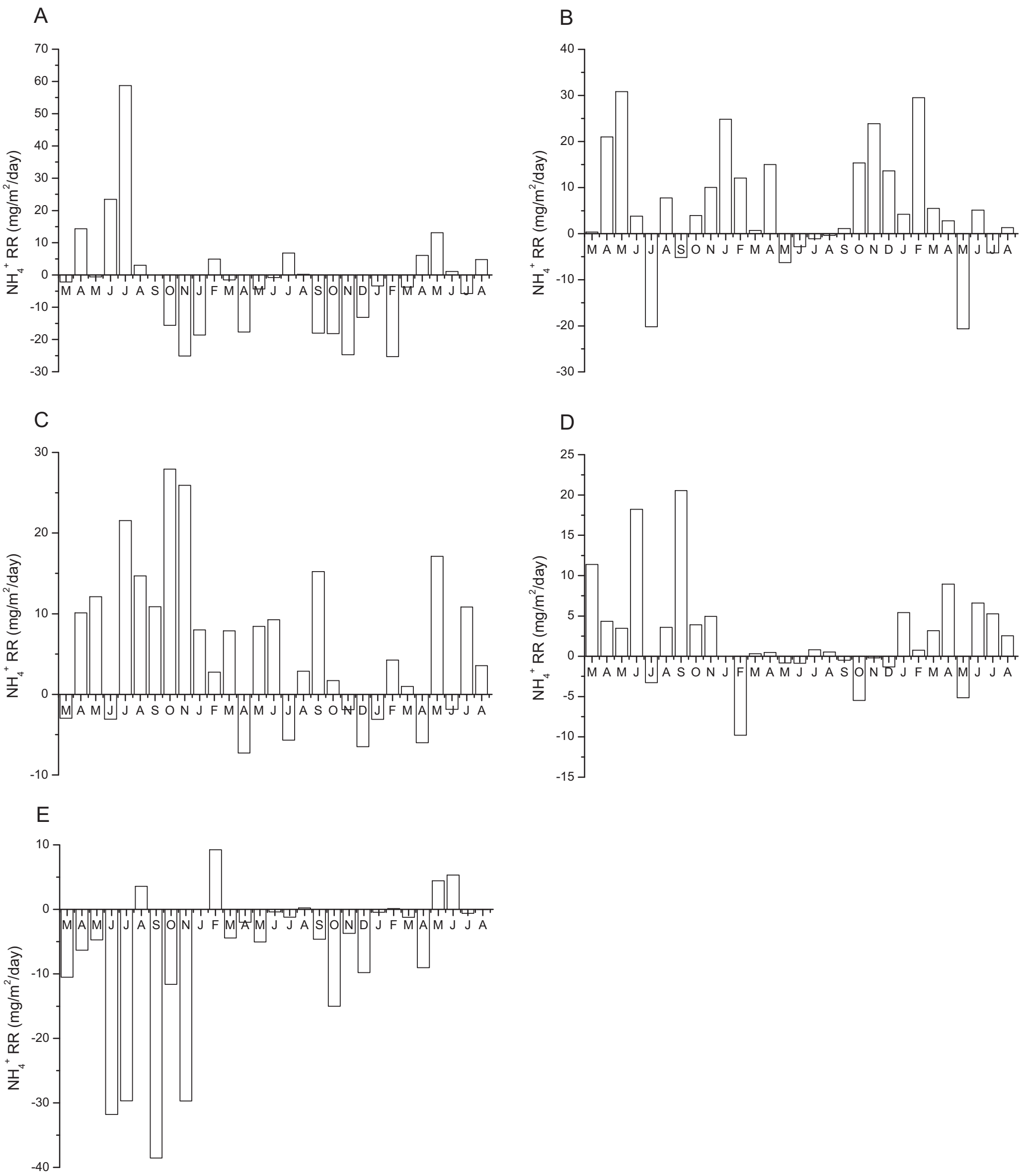


Figure C-7: Ammonium (NH_4^+) Removal Rate (mg/m^2/day) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent NH_4^+ release. n = 29

C-3 P removal efficiency

Table C-3: Results of Tukey's multiple comparisons for the performance for: A. PO_4^{3-} removal efficiency; B. PO_4^{3-} removal rate

A	**site 1**	**site 2**	**site 3**	**site 4**	**outflow**
site 1					
site 2	*				
site 3	*	N.S.			
site 4	*	N.S.	N.S.		
outflow	*	N.S.	N.S.	N.S.	

B	**site 1**	**site 2**	**site 3**	**site 4**	**outflow**
site 1					
site 2	*				
site 3	*	N.S.			
site 4	*	N.S.	N.S.		
outflow	N.S.	N.S.	N.S.	N.S.	

*****, Extremely significant difference ($P<0.001$); **, moderately significant difference ($P<0.01$); *, significant difference ($P<0.05$); N.S., no significant ($P>0.05$); n = 29**

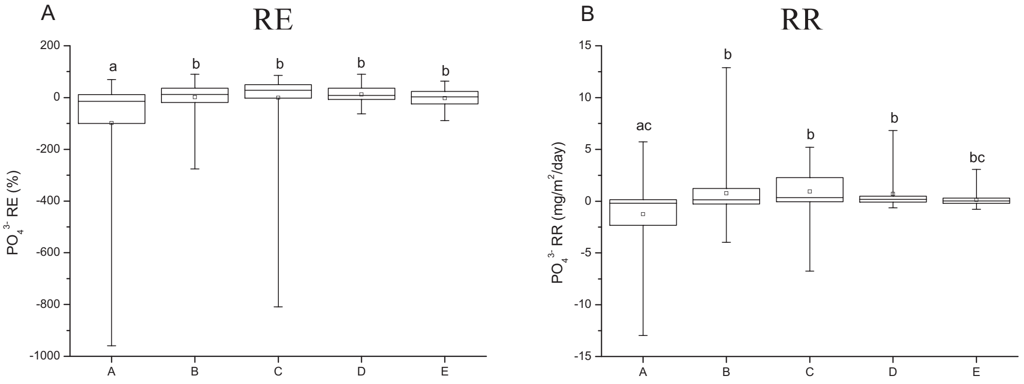


Figure C-8: A. PO_4^{3-} removal efficiency (RE); B. PO_4^{3-} removal rate (RR). The columns marked with different letters indicate significant difference according to Tukey's test (α = 0.05, n= 29). A. site1, B. site2, C. site3, D. site4 and E. outflow.

The Tukey's showed that there are statistically significant differences in the performance within the reed bed. Similar to rest of the other forms of nutrients it showed site 1 had a significant difference from the rest, which was significantly lower regards removal efficiency and removal rate.

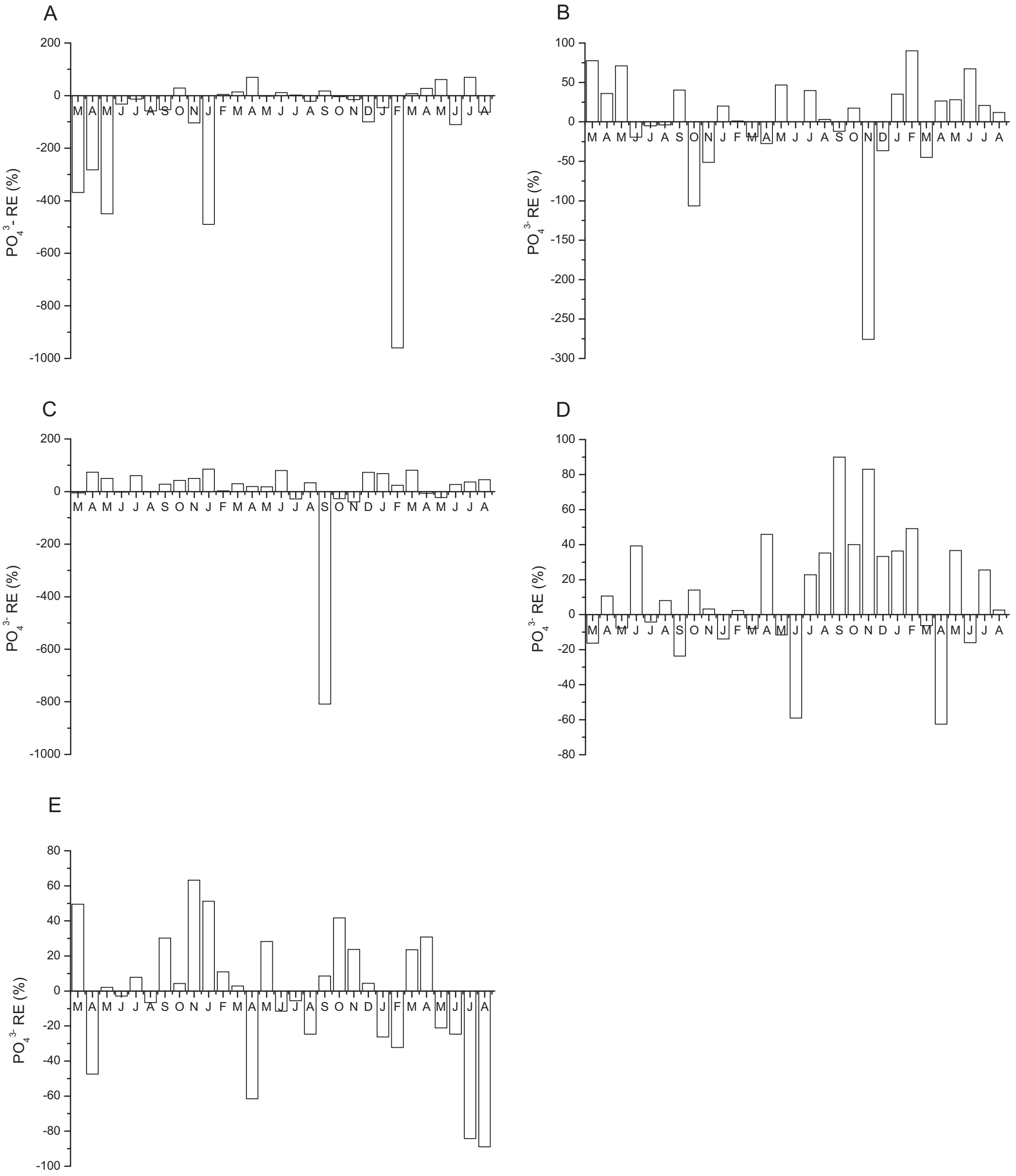


Figure C-9: Phosphate (PO$_4^{3-}$) Removal Efficiency (%) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent PO$_4^{3-}$ release. n = 29

The seasonal pattern for phosphate removal showed that site 1 and site 2 showed low efficiencies of removal during the seasons. In case of site 1 showed that most of the positive performances were during the autumn seasons, but also some of the negative performances were during the autumn seasons. The rest of the sites showed lower and higher efficiencies in regards performances during the growing seasons.

C-4 P removal rate

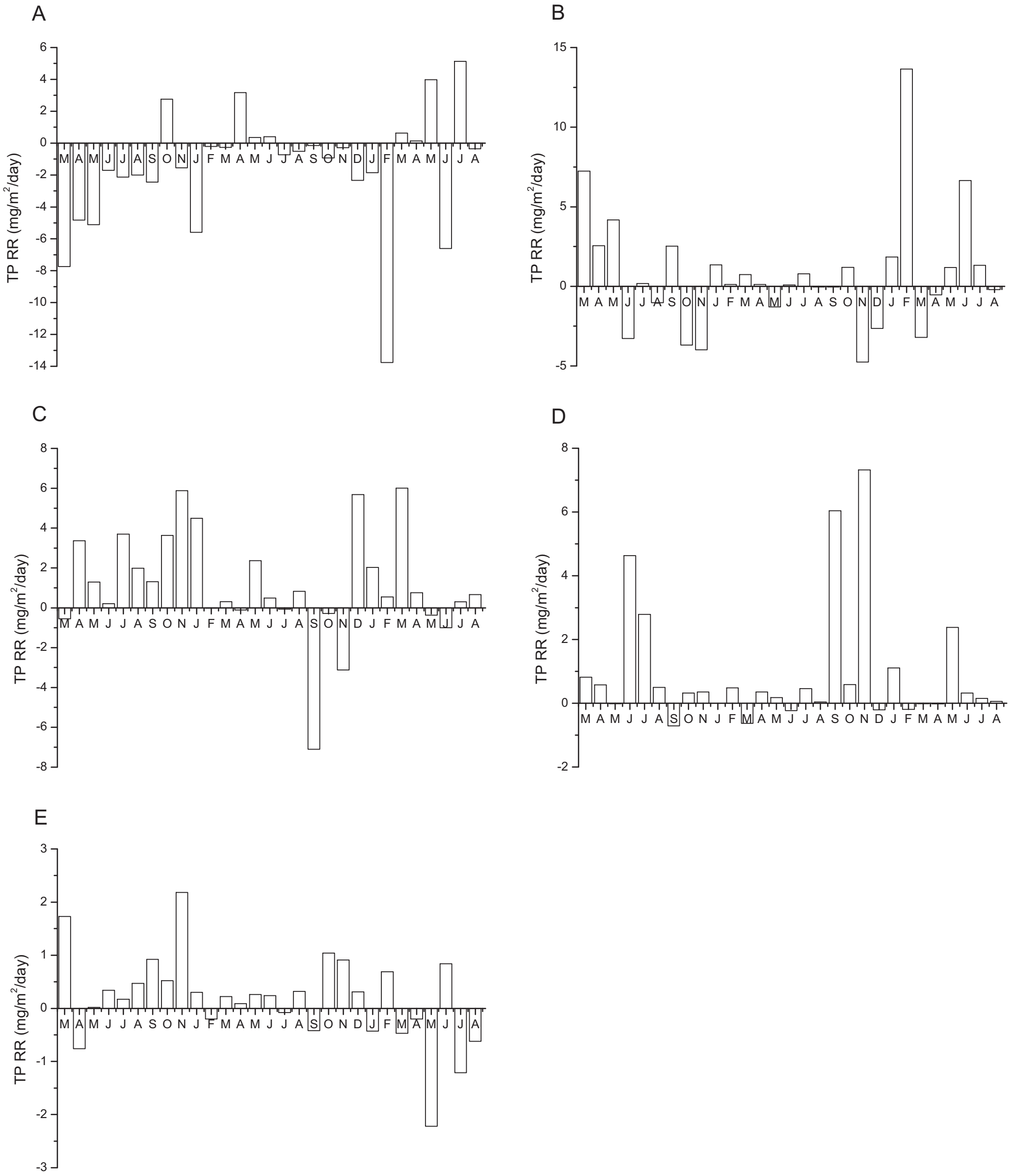


Figure C-10: Total Phosphorus (TP) Removal Rate (mg/m^2/day) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent TP release. n = 29

