A MATHEMATICAL MODEL FOR CHEMICAL PHOSPHORUS REMOVAL

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Abstract

The common view of chemical phosphorus removal is an equilibrium reaction between phosphate and iron or aluminium, resulting in the precipitation of a metal phosphate complex. A comprehensive model based on this was developed by Jenkins and Hermanowicz (1993). This view has been replaced by an alternative interpretation (surface complexation modelling), where the dominant mechanism at typical wastewater pH values is the precipitation of iron or aluminium hydroxide, with subsequent phosphate adsorption onto the hydroxide surface (Takács *et al.*, 2006, 2011; Smith *et al.*, 2008a, 2008b, 2011; Szabó *et al.* 2008) and has been accorded the status of the current best understanding of chemical phosphorus removal (WERF, 2008; WEF, 2008).

The Smith model has been extended to include the effects of alkalinity and sulphide on precipitation, competition for hydroxide surface by COD, the inclusion of temperature sensitivity, and the inclusion of pH as a calculated output.

WRc, supported by UK water companies, has evaluated this model at five UK sites. The model has one site-specific calibration parameter and the paper will describe the range found for the five sites, which is larger than that proposed in the original papers. The model explains why there can be an order of magnitude difference in performance between different sites for the same chemical dose.

Keywords

chemical treatment, phosphorus, surface complexation model

Introduction

Until 2006, chemical phosphorus removal was understood as a chemical precipitation reaction, where ferric or aluminium reacted with phosphate to form ferric or aluminium phosphate precipitates (Takács *et al.,* 2006). A simple one mole of ferric (or aluminium) to one mole of phosphorus was required for removal. This model was enhanced by allowing for complexes with hydroxide, and for allowing the precipitate to be regarded as a more complex material that had apparently non-integer ratios of ferric (or aluminium) to phosphorus (Jenkins and Hermanowicz, 1993).

Then, in 2006, Scott Smith with various co-workers began a series of publications (Takács *et al.*, 2006, 2011; Smith *et al.*, 2008a, 2008b, 2011; Szabó *et al.* 2008) that replaced this interpretation with a surface complexation model. While the wastewater industry regarded ferric phosphate precipitate as taking place at pH values around 6 – 7, typical of wastewater, the mainstream precipitation models, used by the mineral/groundwater industry, predicted that precipitation would not occur. Figure 1(a) shows the equilibrium curves for the disassociation of phosphate, while Figure 1(b) shows that for the precipitation of iron ferric phosphate and ferric hydroxide. The precipitation of ferric phosphate at lower pH values than normally encountered in wastewater treatment can be seen in Figure 1(b), and the corresponding effect on the liquid equilibrium, creating a notch in the shape for $H_2PO_4^-$, Smith demonstrated that this was the case. So, how was phosphate removed, since it clearly was? Smith proposed a new model, based on surface complexation theory. Ferric hydroxide precipitated, not ferric phosphate. Phosphate was then adsorbed onto the hydroxide surface. Adsorption was commonly modelled using isotherms, commonly Freundlich (no limiting adsorption value) or Langmuir (saturation of the adsorbate possible). But the surface complexation model, SCM, used a new approach, where the adsorption was written as a reversible reaction in a similar manner to normal chemical equilibrium. This made it straightforward to generalise the model to allow for competition for the surface by different chemicals.