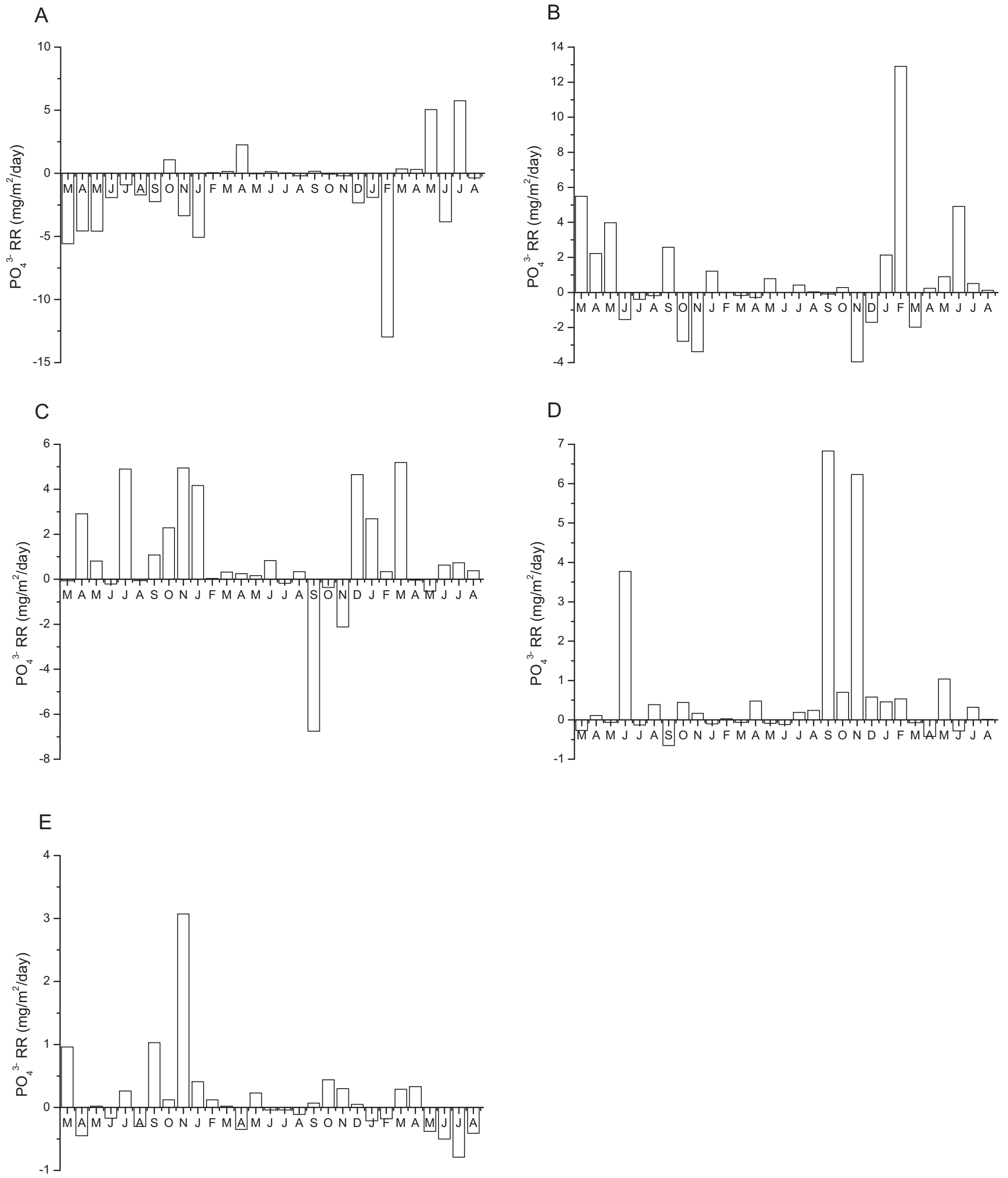


Figure C-11: Phosphate (PO_4^{3-}) Removal Rate (mg/m^2/day) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent PO_4^{3-} release. n = 29

C-5 DOC removal rate

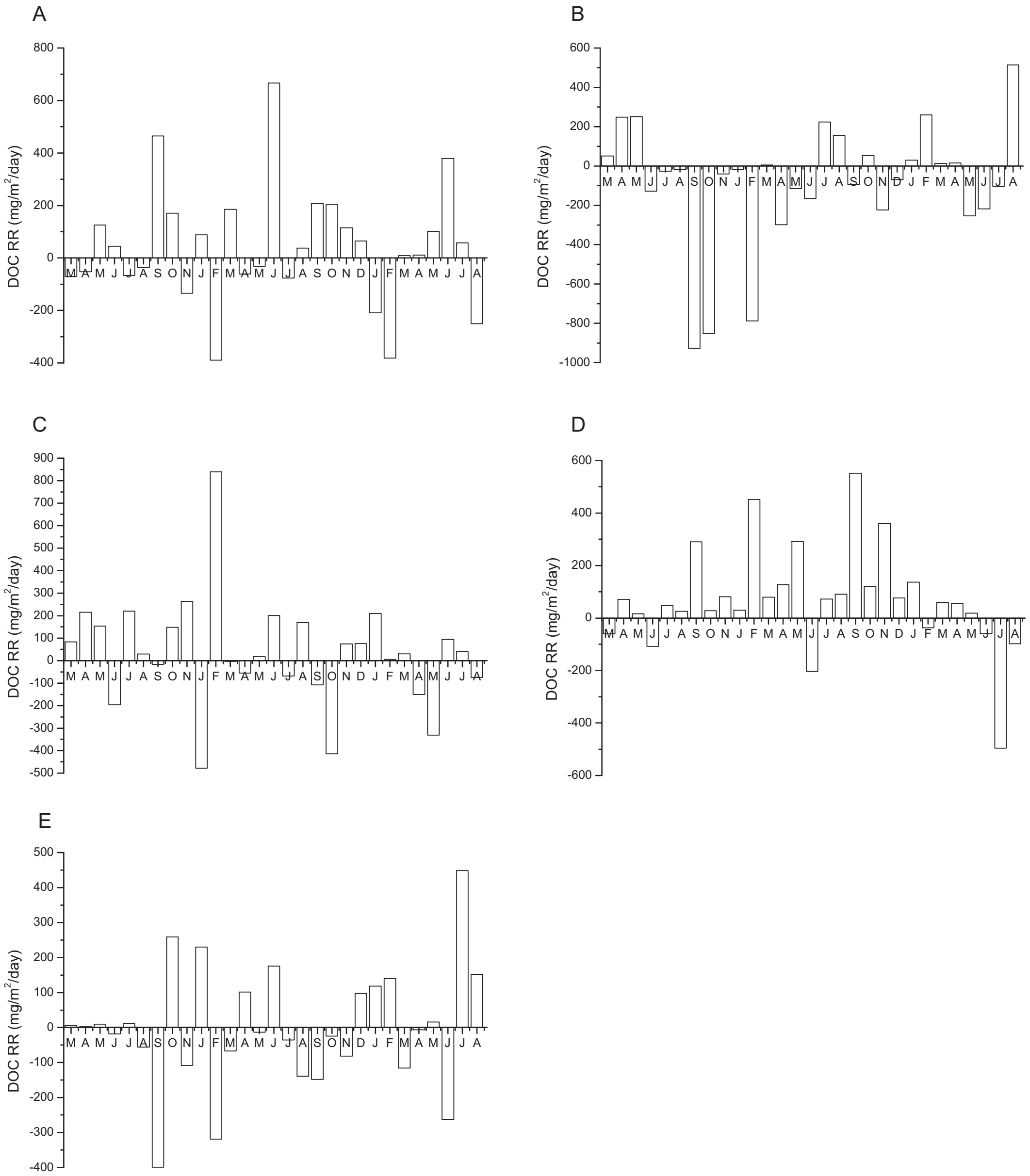


Figure C-12: Dissolved organic carbon (DOC) Removal Rate (mg/m^2/day) for the different sites (A. site 1, B. site 2, C. site 3, D. site 4, E. outflow). Negative columns represent DOC release. n = 29

C-6 Nutrient removal rate in relationship with residence time

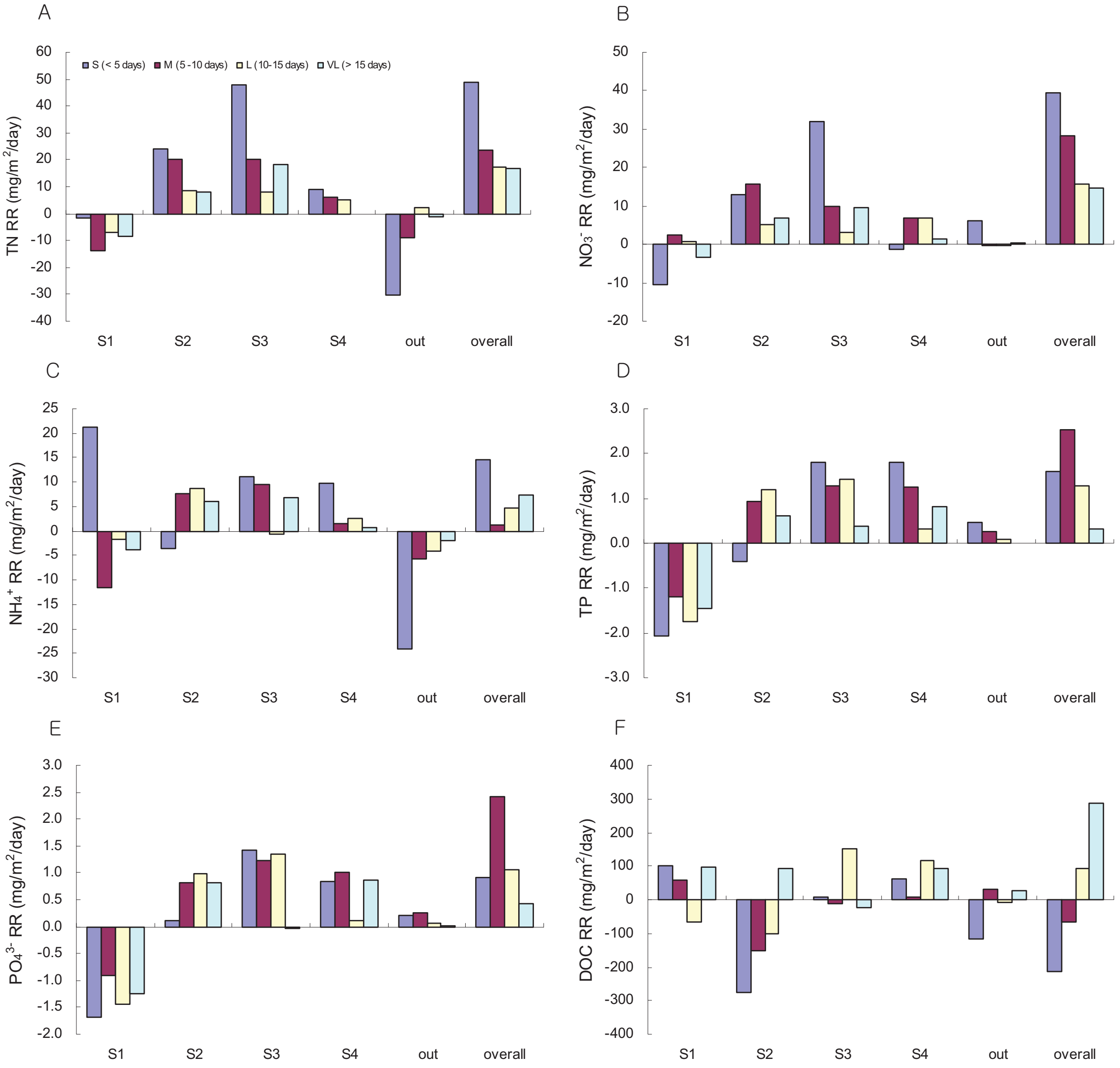


Figure C-13: Nutrient removal rates for the different collection sites at different residence time categories. A. Total Nitrogen, B. Nitrate, C. Ammonium, D. Total Phosphorus, E. Phosphate and F. Dissolved Organic Carbon

Appendix D

D-1 Hypsographic curve

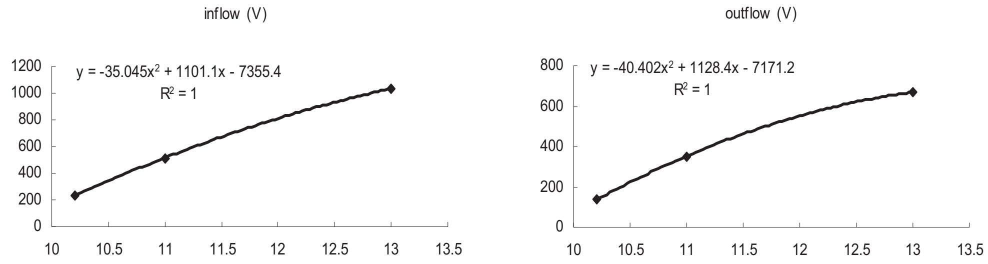


Figure D-1: Hypsographic curve for inflow and outflow area of reed bed pond

Appendix E

E-1 Nitrate

Prediction of Nitrate concentration at the outflow using HEA

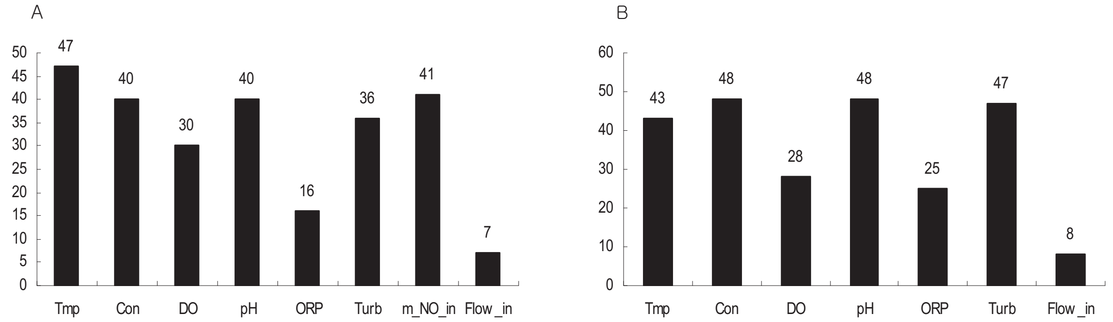


Figure E-1: Input variables used for the prediction of NO_3^- concentration at the outflow area. A. model 1 and B. model 2

A

IF ((Con*(Con*123.557))<8.533)

THEN =(((4.675/(pH/Temp))/pH)/pH)

ELSE =((Turb/((Turb+372.984)+(86.996-ORP)))/Con)

Total error=0.0759 R^2 value=0.48

B

IF (Temp<21.166)

THEN =((((Temp+7.181)+(1.474/DO))-pH)/(((ORP/Temp)+(Temp+22.776))+(Con*254.800)))

ELSE =(Con-(((28.177-ORP)*(Turb*Turb))/((Flow_in+7.025)+(ORP*73.999))))

Total error=0.0751 R^2 value=0.48

Figure E-2: Rule sets developed by HEA. A. model 1 and B. model 2

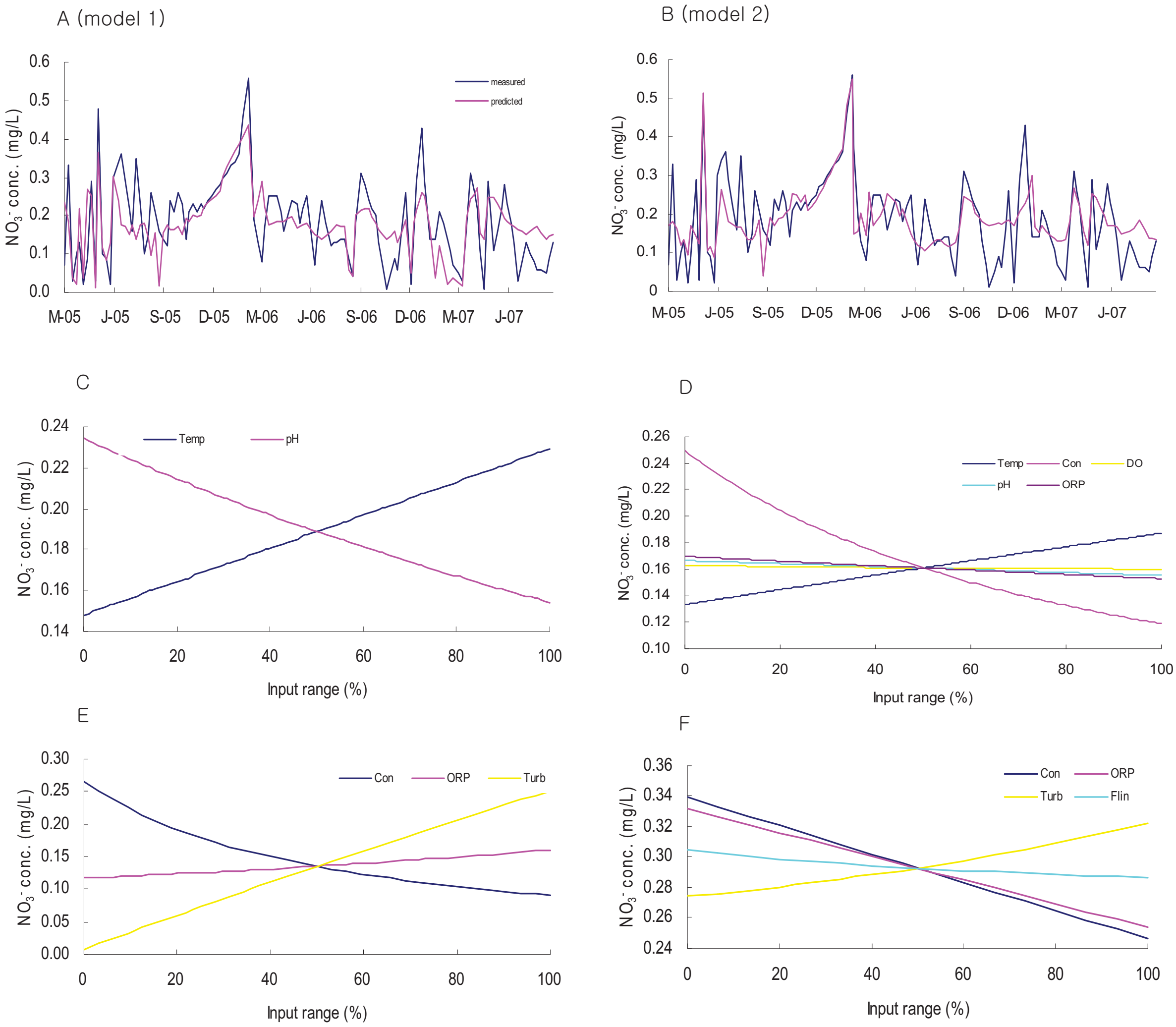


Figure E-3: HEA results for NO_3^- at outflow site. A (model 1) and B (model 2). Comparison between the measured and predicted NO_3^- concentrations; C. & D. Sensitivity for THEN branch and E. & F. Sensitivity for ELSE branch

7 days ahead forecasting of Nitrate using HEA

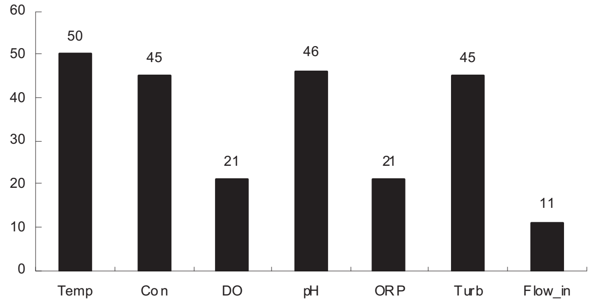


Figure E-4: Input variables used for the forecasting of NO_3^- concentration

IF ((pH/DO)>2.618)

THEN =(Temp/(((-334.901)/(ORP+87.352))+(168.125-(Turb-(-56.694)))))

ELSE =(Temp/(((pH*44.763)-148.679)-84.261))

Total error=0.0825 R^2 value=0.38

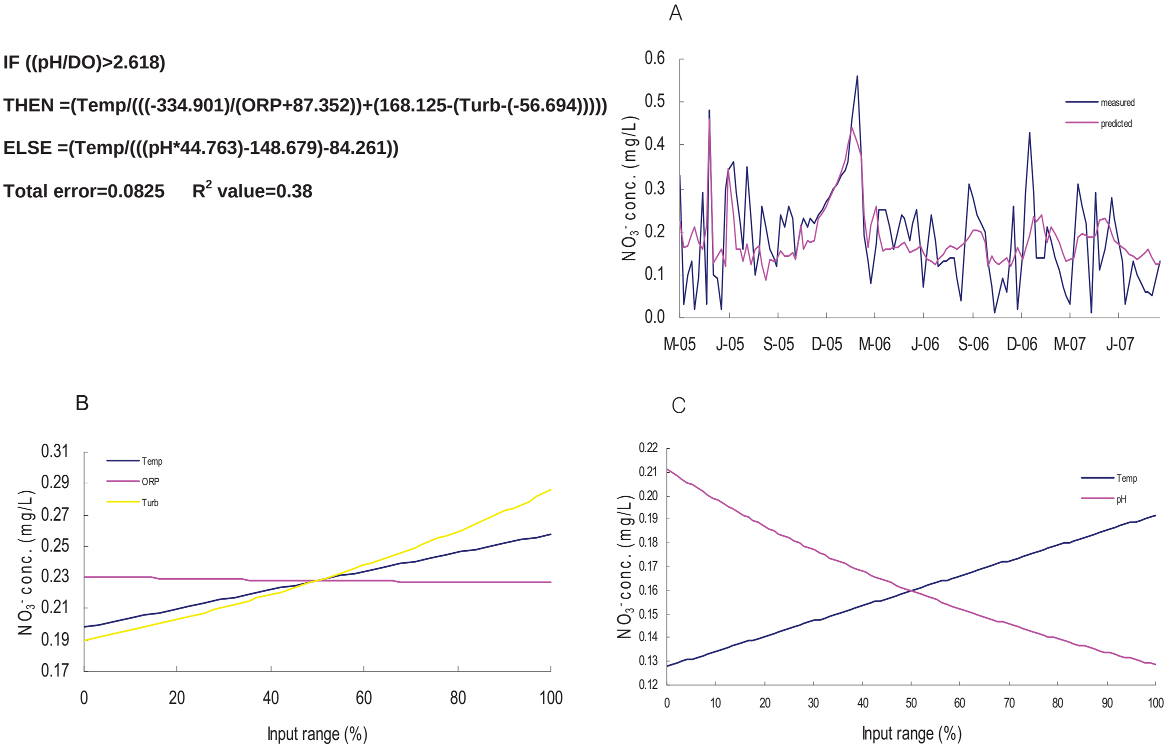


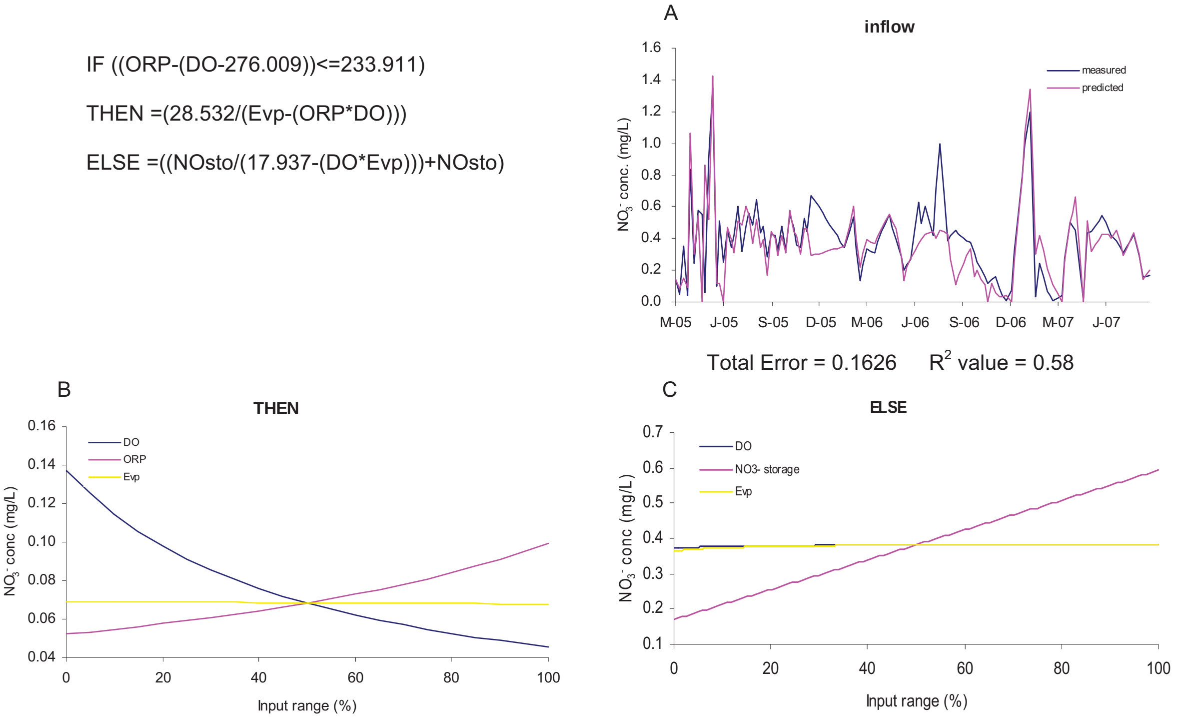
Figure E-5: 7 days ahead forecasting results for NO_3^- at the outflow site. A. Comparison between the measured and predicted TN concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

Knowledge discovery using HEA for prediction of Nitrate

Table E-1: Input variables selected for HEA modeling of NO_3^-

inflow	site 1	site 2	site 3	site 4	outflow
WT	WT	WT	WT	WT	WT
Con	Con	Con	Con	Con	Con
DO	DO	DO	DO	DO	DO
pH	pH	pH	pH	pH	pH
ORP	ORP	ORP	ORP	ORP	ORP
Turb.	Turb.	Turb.	Turb.	Turb.	Turb.
$NO_3^-{}_{(w)}$ conc. (sto)	$NO_3^-{}_{(w)}$ conc. (in)	$NO_3^-{}_{(w)}$ conc. (S1)	$NO_3^-{}_{(w)}$ conc. (S2)	$NO_3^-{}_{(w)}$ conc. (S3)	$NO_3^-{}_{(w)}$ conc. (S4)
$TN_{(sed)}$ (in)	$TN_{(sed)}$ (S1)	$TN_{(sed)}$ (S2)	$TN_{(sed)}$ (S3)	$TN_{(sed)}$ (S4)	$TN_{(sed)}$ (out)
Evp.	Evp.	Evp.	Evp.	Evp.	Evp.
Rainfall	Rainfall	Rainfall	Rainfall	Rainfall	Rainfall

w = water, sed = sediment
sto=storage, in = inflow, S1 = Site 1, S2 = Site 2, S3 = Site 3, S4 = Site 4, out = outflow
WT = Water Temperature, Con = Conductivity, DO = Dissolved Oxygen, ORP = Redox Potential, Turb. = Turbidity and Evp. = Evaporation



IF ((ORP-(DO-276.009))<=233.911)

THEN =(28.532/(Evp-(ORP*DO)))

ELSE =((NOsto/(17.937-(DO*Evp)))+NOsto)

Figure E-6: HEA results for NO_3^- at inflow site. A. Comparison between the measured and predicted NO_3^- concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

IF (Turb<96.337)

THEN =(((prevS*Temp)+DO)/28.130)

ELSE =((Con/Temp)*((prevS*50.438)+(3.444/Con)))

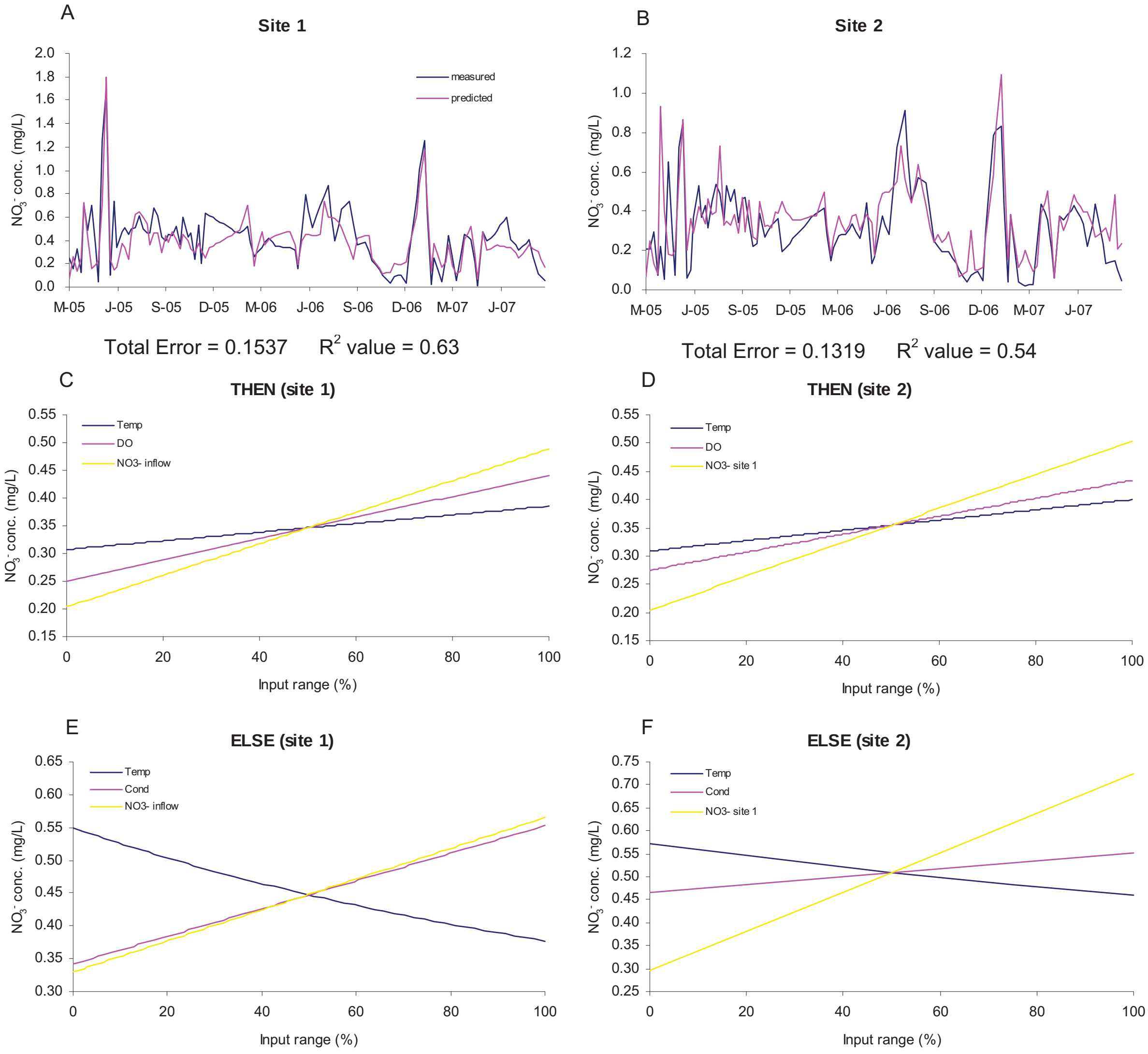


Figure E-7: HEA results for NO_3^- at site 1 and 2. A. Comparison between the measured and predicted NO_3^- concentrations at site 1; B. Comparison between the measured and predicted NO_3^- concentrations at site 2; C. & D. Sensitivity for THEN branch (site 1 & 2); E. & F. Sensitivity for ELSE branch (site 1 & 2)