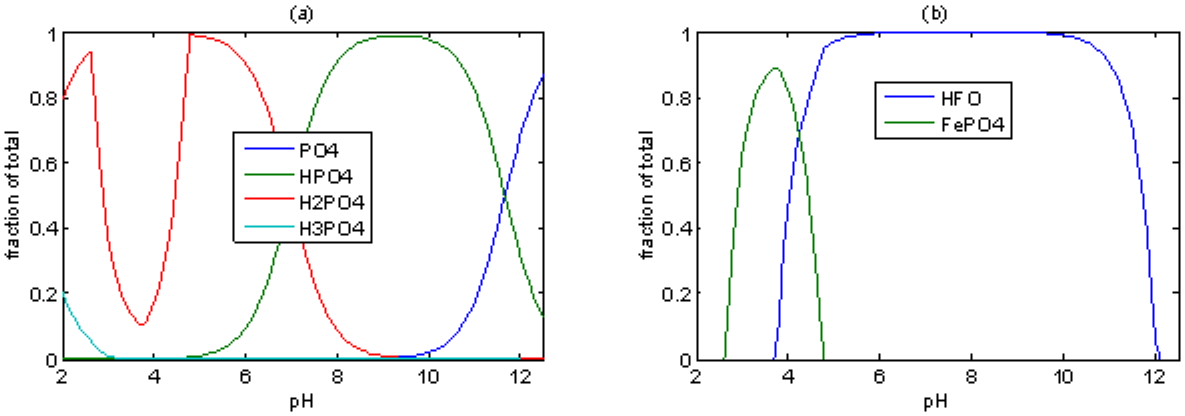

Figure 1: **Phosphorus equilibrium curve (a) and precipitation (b)**

The standard surface complexation model

Smith published the ferric model in its definitive form in 2008 (Smith *et al.*, 2008a), and the aluminium model a few years later (Smith *et al.*, 2011). The ferric model is reproduced in tableau format as Tables 1 and 2. The model has one site-specific factor, the active surface factor (ASF), a numbe,r which lies in the range of 0 to 6. A value for the ASF of six means that all the surface area of precipitate is exposed for adsorption. A value of zero means that mixing is so bad that none of the precipitate is available for adsorption. The upper limit of six is based on the analysis of how many phosphate ions may bind to a ferric hydroxide molecule, charged through the loss of a hydrogen ion.

A tableau format is used for describing the model, where a small number of basis substances are used from which all other species are calculated through the use of equilibrium reactions. As an example, from Table 1, hydroxide is calculated as $10^{-14.04}$ H^{-1}. The model proceeds in two steps. The first is a standard equilibrium process, calculating any precipitate if formed. A mass balance is written around the components, and the equations solved by a modified form of the Newton Raphson equation. This step uses the data in Table 1. If a precipitate is formed then a specific SCM calculation is carried out, using the concentration of precipitate calculated in the previous step. The precipitate is assumed to have two forms of exposed surface, described as S1 and S3[1],

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[1] S1 is a singly coordinated surface oxygen, meaning that the surface oxygen is bound to only 1 iron atom (FeO). S3 is triply coordinated (Fe_3O), meaning that the surface oxygen is shared with 3 iron atoms.

where the standard default used by Smith is that the concentration of each is the same as the concentration of ferric (or aluminium) hydroxide precipitated multiplied by the ASF. The SCM step uses the data in Table 2.

Smith published default values for ASF for ferric and aluminium, as 1.2 (ferric, intense mixing), 0.3 (ferric, poor mixing), 1.0 (aluminium, high dose) and 1.2 (aluminium, low dose). WRc applied the Smith model to data published in Smith's various papers, and found that the ASF varied from data set to data set. The ASF provides a framework for explaining the performance, but the variation makes the model less useful for design purposes.

Table 1: Equilibrium equations for iron (III) phosphate and hydroxide precipitation

ID	Species	H^+	PO_4^{3-}	Fe^{3+}	Log K
1	OH^-	-1	0	0	-14.04
2	HPO_4^{2-}	1	1	0	11.66
3	$H_2PO_4^{2-}$	2	1	0	18.64
4	H_3PO_4	3	1	0	20.05
5	$FeOH^{2+}$	-1	0	1	-2.77
6	$Fe(OH)_2^+$	-2	0	1	-6.29
7	$Fe(OH)_4^-$	-4	0	1	-21.77
8	$FeHPO_4^+$	1	1	1	19.96
9	$FeH_2PO_4^{2+}$	2	1	1	22.11
10	$Fe(OH)_3(s)$	-3	0	1	-6.0
11	$FePO_4(s)$	0	1	1	21.9

Table 2: SCM equations for iron (III) hydroxide

Species	H^+	PO_4^{3-}	S1	S3	Log K
$S1H_2PO_4$	2	1	2	0	27.65
$S3H_3PO_4$	3	1	2	0	33.8
$S3HPO_4$	1	1	0	1	15.5
S1H	1	0	1	0	4.2
S3H	1	0	0	1	4.2

Enhancing the standard

Smith's results showed that alkalinity and COD had an effect on the performance of phosphorus removal. WRc, with the support of Anglian Water, Dwr Cymru, Southern Water, Thames Water and Wessex Water, looked at enhancing the model to include these effects. Temperature was also included, and, at the request of the water companies, hydrogen sulphide.

The structure of the SCM makes adding new processes straightforward. Numerical coefficients in the model were adjusted to match against data taken from the general literature. The final model is given in Tables 3 and 4 for iron (III) and Tables 5 and 6 for aluminium (III). The performance of the model using data from Szabó *et al.* (2008) is shown in Figures 2 and 3, where the model matches the effect of alkalinity and COD on the removal efficiency.

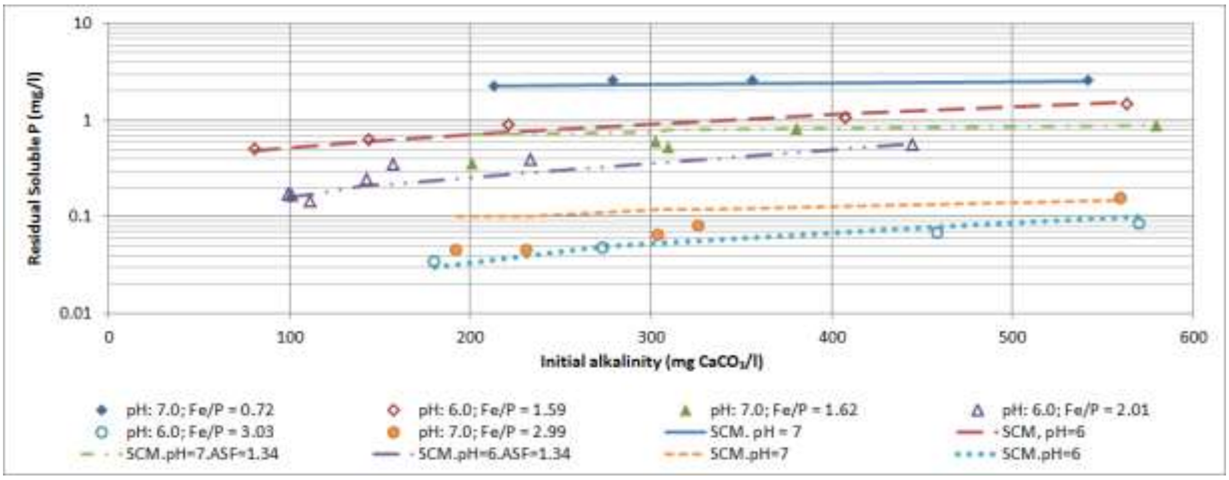

Figure 2: **Effect of initial alkalinity on phosphorus removal (Szabó *et al.*, 2008)**