IF (pH>6.723)

THEN =((Temp+(prevS*19.440))/(((pH*73.924)*Con)+(ORP/pH)))

ELSE =((Temp+(prevS*46.890))/(((104.855-Evp)-ln(|Con|))+19.440))

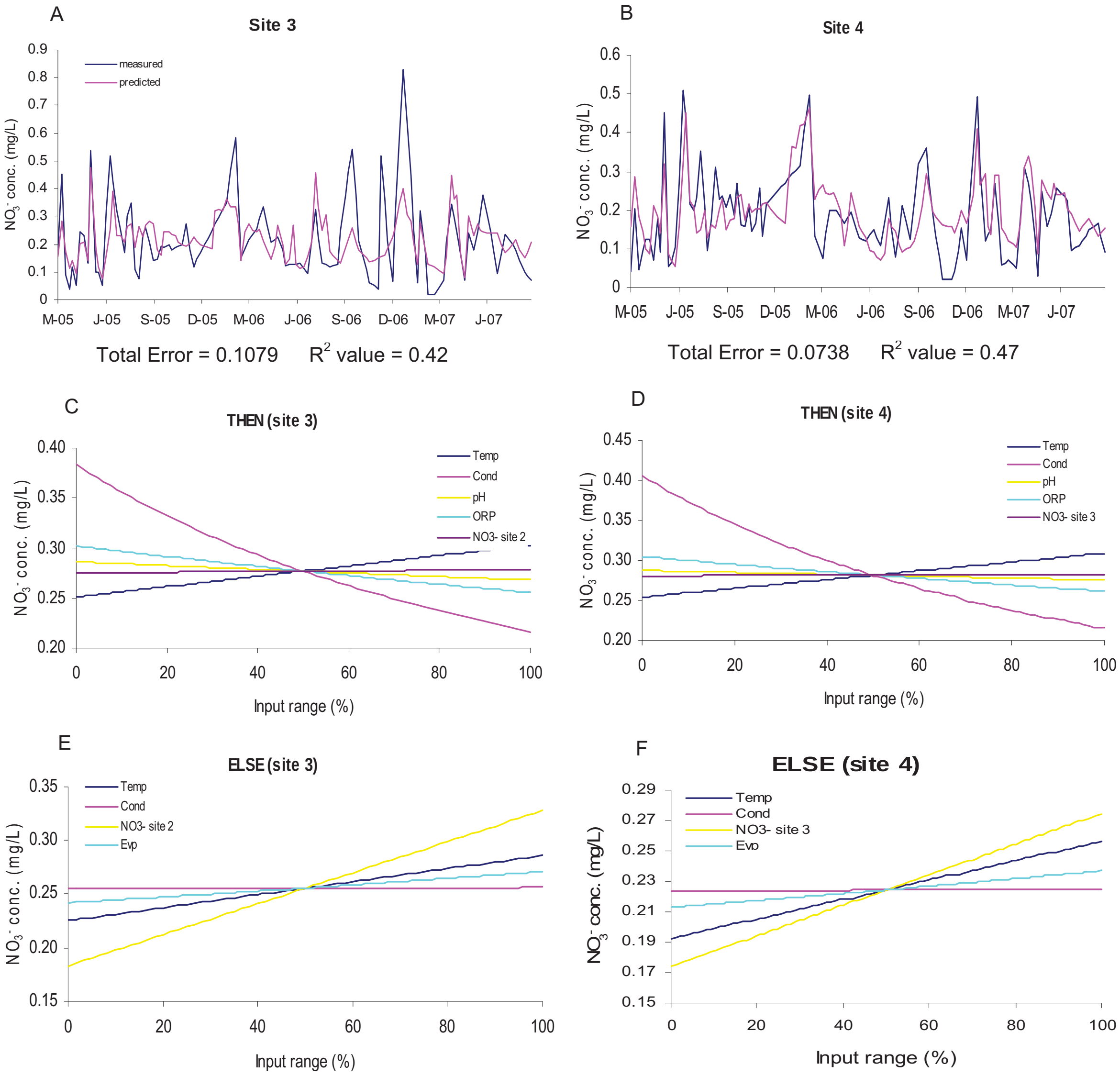


Figure E-8: HEA results for NO_3^- at site 3 and 4. A. Comparison between the measured and predicted NO_3^- concentrations at site 3; B. Comparison between the measured and predicted NO_3^- concentrations at site 4; C. & D. Sensitivity for THEN branch (site 3 & 4); E. & F. Sensitivity for ELSE branch (site 3 & 4)

IF (exp((ORP-73.421))>86.267)

THEN =((NO site4/(338.077/ln(|Temp|)))*(ln(|exp(Rain)|)+115.02

ELSE =((Temp/ln(|(sedTN*(-265.252))|))/pH)

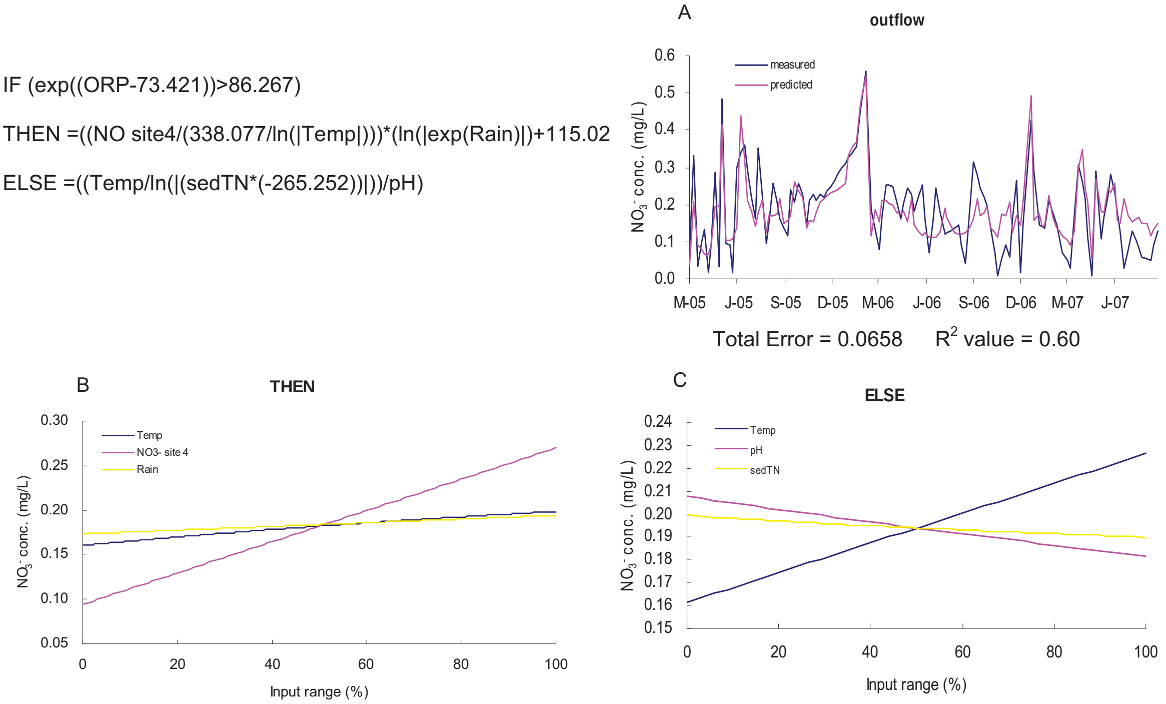


Figure E-9: HEA results for NO_3^- at outflow site. A. Comparison between the measured and predicted NO_3^- concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

General rule for Nitrate prediction using HEA

Rule set selected for general rule application for all the sites in the reed bed pond is the rule set used for the prediction of site3 and 4.

Rule set: IF (pH>6.723)

THEN =((Temp+(prevS*19.440))/(((pH*73.924)*Con)+(ORP/pH)))

ELSE =((Temp+(prevS*46.890))/(((104.855-Evp)-ln(|Con|))+19.440))

Table E-2: R^2 and total error of the rule set for the different sites

	inflow	site 1	site 2	site 3	site 4	outflow
Total Error	0.2232	0.2457	0.1592	0.1079	0.0738	0.0794
R^2	0.06	0.06	0.32	0.42	0.47	0.43

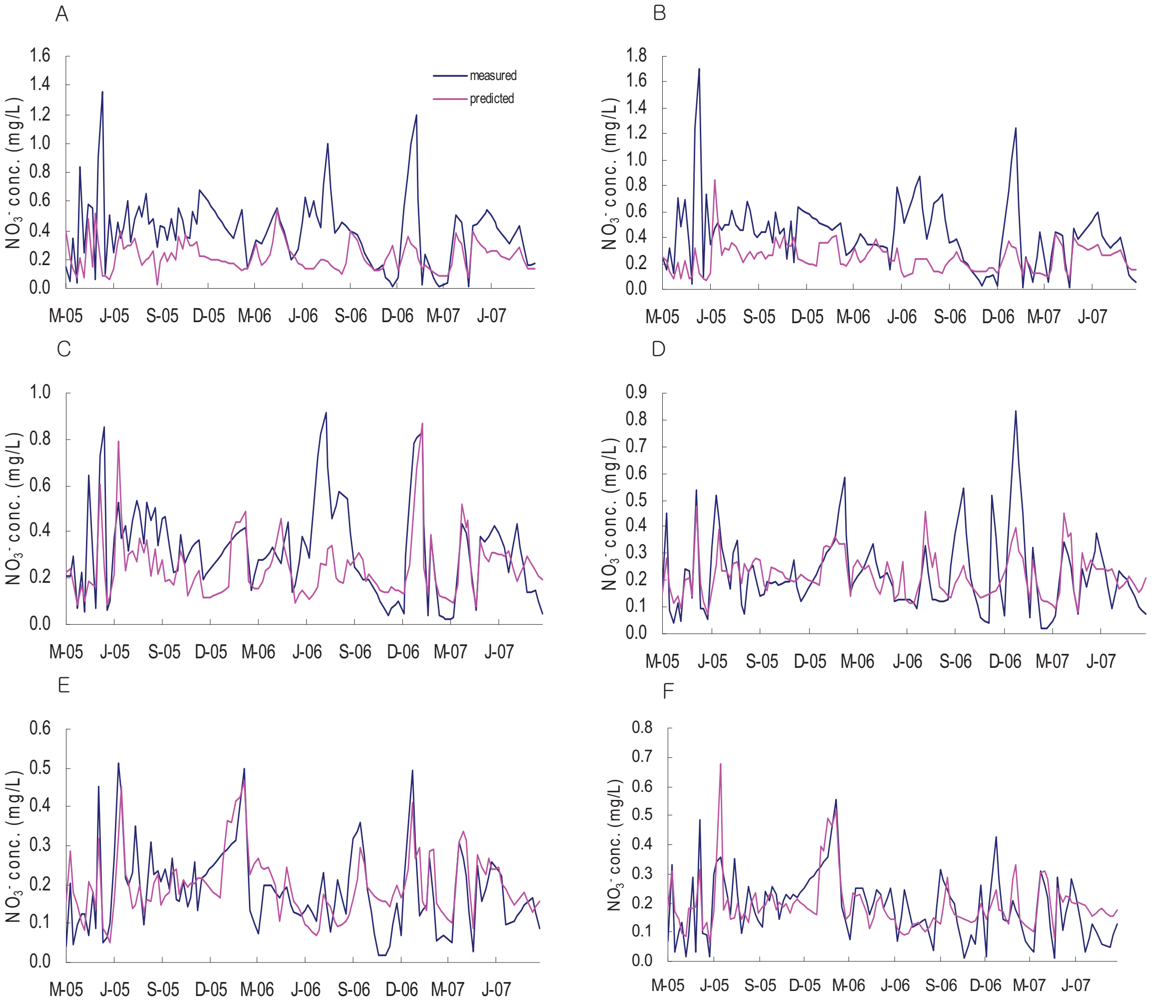


Figure E-10: General rule application for prediction of NO_3^-. A. inflow; B. site 1; C. site 2; D. site 3; E. site 4 and F. outflow

E-2 Ammonium

Prediction of Ammonium concentration at the outflow using HEA

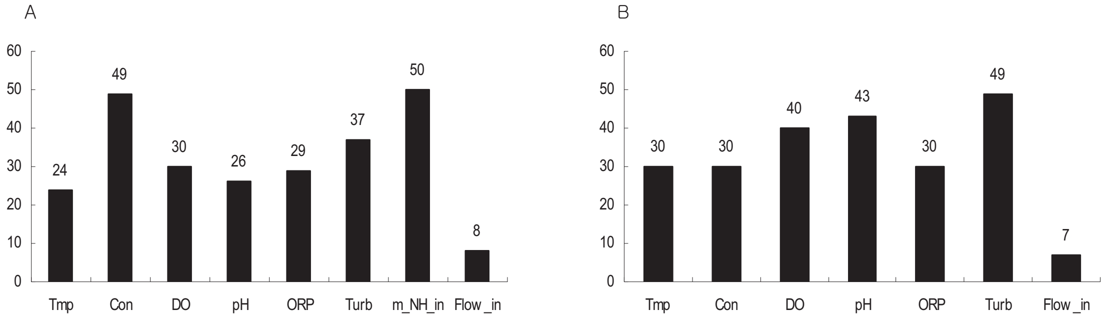


Figure E-11: Input variables used for the prediction of NH_4^+ concentration at the outflow area. A. model 1 and B. model 2