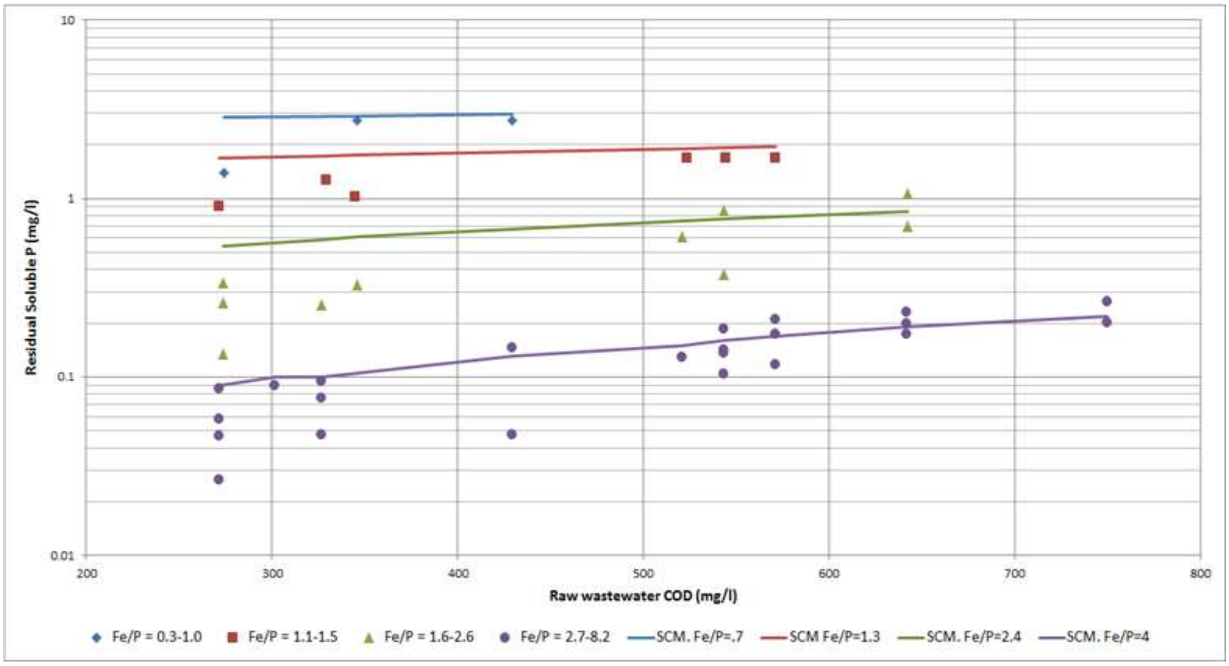

Figure 3: **Effect of COD on phosphorus removal (Szabó *et al.*, 2008)**

The hydrogen sulphide model, for ferric precipitation, is based on a common misperception. Ferrous sulphide is a stable compound that will precipitate from ferric solution. Ferric sulphide is unstable and does not exist at normal conditions found at sewage works. Despite this, the literature contains many references to it (Brown and Holme, 2009), including equilibrium constants for the precipitation reaction. The true reaction is probably 2 Fe^{3+} + 3 HS^{-} = 2 Fe^{2+} + 2 HS^{-} + S(s) + H^{+} = 2 FeS(s) + S(s) + 3 H^{+}, but for simplicity the false reaction (2 Fe^{3} + 3 HS^{-} = Fe$_2$S$_3$(s) + 3 H^{+}) was used as a surrogate.

Table 3: **Equilibrium equations for iron (III) phosphate and hydroxide precipitation in the WRc enhanced model**

Species	log K	H+	PO4---	Fe+++	HS	CO3--
H+	0	1	0	0	0	0
PO4---	0	0	1	0	0	0
Fe+++	0	0	0	1	0	0
HS	0	0	0	0	1	0
CO3--	0	0	0	0	0	1
OH-	-13.9946	-1	0	0	0	0
HPO4--	12.17865	1	1	0	0	0
H2PO4-	19.37804	2	1	0	0	0
H3PO4	21.52629	3	1	0	0	0
H2S	6.982527	1	0	0	1	0
S	-15.1919	-1	0	0	1	0
HCO3-	10.32965	1	0	0	0	1
H2CO3	16.68075	2	0	0	0	1
FeCO3OH	7.7	-1	0	1	0	1
Fe(CO3)2-	10.69	0	0	1	0	2
Fe(CO3)3---	24	0	0	1	0	3
FeOH++	-2.77	-1	0	1	0	0
Fe(OH)2+	-6.29	-2	0	1	0	0
Fe(OH)4-	-21.77	-4	0	1	0	0
FeHPO4+	19.96	1	1	1	0	0
FeH2PO4++	22.11	2	1	1	0	0
Solids						
Fe(OH)3(s)	-6	-3	0	1	0	0
FePO4(s)	21.9	0	1	1	0	0
FeS	26.5	-3	0	2	3	0

Table 4: **SCM equations for iron (III) hydroxide in the WRc enhanced model**

Species	log K	H+	PO4---	S1	S3	COD	HS
S1H2PO4	27.65	2	1	2	0	0	0
S1H3PO4	33.8	3	1	2	0	0	0
S3HPO4	15.5	1	1	0	1	0	0
S1H	4.2	1	0	1	0	0	0
S3H	4.2	1	0	0	1	0	0
S1COD	2.7	0	0	1	0	1	0
S3COD	2.7	0	0	0	1	1	0
S1S	0	0	0	1	0	0	1
S3S	0	0	0	0	1	0	1

Table 5: **Equilibrium equations for aluminium (III) phosphate and hydroxide precipitation in the WRc enhanced model**

Species	log K	H+	PO4---	Al+++	HS	CO3--
H+	0	1	0	0	0	0
PO4---	0	0	1	0	0	0
Al+++	0	0	0	1	0	0
HS	0	0	0	0	1	0
CO3--	0	0	0	0	0	1
OH-	-13.9946	-1	0	0	0	0
HPO4--	12.17865	1	1	0	0	0
H2PO4-	19.37804	2	1	0	0	0
H3PO4	21.52629	3	1	0	0	0
H2S	6.982527	1	0	0	1	0
S	-15.1919	-1	0	0	1	0
HCO3-	10.32965	1	0	0	0	1
H2CO3	16.68075	2	0	0	0	1
AlOH++	-4.82	-1	0	1	0	0
Al(OH)2+	-10.55	-2	0	1	0	0
Al(OH)3	-16.95	-3	0	1	0	0
Al(OH)4-	-22.86	-4	0	1	0	0
AlHPO4+	18.5	1	1	1	0	0
AlH2PO4++	22.28	2	1	1	0	0
Solids						
Al(OH)3(s)	-8.55	-3	0	1	0	0
AlPO4	18.34	0	1	1	0	0
Al2S3	6.7	-3	0	2	3	0

Table 6: **SCM equations for aluminium (III) hydroxide in the WRc enhanced model**

Species	log K	H+	PO4---	S1	S3	COD	HS
(S1)2H2PO4	29.61	2	1	2	0	0	0
(S1)2H3PO4	35.08	3	1	2	0	0	0
S3HPO4	10.8	1	1	0	1	0	0
S1H	5.2	1	0	1	0	0	0
S3H	5.2	1	0	0	1	0	0
S1COD	2.7	0	0	1	0	1	0
S2COD	2.7	0	0	0	1	1	0
S1S	0	0	0	1	0	0	1
S3S	0	0	0	0	1	0	1

Temperature dependencies were included where there was no published relationship. pK values can be approximated as having the temperature dependence.

$\log_{10} K = \Delta G / 2.303\ R\ T$ (Atkins and de Paula, 2006)

from which $\log_{10} K = \log_{10} K_{ref}\ T_{ref} / T$

where T_{ref} reference temperature
ΔG Gibbs free energy of formation
R ideal gas constant
T temperature, Kelvin

The model was evaluated at five sites, four of which used ferric and the fifth aluminium. For aluminium a first approximation to the effect of mixing intensity on ASF was produced, given in Figure 4. This shows that a constant ASF of 1.6 (rather than the 0.3 – 1.2 recommended by Smith) is a better initial value.