A

IF (ORP<121.628)

THEN =(((NHin*(Turb+56.674))+0.590)/(((NHin*73.304)*(Con*pH))+33.247))

ELSE =(((NHin*191.461)+Temp)/((DO+(DO+150.269))+137.011))

Total error=0.1408 R^2 value=0.70

B

IF (((DO+82.578)<=86.703)OR(ORP>=87.497))

THEN =(2.275/((pH-(Turb/ORP))-(Turb/(DO*47.852))))

ELSE =((-197.271)/((pH-(Turb/40.518))*((pH-Temp)*pH)))

Total error=0.2007 R^2 value=0.39

Figure E-12: Rule sets developed by HEA. A. model 1 and B. model 2

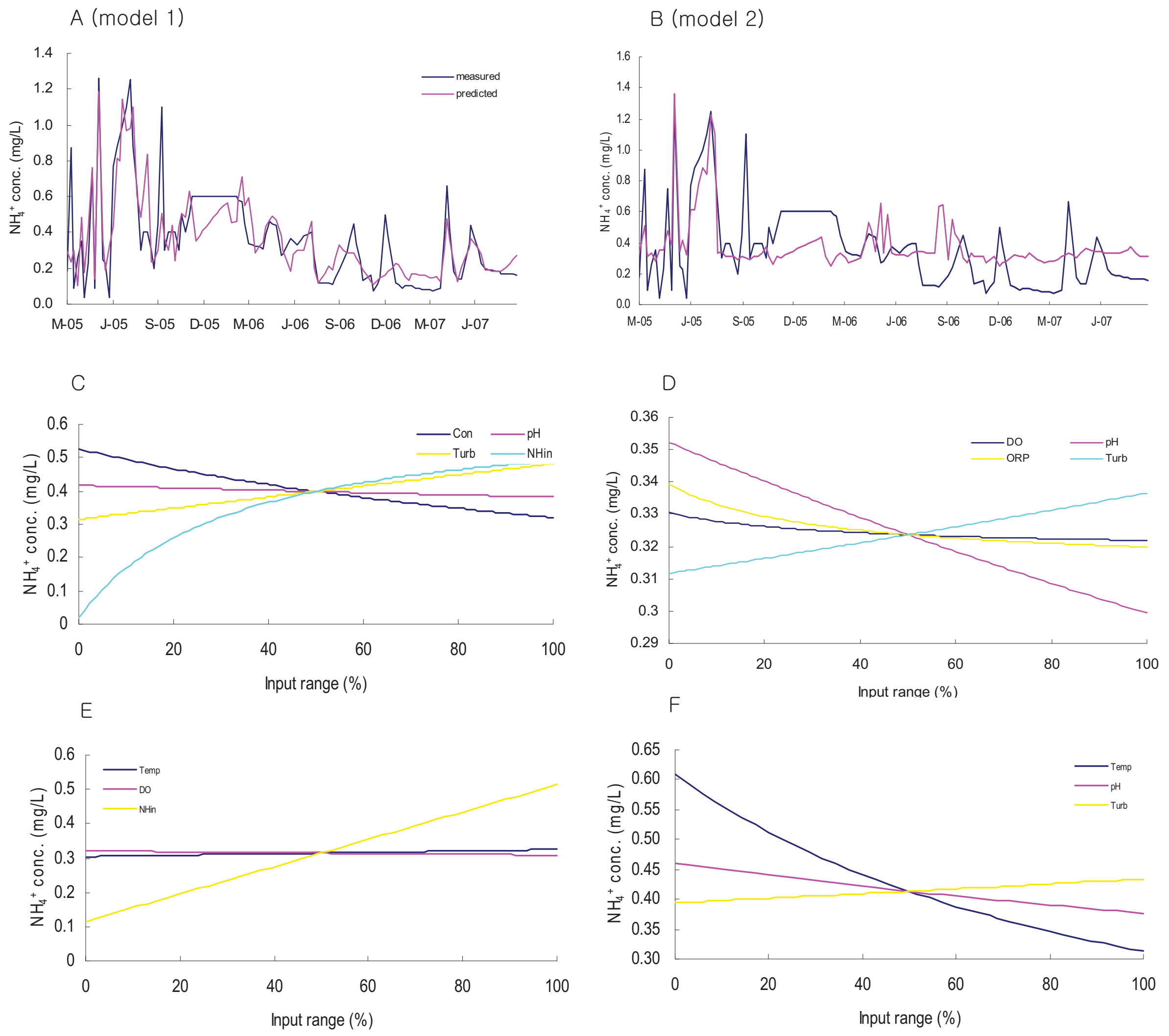


Figure E-13: HEA results for NH_4^+ at outflow site. A (model 1) and B (model 2). Comparison between the measured and predicted NH_4^+ concentrations; C. & D. Sensitivity for THEN branch and E. & F. Sensitivity for ELSE branch

7 days ahead forecasting of Ammonium using HEA

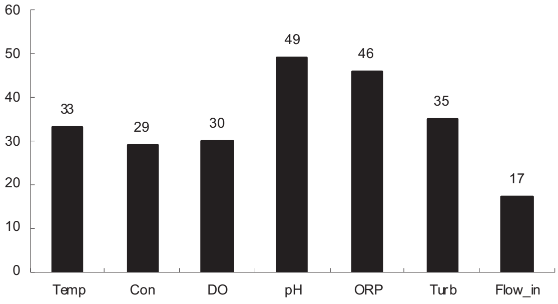


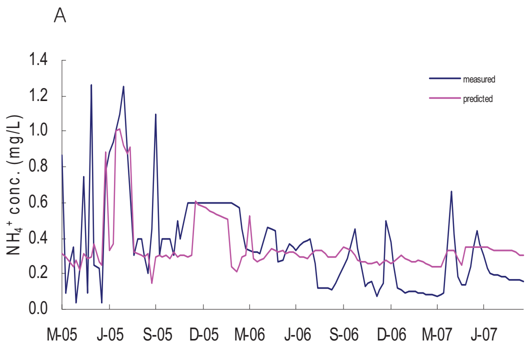
Figure E-14: Input variables used for the forecasting of NH_4^+ concentration

IF
(((Temp<13.019)OR(Temp>21.878))AND((ORP<=91.022)OR(ORP<=94.802)))

THEN =(121.608/(((pH*Temp)+(Con*85.019))+Turb))

ELSE
=(84.943/(((pH*16.422)+(Con*121.608))+((pH*14.914)+(Con*141.090))))

Total error=0.2055 R^2 value=0.36



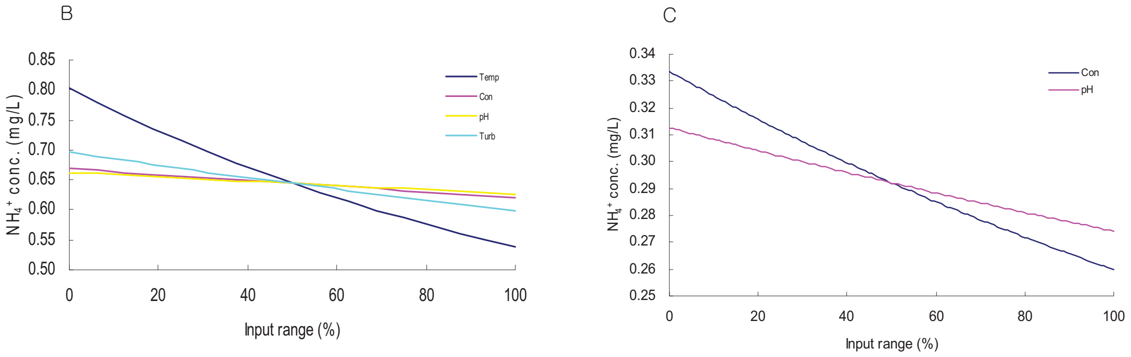


Figure E-15: 7 days ahead forecasting results for NH_4^+ at the outflow site. A. Comparison between the measured and predicted TN concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

Knowledge discovery using HEA for prediction of Ammonium

Table E-3: Input variables selected for HEA modeling of NH_4^+

inflow	site 1	site 2	site 3	site 4	outflow
WT	WT	WT	WT	WT	WT
Con	Con	Con	Con	Con	Con
DO	DO	DO	DO	DO	DO
pH	pH	pH	pH	pH	pH
ORP	ORP	ORP	ORP	ORP	ORP
Turb.	Turb.	Turb.	Turb.	Turb.	Turb.
$NH_4^+{}_{(w)}$ conc. (sto)	$NH_4^+{}_{(w)}$ conc. (in)	$NH_4^+{}_{(w)}$ conc. (S1)	$NH_4^+{}_{(w)}$ conc. (S2)	$NH_4^+{}_{(w)}$ conc. (S3)	$NH_4^+{}_{(w)}$ conc. (S4)
$TN_{(sed)}$ (in)	$TN_{(sed)}$ (S1)	$TN_{(sed)}$ (S2)	$TN_{(sed)}$ (S3)	$TN_{(sed)}$ (S4)	$TN_{(sed)}$ (out)
Evp.	Evp.	Evp.	Evp.	Evp.	Evp.
Rainfall	Rainfall	Rainfall	Rainfall	Rainfall	Rainfall

w = water, sed = sediment
sto=storage, in = inflow, S1 = Site 1, S2 = Site 2, S3 = Site 3, S4 = Site 4, out = outflow
WT = Water Temperature, Con = Conductivity, DO = Dissolved Oxygen, ORP = Redox Potential, Turb. = Turbidity and Evp. = Evaporation

IF ((exp((Con*Temp))>=58.437)AND(Temp<16.231))

THEN =(Turb/ln(|(exp(DO)*(34.903/NH sto))|))

ELSE =(NH sto+(NH sto/((DO/NH sto)+exp(Con))))

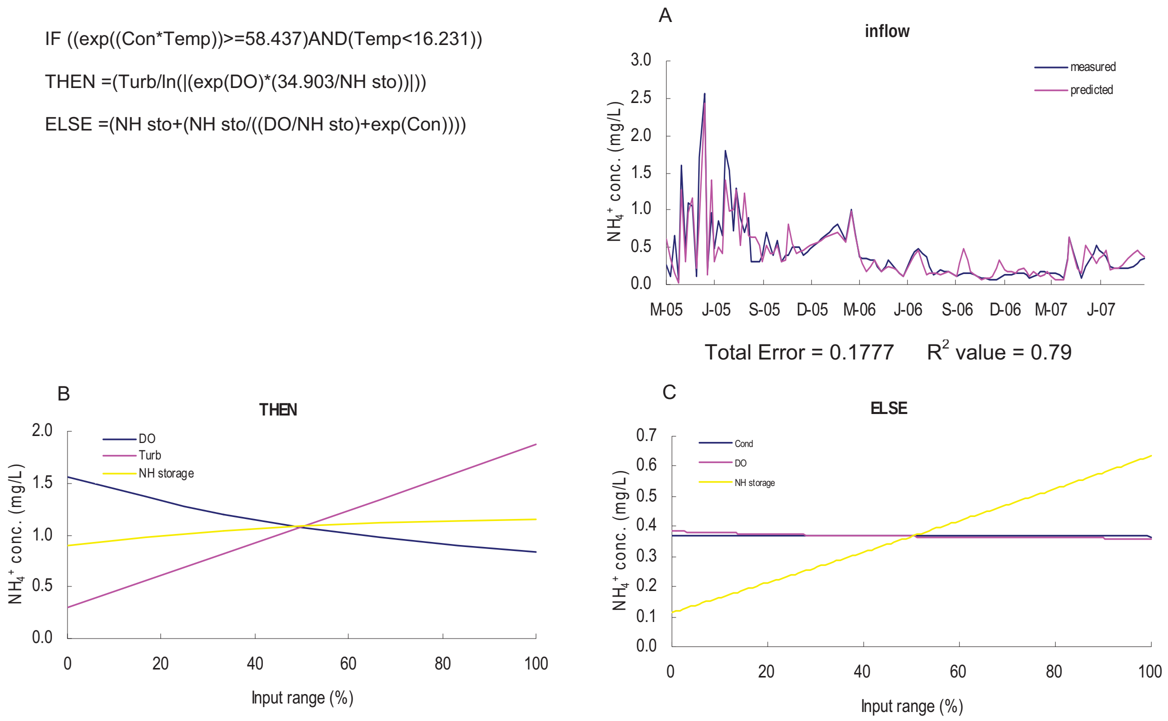
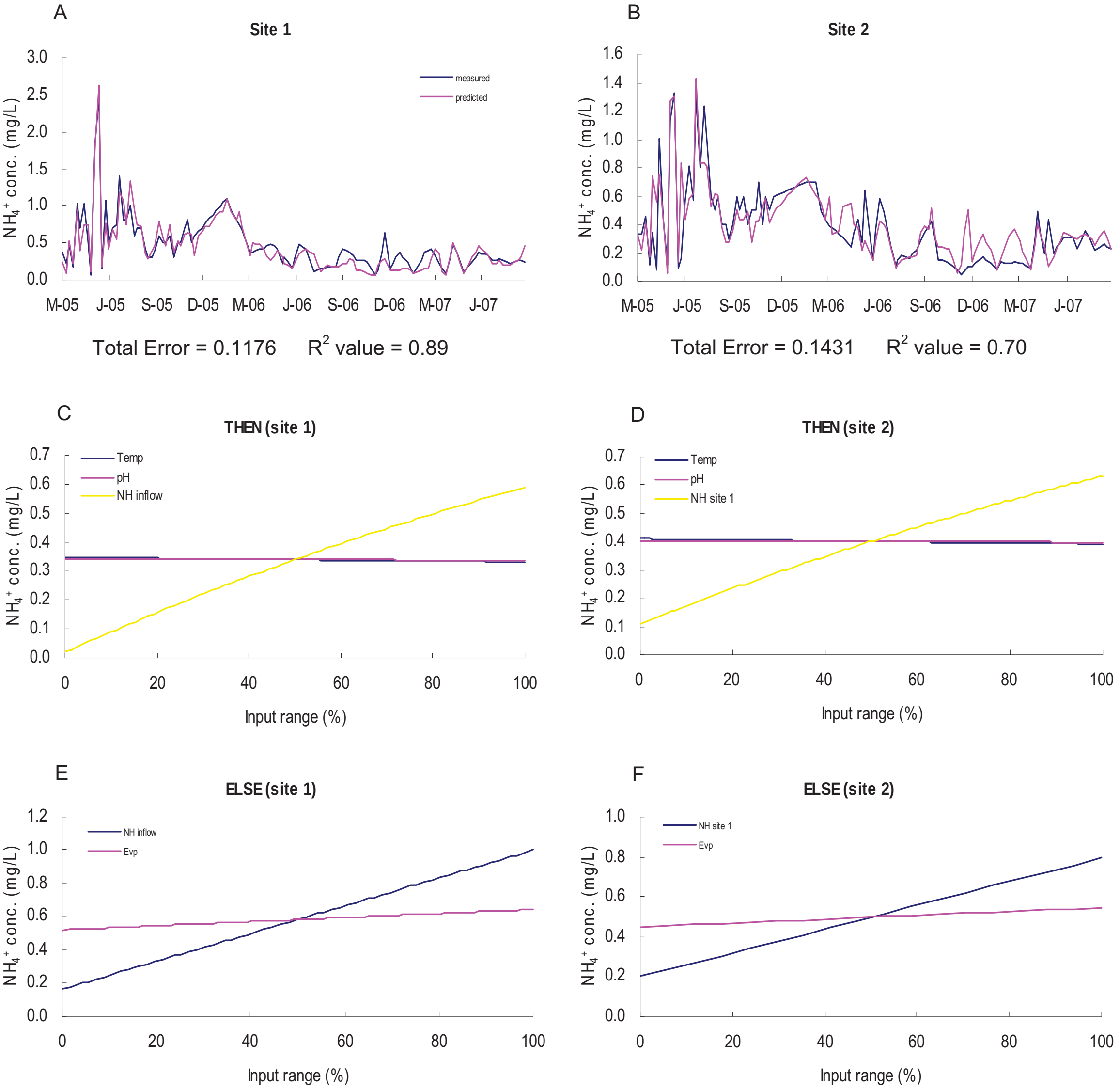