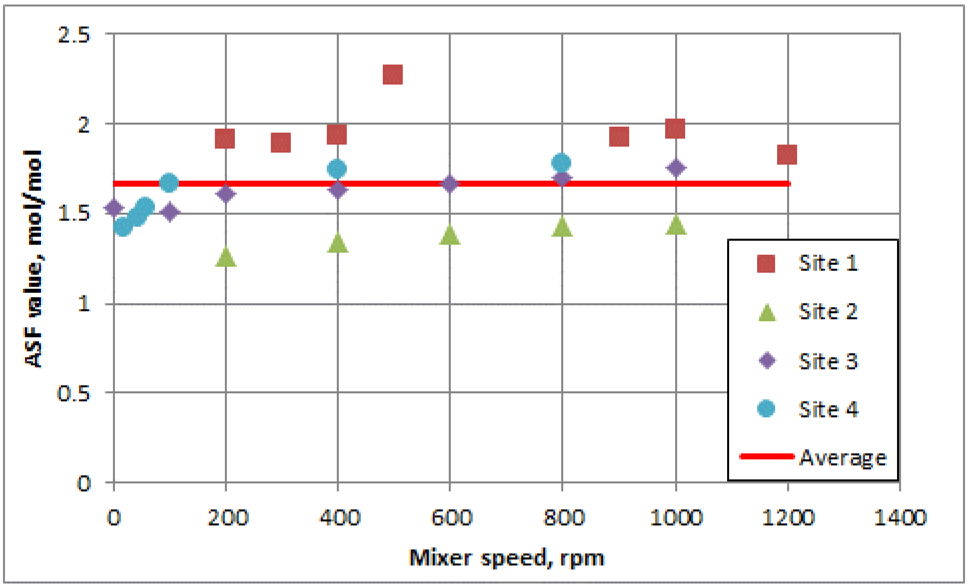

Figure 4: **ASF values for all four sites**

Using the model

The model was tested at sewage works from each of the project supporters. At each site jar tests were carried out, and the model ran against the jar tests. Works data was also collected, and the model applied against the site data. The jar testing equipment that was used was relatively inefficient, and several of the full-scale contacting processes had higher values for the ASF to match the data than was the case for the jar tests; however, simple dosing of chemicals into a flume had a lower value for ASF than did the jar test mixing vessels. The performance of the model is given in Figures 5 to 7 for one of the sites, showing (Figure 5) that the model can represent performance at a fixed mixing speed over a range of doses, using a constant value for the ASF, but that the best value for ASF varies with mixing speed (Figure 6).