Figure E-16: HEA results for NH_4^+ at inflow site. A. Comparison between the measured and predicted NH_4^+ concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

```
IF (((Turb/ln(|ORP|))/ln(|ORP|))<=10.242)
THEN =(prevS*exp(((pH/(-368.638))*(prevS*Temp))))
ELSE =(prevS-(Evp/(-92.680)))
```



Total Error = 0.1176 R^2 value = 0.89

Total Error = 0.1431 R^2 value = 0.70

Figure E-17: HEA results for NH_4^+ at site 1 and 2. A. Comparison between the measured and predicted NH_4^+ concentrations at site 1; B. Comparison between the measured and predicted NH_4^+ concentrations at site 2; C. & D. Sensitivity for THEN branch (site 1 & 2); E. & F. Sensitivity for ELSE branch (site 1 & 2)

IF (ln(|ln(|Rain|)|)>65.234)

THEN =(204.487/(sedTN+((92.110/prevS)-ln(|prevS|))))

ELSE =(113.518/((ORP/Evp)+((121.647/prevS)-(DO-Evp))))

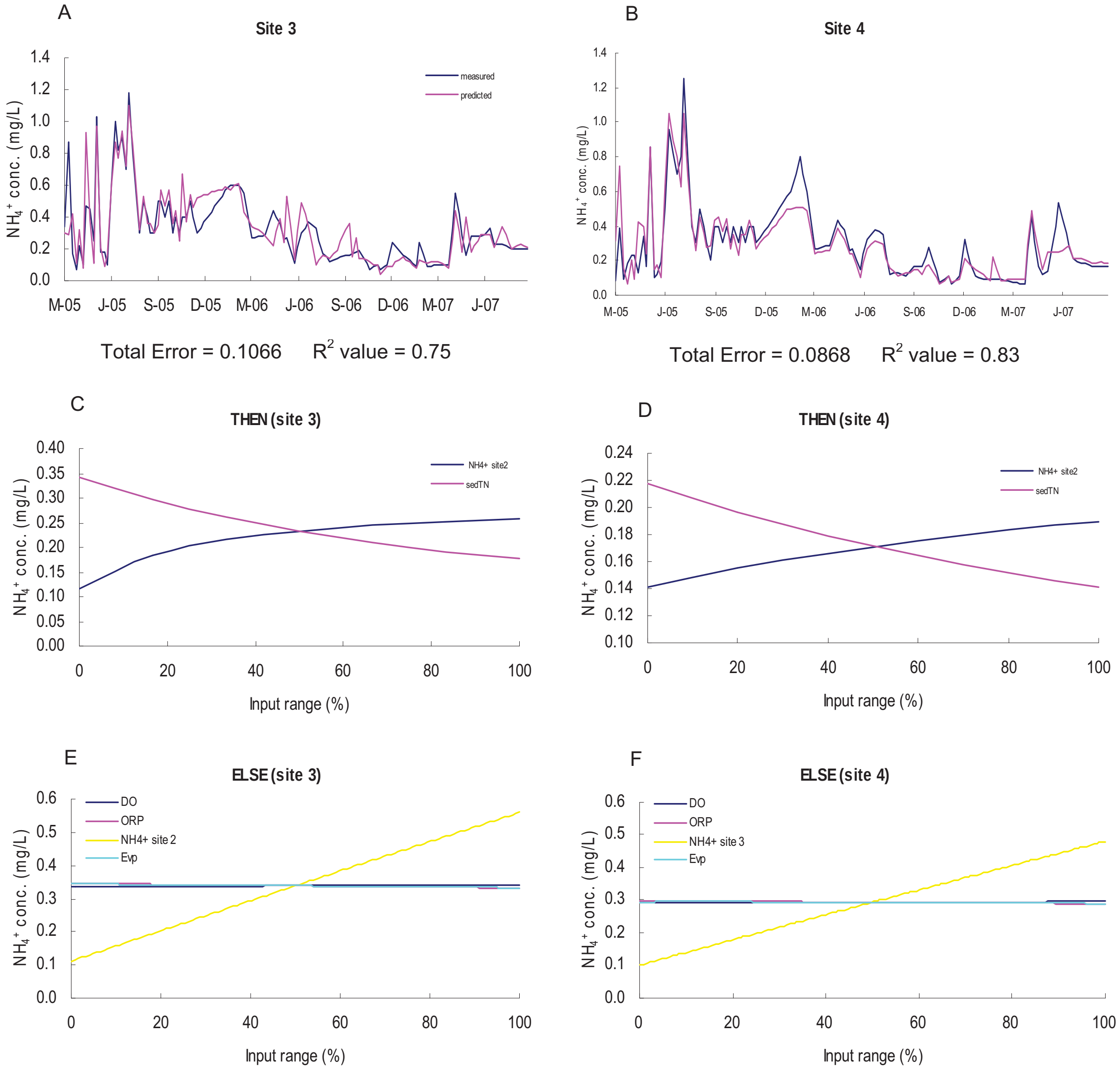


Figure E-18: HEA results for NH_4^+ at site 3 and 4. A. Comparison between the measured and predicted NH_4^+ concentrations at site 3; B. Comparison between the measured and predicted NH_4^+ concentrations at site 4; C. & D. Sensitivity for THEN branch (site 3 & 4); E. & F. Sensitivity for ELSE branch (site 3 & 4)

IF (ln(|Rain|)<3.542)

THEN =(NH site4+((25.428/Evp)/(ORP+(408.199/DO))))

ELSE =(NH site4+((NH site4*54.757)/((ORP+198.679)-(Evp*2.627))))

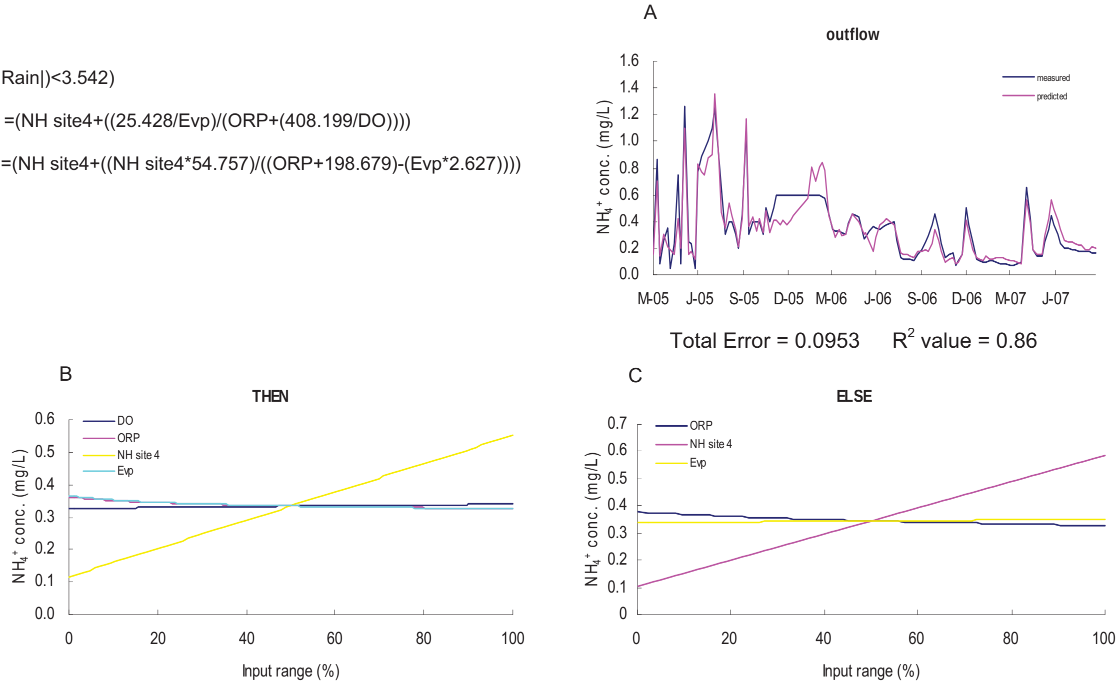


Figure E-19: HEA results for NH_4^+ at outflow site. A. Comparison between the measured and predicted NH_4^+ concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

General rule for Ammonium prediction using HEA

Rule set selected for general rule application for all the sites in the reed bed pond is the rule set used for the prediction of site1 and 2.

Rule set: IF (((Turb/ln(|ORP|))/ln(|ORP|))<=10.242

THEN =(prevS*exp(((pH/(-38.638))*(prevS*Temp))))

ELSE =(prevS-(Evp/(-92.680)))

Table E-4: R^2 and total error of the rule set for the different sites

	inflow	site 1	site 2	site 3	site 4	outflow
Total Error	0.3052	0.1176	0.1431	0.1347	0.0979	0.1325
R^2	0.39	0.88	0.70	0.60	0.78	0.73

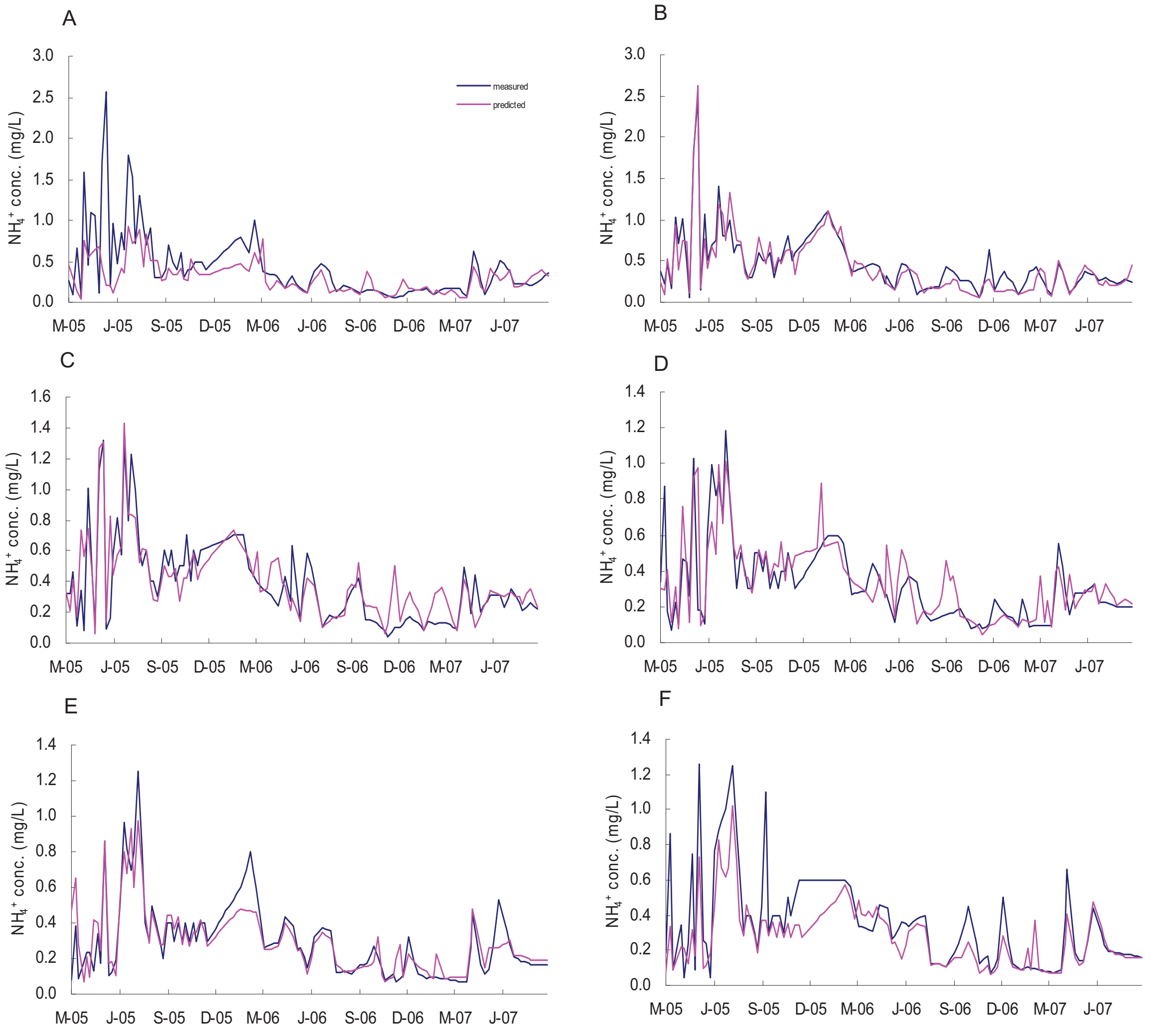


Figure E-20: General rule application for prediction of NH_4^+. A. inflow; B. site 1; C. site 2; D. site 3; E. site 4 and F. outflow

E-3 Phosphate

Prediction of Phosphate concentration at the outflow using HEA

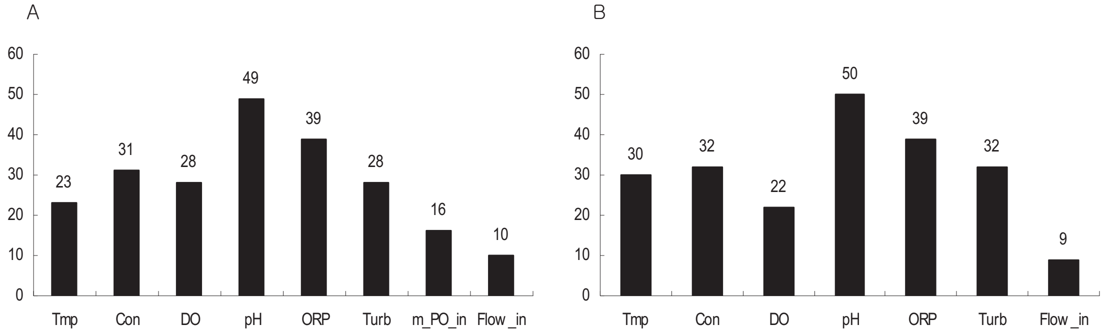


Figure E-21: Input variables used for the prediction of PO_4^{3-} concentration at the outflow area. A. model 1 and B. model 2

A

IF ((ORP*(ORP+31.143))<78.897)

THEN =((((229.253/Temp)-pH)/pH)/(pH/Con))

ELSE =((((Con+296.235)/pH)/((296.235/Turb)+461.735))/pH)

Total error=0.0052 R^2 value=0.57

B

IF (((Con*65.347)+Con)>=16.534)

THEN =((158.548/((ORP-Turb)+(pH*Temp)))/(Temp+(pH*pH)))

ELSE =((-15.738)/(((pH*(-184.432))+(Turb+ORP))+((ORP+Turb)-173.105)))

Total error=0.0054 R^2 value=0.53

Figure E-22: Rule sets developed by HEA. A. model 1 and B. model 2

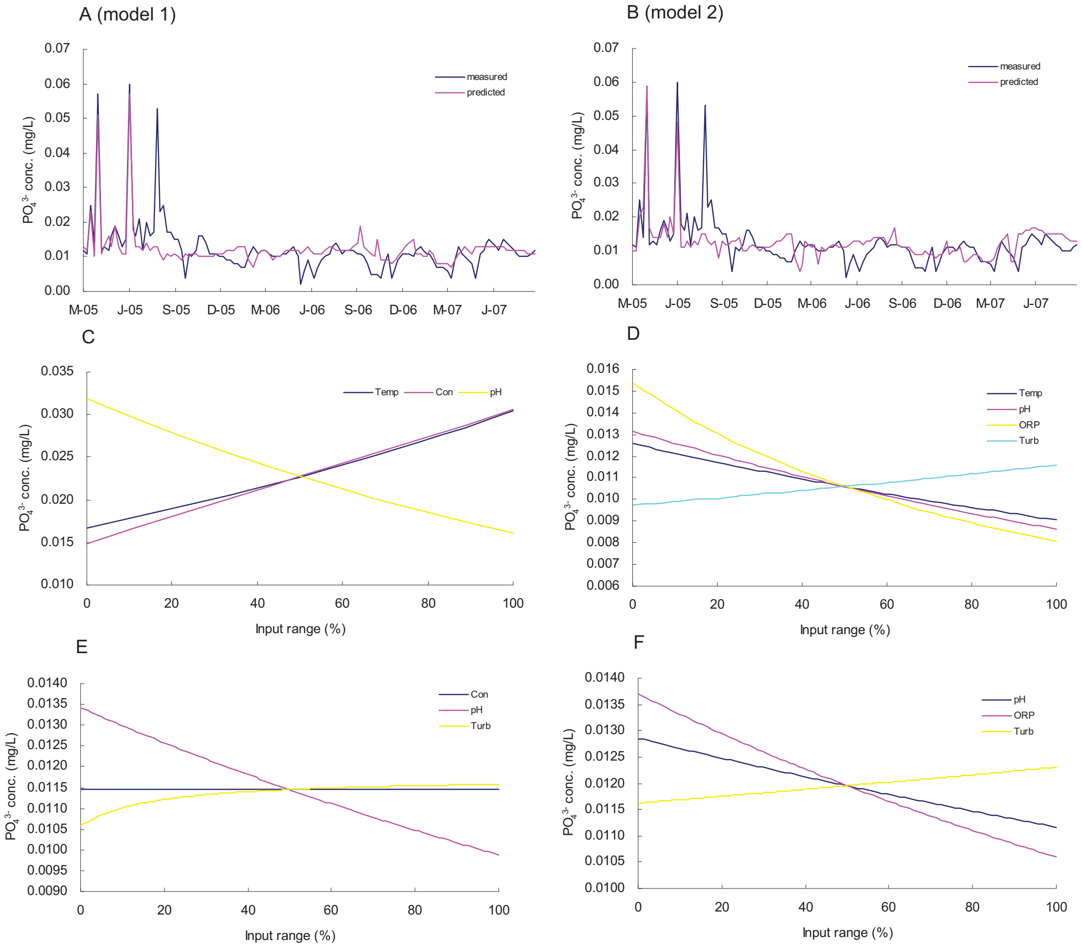


Figure E-23: HEA results for PO$_4^{3-}$ at outflow site. A (model 1) and B (model 2). Comparison between the measured and predicted PO$_4^{3-}$ concentrations; C. & D. Sensitivity for THEN branch and E. & F. Sensitivity for ELSE branch

7 days ahead forecasting of Phosphate using HEA

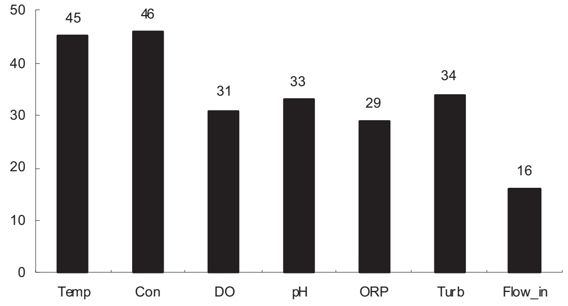


Figure E-24: Input variables used for the forecasting of PO_4^{3-} concentration

IF ((Con*(Con*(Con*419.798)))<34.622)

THEN =(7.312/((Con*245.798)*((Temp+10.820)-(Con*57.442))))

ELSE =((-342.651)/((Con*(Turb*DO))*(-349.774)))

Total error=0.0056 R^2 value=0.52

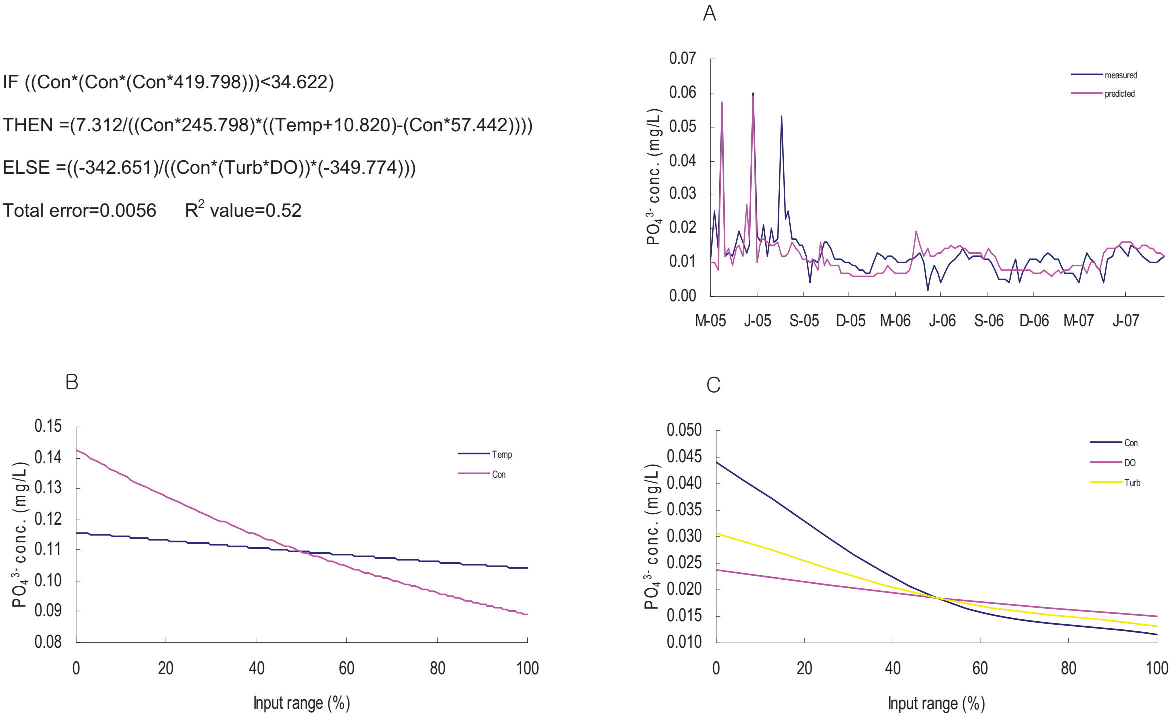


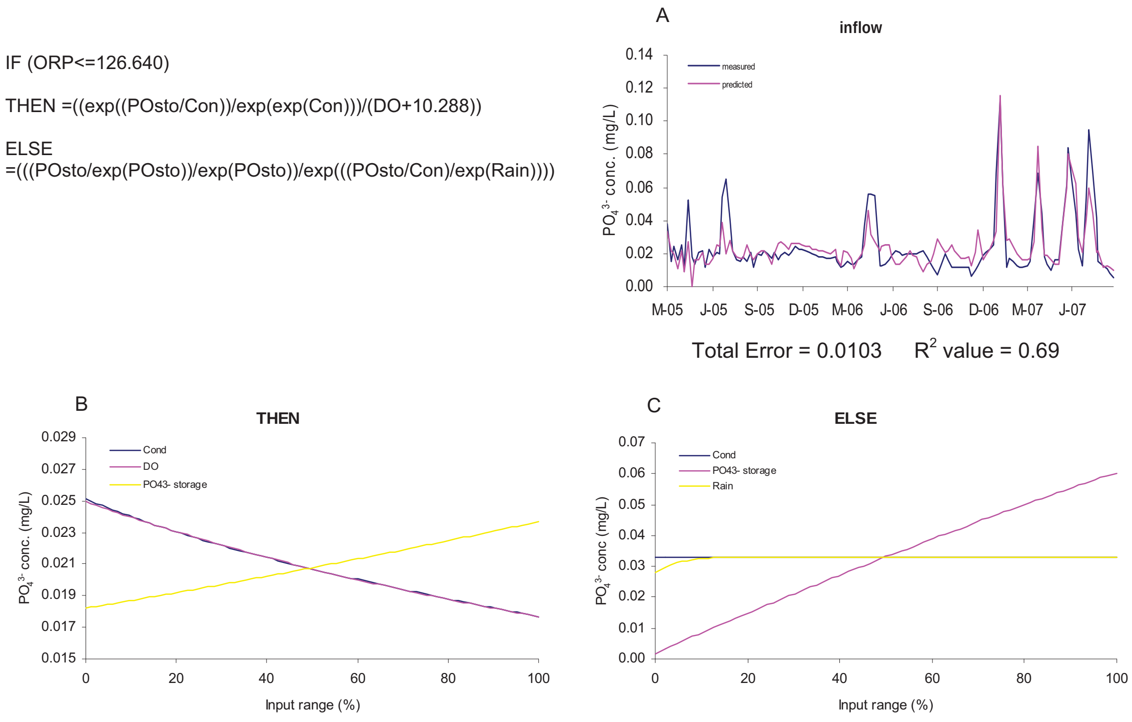
Figure E-25: 7 days ahead forecasting results for PO_4^{3-} at the outflow site. A. Comparison between the measured and predicted TN concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

Knowledge discovery using HEA for prediction of Phosphate

Table E-5: Input variables selected for HEA modeling of PO_4^{3-}

inflow	site 1	site 2	site 3	site 4	outflow
WT	WT	WT	WT	WT	WT
Con	Con	Con	Con	Con	Con
DO	DO	DO	DO	DO	DO
pH	pH	pH	pH	pH	pH
ORP	ORP	ORP	ORP	ORP	ORP
Turb.	Turb.	Turb.	Turb.	Turb.	Turb.
$PO_4^{3-}{}_{(w)}$ conc. (sto)	$PO_4^{3-}{}_{w)}$ conc. (in)	$PO_4^{3-}{}_{w)}$ conc. (S1)	$PO_4^{3-}{}_{w)}$ conc. (S2)	$PO_4^{3-}{}_{w)}$ conc. (S3)	$PO_4^{3-}{}_{(w)}$ conc. (S4)
$TP_{(sed)}$ (in)	$TP_{(sed)}$ (S1)	$TP_{(sed)}$ (S2)	$TP_{(sed)}$ (S3)	$TP_{(sed)}$ (S4)	$TP_{(sed)}$ (out)
Evp.	Evp.	Evp.	Evp.	Evp.	Evp.
Rainfall	Rainfall	Rainfall	Rainfall	Rainfall	Rainfall

w = water, sed = sediment
sto=storage, in = inflow, S1 = Site 1, S2 = Site 2, S3 = Site 3, S4 = Site 4, out = outflow
WT = Water Temperature, Con = Conductivity, DO = Dissolved Oxygen, ORP = Redox Potential, Turb. = Turbidity and Evp. = Evaporation


IF (ORP<=126.640)

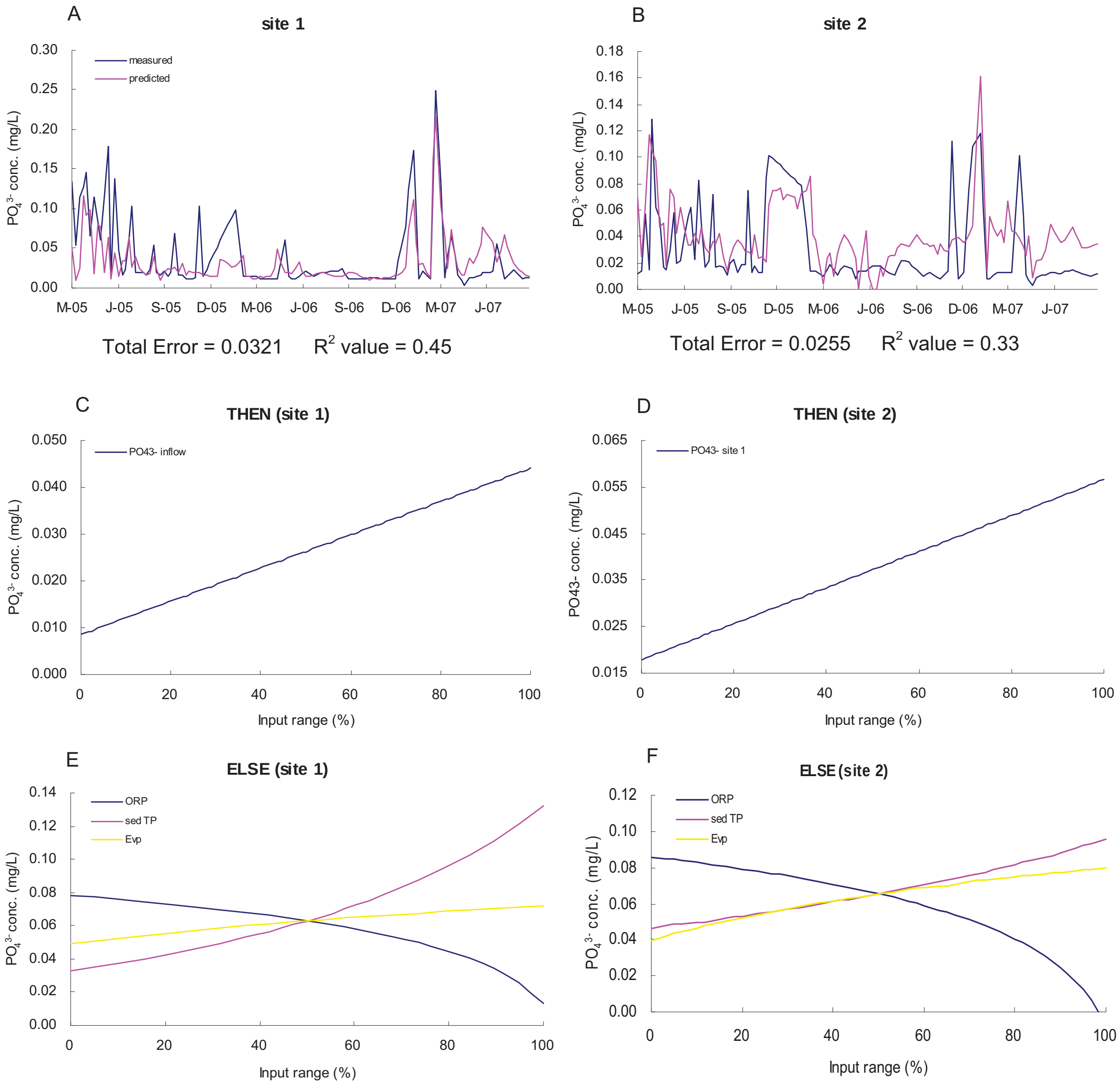
THEN =((exp((POsto/Con))/exp(exp(Con)))/(DO+10.288))