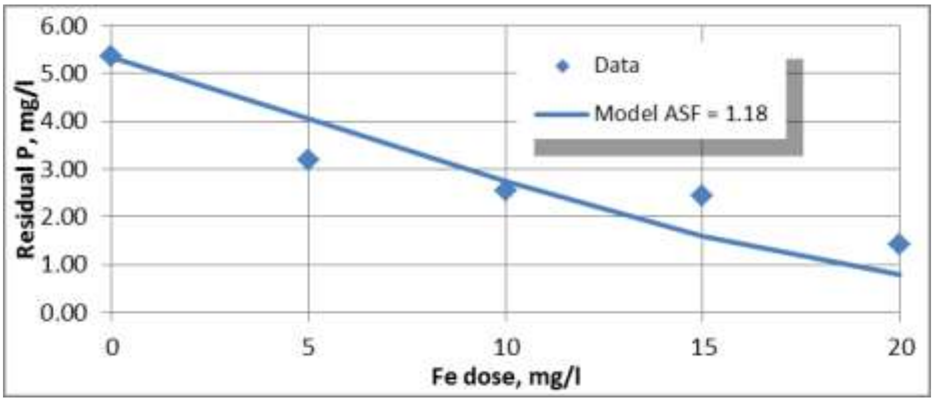

Figure 5: **Site 1 – effect of dose on removal**

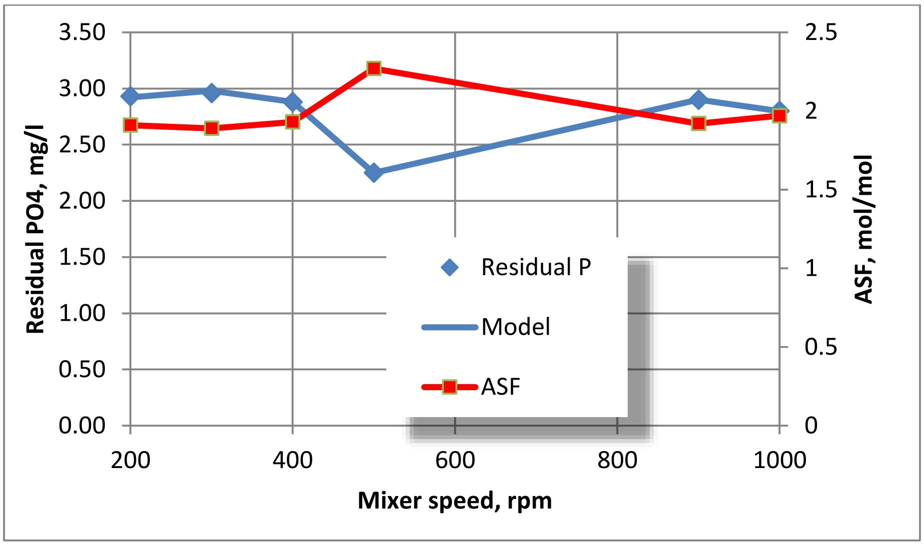

Figure 6: **Site 1 – effect of mixing speed on removal**

Figure 7 is a comparison of the model predictions of the effluent total phosphorus concentration compared to the measured values, using samples collected over a 24-hour period. The model produces a reasonable prediction.

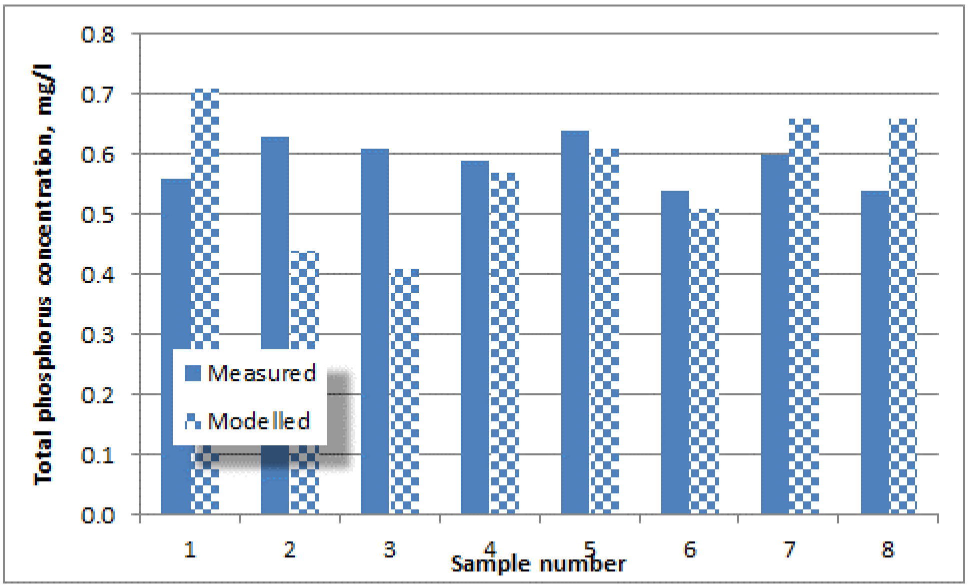

Figure 7: **Comparison between model and measurements for final effluent at Site 1**

Conclusions

Surface complexation modelling provides a new approach to understanding chemical phosphorus removal. At present there is no means of predicting the appropriate value for the ASF, which limits the model to being a means of reviewing the performance of existing sites, and identifying, by looking at the value for ASF, if there is scope for improved dosing.

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