ELSE
=(((POsto/exp(POsto))/exp(POsto))/exp(((POsto/Con)/exp(Rain))))

Total Error = 0.0103 R^2 value = 0.69

Figure E-26: HEA results for PO_4^{3-} at inflow site. A. Comparison between the measured and predicted PO_4^{3-} concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

```
IF ((Con*59.846)<=20.104)
THEN =prevS
ELSE =(ln(|((118.193/ORP)/Evp)|)/(((118.193/sedTP)*(-199.173))-(-55.743)))
```



Total Error = 0.0321 R^2 value = 0.45

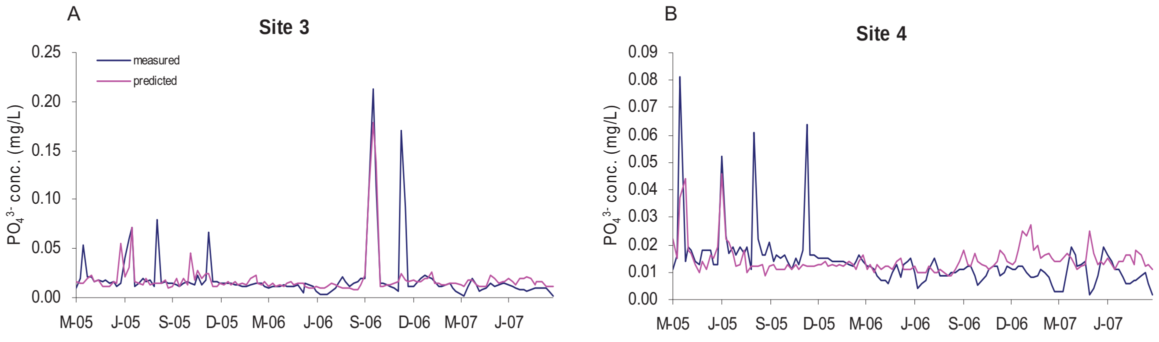
Total Error = 0.0255 R^2 value = 0.33

Figure E-27: HEA results for PO_4^{3-} at site 1 and 2. A. Comparison between the measured and predicted PO_4^{3-} concentrations at site 1; B. Comparison between the measured and predicted PO_4^{3-} concentrations at site 2; C. & D. Sensitivity for THEN branch (site 1 & 2); E. & F. Sensitivity for ELSE branch (site 1 & 2)

IF ((DO*(Turb+DO))>417.513)

THEN =(DO/(Rain+(Rain+(Rain+89.102))))

ELSE =(ln(|((Rain*Turb)+67.643)|)/(ORP+324.932))



Total Error = 0.0183 R^2 value = 0.58 Total Error = 0.0096 R^2 value = 0.12

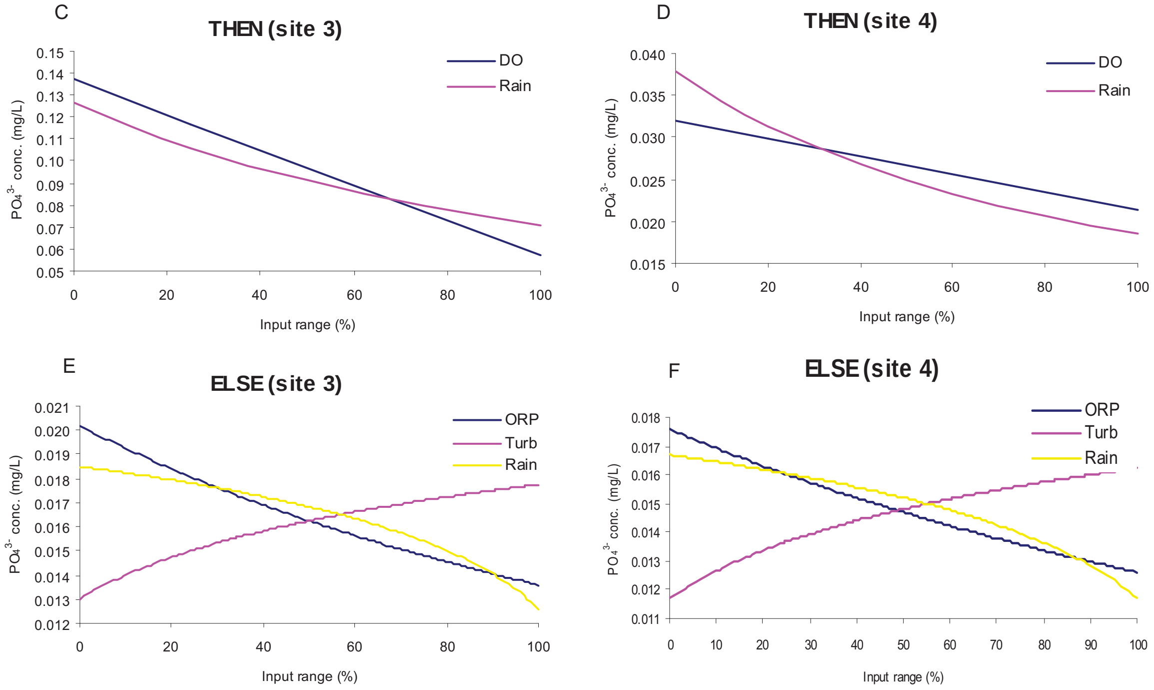


Figure E-28: HEA results for PO_4^{3-} at site 3 and 4. A. Comparison between the measured and predicted PO_4^{3-} concentrations at site 3; B. Comparison between the measured and predicted PO_4^{3-} concentrations at site 4; C. & D. Sensitivity for THEN branch (site 3 & 4); E. & F. Sensitivity for ELSE branch (site 3 & 4)

IF (((Temp*Turb)>113.333) AND (Turb<=22.429))

THEN =(DO/(((pH*104.198)+ORP)+(-421.971)))

ELSE =(6.053/((pH*(Evp+59.720))+ORP))

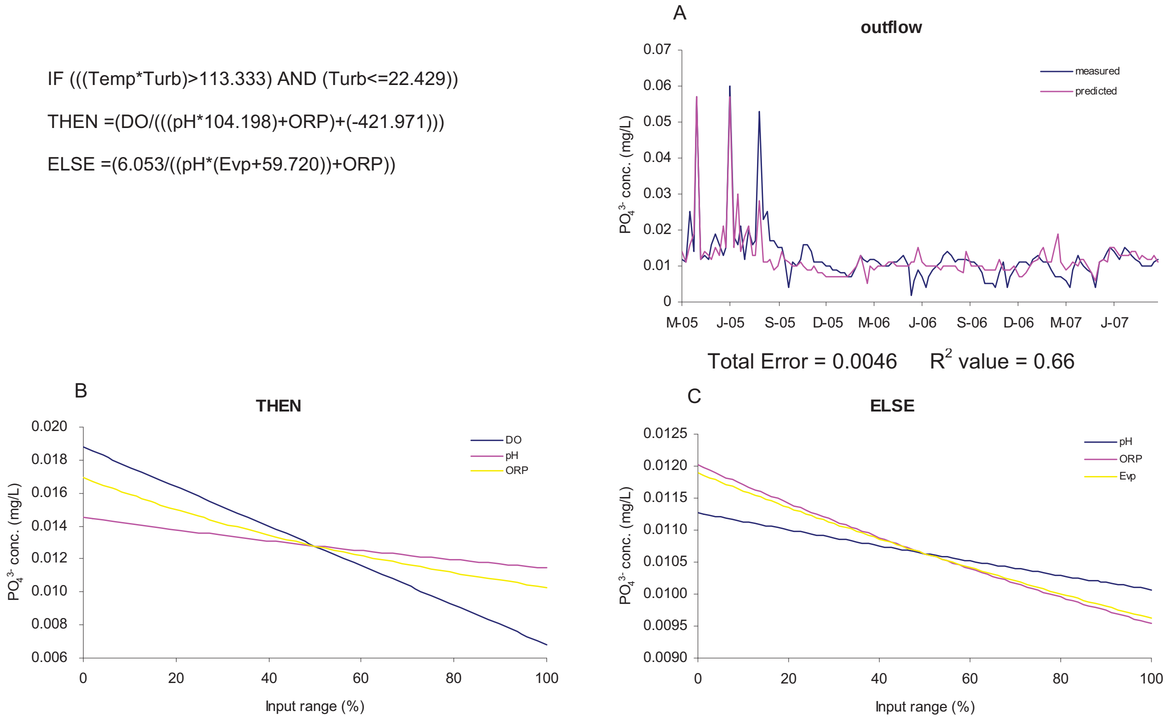


Figure E-29: HEA results for PO_4^{3-} at outflow site. A. Comparison between the measured and predicted PO_4^{3-} concentrations; B. Sensitivity for THEN branch and C. Sensitivity for ELSE branch

General rule for Phosphate prediction using HEA

Rule set selected for general rule application for all the sites in the reed bed pond is the rule set used for the prediction of site1 and 2.

Rule set: IF ((Con*59.846)<=20.104)
THEN =prevS
ELSE =(ln(|((118.193/ORP)/Evp)|)/(((118.193/sedTP)*(-199.173))-(-55.743)))

Table E-6: R^2 and total error of the rule set for the different sites

	inflow	site 1	site 2	site 3	site 4	outflow
Total Error	0.0156	0.0321	0.0255	0.0102	0.0283	0.0075
R^2	0.30	0.45	0.33	0.00	0.00	0.12

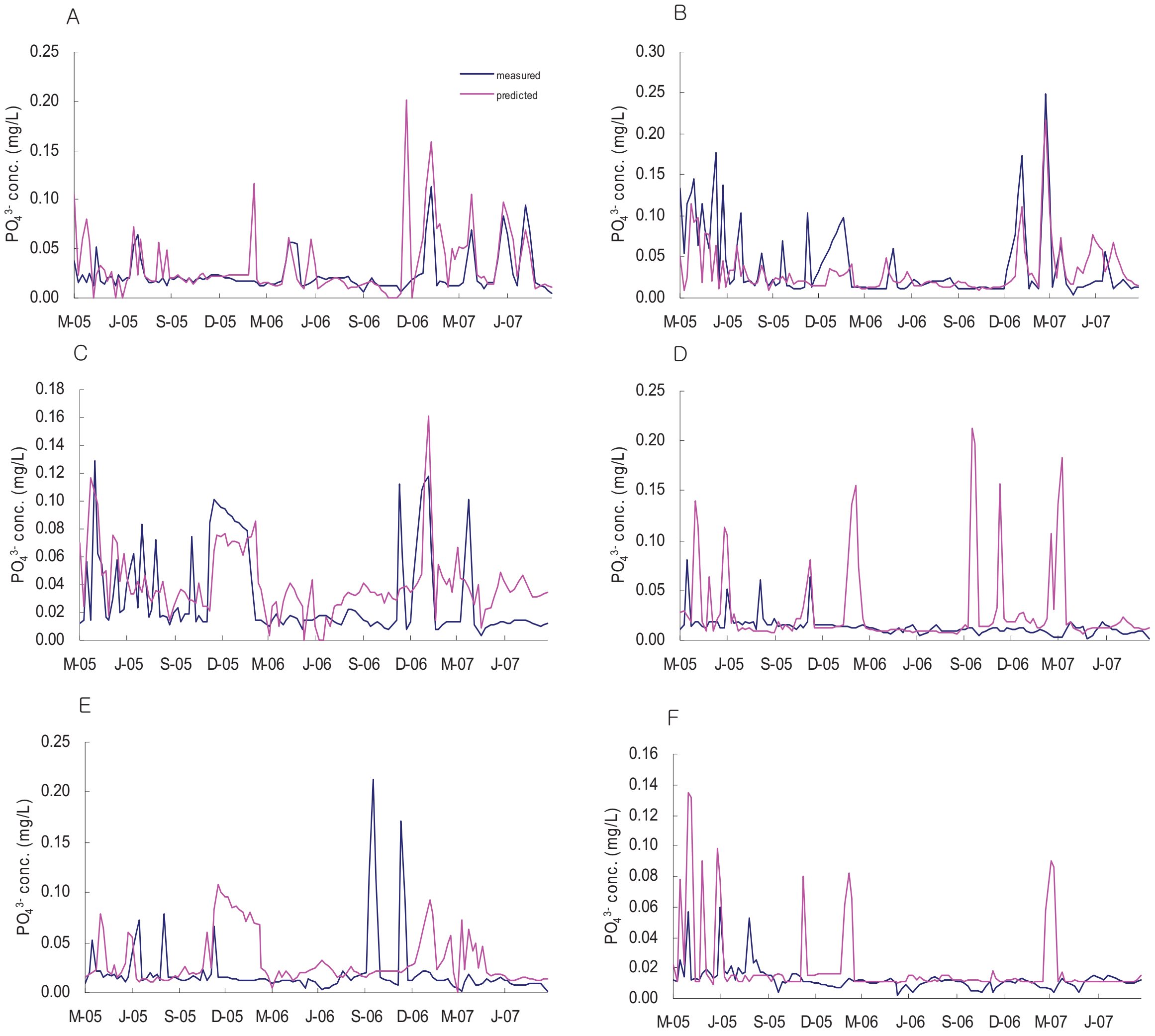


Figure E-30: General rule application for prediction of PO_4^{3-}. A. inflow; B. site 1; C. site 2; D. site 3; E. site 4 and F. outflow

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